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S. Suresh
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Contents

Waste Cooking Oil (WCO) Biodiesel Production Using Calcined Chalk as Heterogeneous Catalyst

Amit Pal, Balbir Singh and Shashank Mohan

Abstract Biodiesel is a low emission, renewable and a potential alternative of petro diesel made from vegetable oil, waste lipid and animal fat. Transesterification is a very common method to produce biodiesel from raw oil. Other three methods of production of biodiesel are: Direct use and blending of raw oils, micro-emulsion and thermal cracking. The study deals with heterogeneous catalyst based transesterification reaction for conversion of raw WCO into biodiesel. Calcium oxide used as heterogeneous catalyst was prepared from easily available and cheap white chalk ($CaCO_3$) by the process of calcinations. The heterogeneous catalyst was easily separated from the crude biodiesel produced by transesterification reaction. Further, catalyst separation did not require water washing process during purification process of biodiesel. Biodiesel production was investigated for various factors like methanol to oil molar ratio, reaction time and wt% of catalyst to oil with the help of recycled heterogeneous catalyst. Sustainable yields were obtained when the proposed catalyst was used in mechanical stirring, hydrodynamic cavitation and ultrasonic cavitation methods. The present research has the potential to ease the process of biodiesel production without environmental degradation from low quality feedstocks.

1 Introduction

Industrial development and increased transportation worldwide has created a huge demand for liquid fuel which is mainly derived from petroleum [1]. These fuel reserves being exploited extensively will not able to cater the need of future. The petroleum reserves are very limited and only available with few countries due to

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which other countries bound to import high priced crude petroleum thus facing energy and economy crisis. The environment pollution is the another curse of using petroleum based fuel due to emission of carbon monoxide (CO), nitrogen oxides, sulphur dioxide and particulate matters leading to climate change and health problems across the world. Therefore, to increase energy security for economic development and to minimize emission, the need to search for an alternative and environment friendly source of energy such as biodiesel is necessary [2]. Moreover biodiesel can be used with little or no modification in existing Compressed Ignition (C. I.) engines. Unlike fossil fuel, molecular structure of biodiesel contains oxygen which helps in increasing the rate of combustion of fuel in C. I. engines resulting in reduction in emission of CO, soot etc. [3].

Biodiesel is mono alkyl esters of fatty acids which are derived from vegetable oils (edible and non-edible) and animal fats. The feed-stocks from which more than 95% of biodiesel is produced in world are in edible category as theses are only largely and mainly produced. The properties of biodiesel prepared from such oils proved to be compatible to be used with petroleum diesel [4]. But the use of edible oil for producing biodiesel will cause scarcity of edible oil in the market. Whereas waste cooking oil is not suitable for human consumption and thus it can be a potential source of feedstock for biodiesel production.

There are different methods through which biodiesel can be produced viz. blending of raw oils and direct use, micro-emulsion, pyrolysis and transesterification. Vegetable oils are nothing but a combination of organic compounds. It ranges from simple straight chain compound to complex proteins structure and fat-soluble vitamins while the petroleum diesel fuel is saturated non-branched molecules with carbon atoms in a range of 12–18 [1]. The problem implies with the vegetable oil is its higher viscosity and higher flash point contributing to its lower volatility and the reactivity of unsaturated hydrocarbons [5]. Vegetable oil has a higher viscosity in the range of 35–60 cSt in comparison with the diesel with low viscosity of 4 cSt at 40 °C [6], which creates short-term troubles like starting problem in cold weather, gumming and clogging of filters, pipelines and injectors, knocking problem in engine and long-term troubles like choking of injectors, engine wear etc. [7] when used in existing unmodified direct and indirect diesel engine. When the vegetable oils are used in C. I. engines directly or by diluting it with petro diesel than that method is called direct use and blending of raw oils.

Micro-emulsion is a special class of colloidal dispersion that has attracted a wide attention because of their ability to solubilise material which was not soluble otherwise. Micro-emulsions were found to have lower fuel viscosity and better spraying patterns of fuel during combustion process. However the micro-emulsions have lower cetane number and lower calorific value which makes it unsuitable for use in C. I. engine for long time [6, 8, 9].

Pyrolysis refers to the chemical changes of long chain and saturated vegetable oils or natural fatty acids and animal fats using thermal energy in presence of air [10]. There have been lots of studies on the pyrolysis of triglycerides to obtain products appropriate for diesel engine. Alkanes, alkadines, alkenes, aromatics and carboxylic acids are produced from triglycerides on thermal decomposition.

The products of pyrolysis are chemically alike to petroleum gasoline and diesel. The main disadvantage of Pyrolysis is that it is an energy intensive process and higher cost of production [11].

Transesterification means the exchanging of alkoxy group of an ester compound with alcohol [1]. The reaction needs alcohol to react with vegetable oil (triglycerides) in the presence of a catalyst. Methanol is commonly used alcohol due to its low cost and quick reaction with triglycerides [10]. Transesterification is the very often used method for production of biodiesel. Biodiesel produced through transesterification has higher cetane value, higher efficiency of combustion and low emissions. However the main disadvantage associated with transesterification is safe disposal of by-products (glycerol and waste water) [8, 12, 13]. The reactions mostly use an acid or a base catalyst.

2 Biodiesel Production Process with Catalyzed Reaction

The given flowchart (Fig. 1) shows transesterification process using alkali catalyzed in general. The major shortcoming of alkali catalyst is its rapid reaction with free fatty acids to form soap. Equation (1) represents saponification reaction between FFA and alkali catalyst to form water and soap.

$$\underset{\text{(FFA)}}{R_1-COOH} + \underset{\text{sodium hydroxide}}{NaOH} \rightarrow \underset{\text{(soap)}}{R_1COONa} + \underset{\text{(water)}}{H_2O} \tag{1}$$

The reaction is not desirable because NaOH reaction with free fatty acid produces the soap and the soap lowers the biodiesel yield and the esters separation from the glycerol become more difficult and slow. It also combines with the catalyst and there is more need of catalyst to complete the reaction, hence the process will become costly [14]. The water already present in the oil along with water produced in saponification reaction reacts with triglycerides to form diglyceride and free fatty acids. These undesirable reactions can be avoided by employing acid catalyzed transesterification reaction. Acid catalyst directly transforms free fatty acid in oil into biodiesel [15, 16]. This acid catalyst based reaction has not gain much attention as the alkali-catalyzed transesterification due its slow rate and a need of high methanol to oil molar ratio [17]. The oils with high value of FFA undergo pre-treatment process (before being converted into biodiesel) where the oil undergoes neutralization process in the presence of acidic catalyst. Some drawbacks of transesterification reaction using alkali catalyst are that it needs neutralization and separation from the reaction mixture. The recovery of glycerol is also a difficult process, removal of catalyst from the product requires water washing and alkaline waste water requires treatment which increases the cost of biodiesel production [18]. To avoid the formation of soap and making the purification process simple and cheap, enzymatic catalysts like lipases are used to effectively catalyze the reaction [18]. But due to longer reaction time and higher cost, enzymes are not used

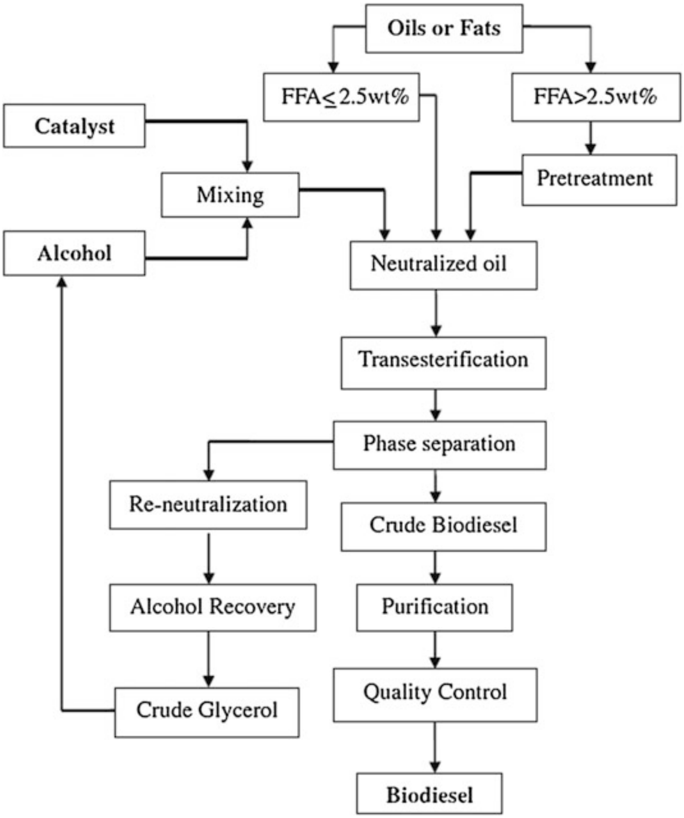


Fig. 1 Simplified process flow chart of alkali-catalyzed biodiesel production [11]

commercially [19]. Another range of catalyst is heterogeneous catalyst (alkaline or acidic) which shows easy recovery from the product of reaction by simple filtration method without water washing and eliminating the need of pre-treatment of feedstocks with high FFA content [20].

3 Homogeneous Catalyst

Homogeneous catalyst is of same phase as the reactants that is liquid. Homogeneous catalysts are dissolved in a solvent with the substrates. Homogeneous base catalysts (NaOH, KOH, CH_3ONa, and CH_3OK etc.) and homogeneous acid catalysts (H_2SO_4, HCl, $Fe_2(SO_4)_3$ etc.) are used for transesterification reaction. These catalysts have well defined active sites, moderate activity level and reasonably well understood reaction mechanism. After gravity separation of glycerol, the crude biodiesel is cleaned by water washing process, dry washing or membrane extraction process to remove any residual catalyst, free glycerol, unreacted alcohol and soap that were formed during transesterification reaction.

4 Heterogeneous Catalyst

These catalysts are in the form of metal oxides in solid state. In contrary to the homogenous system, heterogeneous catalysis involves adsorption of reactants and desorption of products to take place on the surface of the solid catalyst for the reaction to take place at increased rate. To get the desired properties of catalyst, heterogeneous catalysts can be easily tuned so that the presence of free fatty acid or water does not adversely affect the reaction steps during transesterification [21]. Active sites are not well defined and the reaction mechanism is poorly understood. Compared with the former one, solid acid-catalysts is cheaper, offer some advantages for eliminating separation, corrosion, toxicity, and environmental problems, but the reaction rate is slower [22].

5 Materials

Vegetable oils derived from Soybean, Groundnut, Rapeseed, Palm, Olive etc. are very commonly used for frying of food items in hotel and food industries. But after heating above a critical temperature for deep frying, they become unsuitable for further cooking, as their further consumption as food by human beings may lead to cholesterol formation in them. Presently, the WCOs are still lower cost feedstock making biodiesel production more competitive to the production of petroleum based diesel fuel. WCO was brought from 5 star hotel ITC Maurya Sheraton, Delhi. Various properties of biodiesel produced from WCO are represented in Table 1.

Methanol was purchased from nearby local market and white dustless chalk pieces (black board chalk) of Apsara Company containing high quality calcium carbonate are used to produce calcium oxide (CaO). Table 2 presents the details of constituents used for production of biodiesel. Experiments were carried out for different molar ratio of 6:1, 9:1 and 12:1 for 3, 4 and 5% catalyst by weight of oil.

Table 1 Properties of WCO biodiesel

Property	WCO biodiesel
Phase (physical)	Liquid
Colour	Oily
Specific gravity @ 25 °C	0.8849
Kinematic viscosity, mm^2/s @ 40 °C	56.94
Molecular weight (g/mol)	870
Pour point (°C)	6
Cloud point (°C)	12

Table 2 Oil, alcohol and catalyst used for mechanical stirring and ultrasonic cavitation

Molar ratio (alcohol/oil)	WCO (g)	Methanol (g)	Catalyst (CaO)		
			3%	4%	5%
6:1	100	22	3 g	4 g	5 g
9:1	100	33	3 g	4 g	5 g
12:1	100	44	3 g	4 g	5 g

6 Preparation of Heterogeneous Catalyst (CaO) from White Chalk ($CaCO_3$)

A process where ores or solids are brought to a thermal decomposition in presence of air during a thermal treatment process is known as calcinations. The calcinations process generally occurs at temperatures below the melting point but above the thermal decomposition temperature. Thermal decomposition temperature is defined as the temperature at which the standard Gibbs free energy for calcinations reaction is zero. For Calcium carbonate decomposition process, the chemical reaction is shown in (2).

$$\mathrm{CaCO_3} \xrightarrow{\text{Heating at } 850\,^{\circ}\mathrm{C}} \mathrm{CaO} + \mathrm{CO_2(gas)} \tag{2}$$

White chalk pieces were kept in muffle furnace at 850 °C for 2 h. Thermal decomposition started at these temperatures to drive out CO_2 gas and residual is CaO as shown in Fig. 2. The chalk pieces (CaO) were allowed to cool in furnace itself and stored in an airtight container to avoid exposure to air.

7 Preparation of WCO, Catalyst and Methyl Alcohol Mixture

First of all waste cooking oil WCO is cleaned by filtering to remove any impurities. Then the clean raw oil is heated up to a temperature of 110 °C to remove any water content if present in oil to avoid formation of soap during reaction. Then the oil is allowed to cool up to 60 °C temperature. Catalyst (CaO) (crushed to powder form) in 3, 4 and 5% by weight of oil and mixed with methyl alcohol (CH_3OH) with in a molar ratio of 6:1, 9:1 and 12:1.

8 Transesterification by Mechanical Stirring

CH_3OH and recycled powered CaO mixture is poured in a beaker. Then the WCO sample is poured into the beaker. The beaker is now kept on the hot plate of mechanical stirrer. It functions as a source of heat to maintain the temperature of the

Fig. 2 Chalk pieces heated in muffle furnace at a temperature of 850 °C

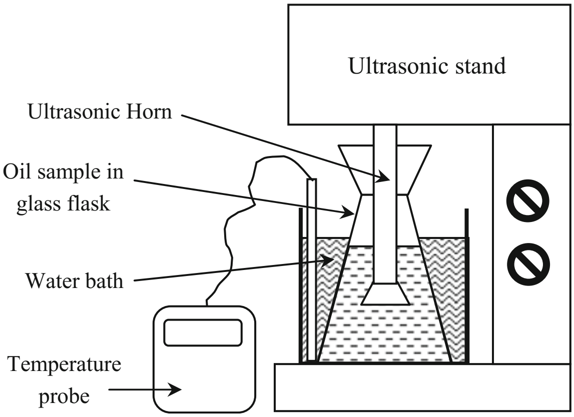
solution to 55–60 °C. The transesterification reaction is carried by conventional mechanical stirring method. A magnetic capsule is dropped in the mixture and rotated with the help of mechanical stirrer. The solution is allowed to stir with a speed of 300 rpm. During the reaction the temperature of mixture is maintained from 55 to 60 °C for the reaction time period of 3, 3½, 4 and 4½ h. After the completion of reaction the sample in the beaker is poured in a separation flask for 2–3 h for the separation. Catalyst CaO, soap, Fatty acid methyl ester (FAME) and methanol settled down in order as per their specific weight (catalyst at the bottom and methanol at the top).

The insoluble catalyst and glycerine recovered by filtration, dried in an oven at 250 °C, sieved and catalyst reused in subsequent reactions. The remaining solution was put into the beaker. The extra methanol present in biodiesel has been removed by distillation process and left over is biodiesel. Biodiesel so produced is measured.

9 Transesterification by Ultrasonic Cavitation

The process of formation of vapour cavities in the mass of liquid i.e. formation of small bubbles or voids in the mass of liquid is known as Cavitation [23]. In this process a bubble in a fluid is forced to oscillate in size or shape due to some form of energy input, as in a case of acoustic field. Such cavitation is often employed in

Fig. 3 Ultrasonic generator



ultrasonic cleaning baths [24]. The transesterification reactions were carried out in an ultrasonic reactor. Ultrasonic horn type processor is shown in Fig. 3.

In horn type reactor, horn is attached with the transducer which produces ultrasonic irradiation in the mixture. Horn type reactor has been used for this experiment. The ultrasonic cavitation generates ultrasonic processor frequency of 25–28 kHz. The transducer horn is clamped in a separate stand having jack type table to support the beaker and for its proper adjustment so that sufficient length of horn is dipped in the sample without touching the boundaries of the beaker. The mixture of oil, methanol and catalyst is kept inside the ultrasonic processor transducer. Adjust the beaker so that ultrasonic horn sufficiently dips in the solution. Reaction time was varied for different samples from half an hour to 2 h with an increment of half an hour. After the completion of reaction the biodiesel is separated in the same way as in mechanical stirring method.

10 Experimental Results

Figures 4, 5 and 6 shows comparison of biodiesel yield for mechanical stirring transesterification process at molar ratio 6:1, 9:1 and 12:1 of methanol to alcohol respectively for varying concentration of recycled heterogeneous catalyst and reaction time. % yield of biodiesel produced was found to increase sharply with increase in reaction time from 3 to 4 h and then achieve almost constant yield with increased reaction time.

Figure 4 shows percentage yield for 5% catalyst by weight for 4 h reaction time was 20% higher than that for 4% catalyst and 2.4% higher than for 3% catalyst for 6:1 molar ratio. The maximum yield was around 85% for 5% CaO catalyst by weight.

Fig. 4 Effect of reaction time and catalyst concentration on biodiesel yield using MR 6:1 in mechanical stirring

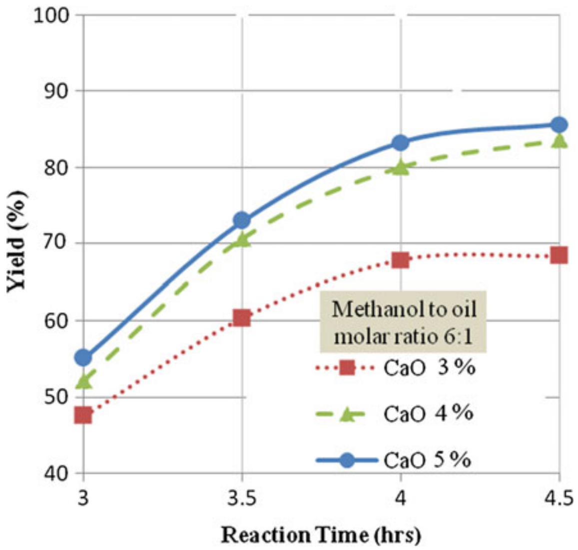


Fig. 5 Effect of reaction time and catalyst concentration on biodiesel yield using MR 9:1 in mechanical stirring

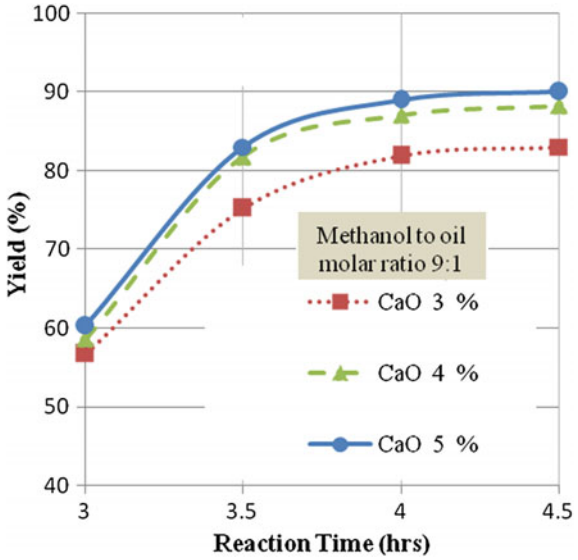


Figure 5 shows percentage yield for 5% catalyst by weight for 4 h reaction time was 7% higher than that for 4% catalyst and 2% higher than for 3% catalyst for 9:1 molar ratio. The maximum yield was around 90% for 5% CaO catalyst by weight.

Figure 6 shows percentage yield for 5% catalyst by weight for 4 h reaction time was 6.5% higher than that for 4% catalyst and 2% higher than for 3% catalyst for 12:1 molar ratio. The maximum yield was around 92% for 5% CaO catalyst by weight.

Fig. 6 Effect of reaction time and catalyst concentration on biodiesel yield using MR 12:1 in Mechanical Stirring

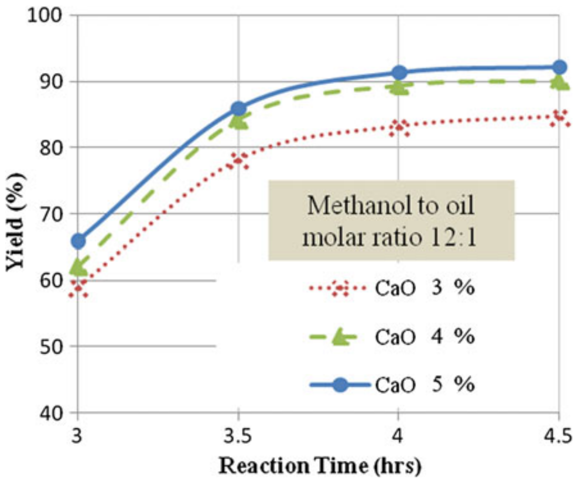
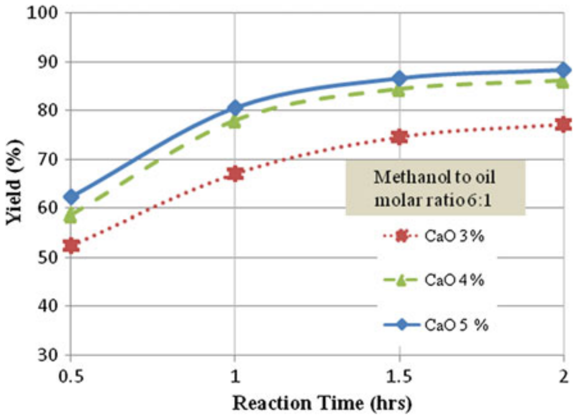


Fig. 7 Effect of reaction time and catalyst concentration on biodiesel yield using MR 6:1 in ultrasonic cavitation



Figures 7, 8 and 9 shows comparison of biodiesel yield for ultrasonic cavitation transesterification process at molar ratio 6:1, 9:1 and 12:1 of methanol to alcohol respectively for varying concentration of recycled heterogeneous catalyst and reaction time. % yield of biodiesel produced was found to increase sharply with increase in reaction time from 0.5 to 1 h and then increases gradually up to 1.5 h and then achieve almost constant yield for increased reaction time.

Figure 4 shows percentage yield for 5% catalyst by weight for 1.5 h reaction time was 12% higher than that for 3% catalyst and almost equal to that for 4% catalyst for 6:1 molar ratio. The maximum yield was around 87% for 5% CaO catalyst by weight.

Figure 6 shows percentage yield for 5% catalyst by weight for 1.5 h reaction time was 10.5% higher than that for 3% catalyst and 3% higher than for 4% catalyst for 9:1 molar ratio. The maximum yield was around 93.5% for 5% CaO catalyst by weight.

Fig. 8 Effect of reaction time and catalyst concentration on biodiesel yield using MR 9:1 in ultrasonic cavitation

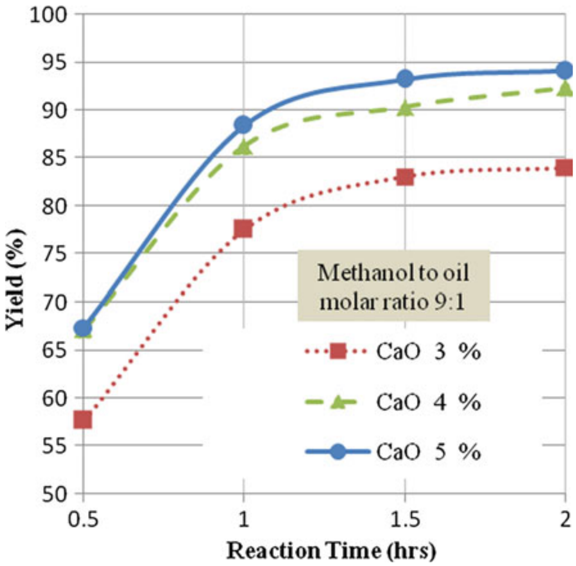


Fig. 9 Effect of reaction time and catalyst concentration on biodiesel yield using MR 12:1 in ultrasonic cavitation

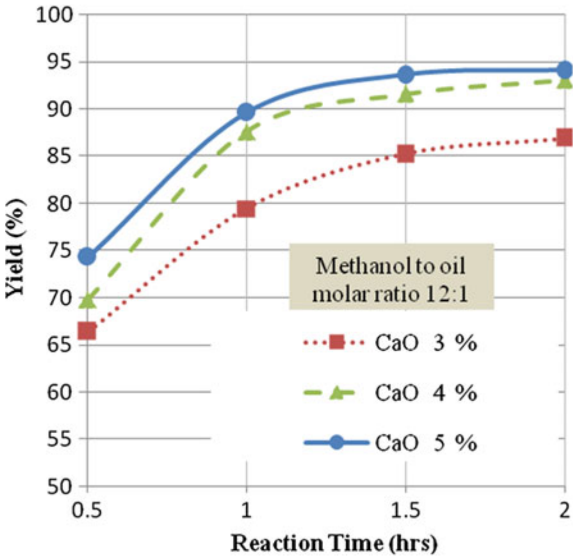


Figure 6 shows percentage yield for 5% catalyst by weight for 1.5 h reaction time was 8.5% higher than that for 3% catalyst and 2.5% higher than for 3% catalyst for 12:1 molar ratio. The maximum yield was around 94% for 5% CaO catalyst by weight.

11 Discussion

An increase in molar ratio (methanol to oil) of 12:1 has given maximum yield for every variation of catalyst concentration. A further increment in molar ratio does not increase the yield in all the methods of production.

An increase in catalyst concentration has given maximum yield for every variation of different molar ratio of methanol. A further increase in catalyst quantity does not increase the yield in all the methods of production. Increase in catalyst quantity beyond 5% raised the viscosity of solution, so the hindrance in the mixing of reactants.

12 Conclusion

Heterogeneous base catalyst has proved to be economical, environmental friendly, easily recyclable, ease in separation and low cost of separation in comparison with homogeneous catalyst, whereas the catalyst preparation is difficult and expensive task. Heterogeneous catalyst transesterification reaction was slow when comparing with homogeneous catalyst. It is probably due to inadequate mass transfer of reactants in the solution, thus improper and inefficient contacts of reactants with the catalyst to complete the reaction. However the rate of reaction increases in ultrasonic cavitation method of transesterification reaction. CaO catalyst leads to sustainable yield even at molar ratio of 12:1 whereas most of the commonly used heterogeneous catalyst requires high molar ratios up to 20:1.

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Synthesis of Biodiesel from Karanja Oil Using Modified Mordenite as a Heterogeneous Catalyst

Shikha Gangil, Virendra Singh Dhakar, Yashwant Parihar, Divya Bhagat, Priyanka Bhawate and Bharat Modhera

Abstract The catalytic performance of alkali leached modified mordenite has been obtained for transesterification of Karanja oil using a rota mantle as experimental setup at 60 °C. Dealumination was found in the alkali leaching calcined catalysts. It was found significant effect on the physical structure and chemical composition of the catalysts. The alkali leached modified mordenite processed transesterification gave the highest methyl ester yield 95.14% with NaOH loading (20% by wt) of in 3 h.

1 Introduction

With the decreasing conventional source of petroleum fuel, it will increase to concern about alternate sources and environmental impacts. That's why, it is crucial to grow eco-friendly biodegradable and renewable alternate source of energy to eliminate this problem.

In this regard, biodiesel proves to be a better alternate of energy. Biodiesel, a combination of long-chain fatty acid methyl esters (FAMEs) or fatty acid ethyl esters (FAEEs) biodiesel can be formed by several methods; transesterification has become the most popular method today. It possesses various benefits like better performance for production of biodiesel in less requisite, etc. [1]. Biodiesel is currently produced by using homogeneous acid or base catalyst. These catalysts include some undesirable features: costly process steps of catalyst/products separation; need to get rid of FFA and water from the feedstock [2].

Generally, Biodiesel was produced with a homogeneous catalyst such as NaOH or KOH. It produces methyl ester with high yield under mild reaction conditions: temperature of 60 °C, atmospheric pressure and reaction time of 1 h. But, before use of this product as a diesel fuel, the base catalyst must be separated from it. Due

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to high basicity of process wastewater, it will environmentally toxic. The total cost of the biodiesel production based with including separation process is not sufficiently viable as compared to the production cost of petroleum diesel oil. For example, soyabean oil transesterification with ETS-10. Zeolites has been studied, conversion in more than 90% was achieved at a reaction temperature of 100 °C [3]. To remove problem corresponding to homogeneous catalyst, people are focusing to the development of heterogeneous catalyst. The heterogeneous catalytic transesterification embraces under Green Technology due to the following reasons: (1) catalyst can be recycled/reused, (2) there is zero waste water or very less amount of waste water produced during the process and (3) separation of biodiesel and glycerol is very easy. During homogeneous catalytic transesterification the glycerol produced is of low quality and requires lengthy process and distillation for purification. Heterogeneous catalyst production rate of biodiesel is slightly slow as compared to homogeneous catalyst but production is economically feasible with recycling nature of catalyst and no more extra utilities requirement [4]. Chemistry of heterogeneous catalyst reported, includes metal hydroxides, metal oxides, metal complexes such as magnesium oxide, calcium oxide, zirconium oxide, hydro calcites, zeolites and supported catalysts. These types of catalysts have been examined as solid catalysts which overwhelmed some of the weakness on use of homogeneous catalysts. Alkaline earth oxide catalysts activity order was observed as BaO > SrO > CaO > MgO [5]. Another concern with biodiesel production is the availability of feedstock. In countries like US and Europe, the main sources for biodiesel production are generally edible oils like soyabean, rapeseed and sunflower. In India, non-edible oils like Karanja and Jatropha are being encouraged on a very large scale, as these can be grown on negligible and waste lands. Saras Vieira et al. modified the ZSM-5 with the citric acid at different concentration and temperature which result as the increase in external surface area and reduction in both Bronsted and Lewis acid sites with the increase in Si/Al ratio from 11 to 15 at 60 °C temperature, sample showed the better result with highest Bronsted acidity result and greatest increase in surface area [6]. Wang et al. performed Na^+ ion exchange process with modifying the low Al zeolites Beta as an effective catalyst in transesterification of triolein in excess methanol. Which resulted that at least eight cycles of transesterification on reaction by reflux method the Na-Zeolite exhibits any significant decrease in catalysts in transesterification of triolein [7]. Wang et al. showed that modified zeolites MCM-22 prepare with NaOH ion exchange process gives the conversion yield of triolein to biodiesel as high as 94.5% achieved in 1 h [8]. Liu et al. showed that calcium meth oxide has excellent catalytic activity and better stability in transesterification of soyabean to biodiesel with methanol and the optimum conditions: 1:1 volume ratio of methanol to oil, addition of 2% $Ca(OCH_3)_2$ catalyst, 65 °C and about 2 h of reaction time. It has the potential to replace homogeneous catalyst [9]. Intarapong and Iangthanarat told that 20% KOH/Mordenite is an better catalyst for palm oil transesterfication with methanol, showing highest activity with methyl ester yield of 96.7 wt% in the tested catalyst. Further, he explained that activity of uncalcined catalyst is better than calcined catalyst [10]. Bhagiyalakshmi et al. synthesized Na-ZSM-5 in alkaline medium and impregnated with cerium oxide by using cerium nitrate as a source for cerium. The maximum yield of transesterification process was resulted to be 90% under the conditions: oil:methanol molar ratio: 1:12; temperature: 60 °C; time: 1 h; catalyst: 5 wt%. Then reaction is catalyzed with ceria and the maximum yield of 93% over 15% Ce-ZSM-5 might be due to the availability more ceria for transesterification [11]. Selvabala et al. experimented that solid catalyst present lower activity as compared to other catalyst in transesterification reaction. This lower activity is compensated by higher reaction temperature. For this much temperature a large amount of energy is required. So research must be done to increase the catalyst efficiency under lower operating temperature [12]. Jiang et al. [13] showed that Na_3PO_4 had excellent activity and stability during transesterification reaction. During the transesterification of rapeseed oil to be biodiesel, the yield attained 95% with a mass ratio of catalyst to oil of 3%, molar ratio methanol: oil of 9:1, reaction temperature of 70 °C and reached equilibrium after 20 min. The dissolution of catalyst in solution was very less. Karmee and Chadha used Hb-zeolite, ZnO and montmorillonite K-10 catalysts for non-edible oil crude Pongammia Pinnate transesterfication with methanol (1:10 Molar ratio of oil: methanol), 0.575 g catalyst (0.115 wt% of oil) in 5 g oil at 120 °C. They found that the highest conversion rate of 83% was obtained with ZnO, while montmorillonite K-10, Hb-zeolite catalyst gave low conversion rates of 47 and 59% respectively in 24 h of reaction time [14].

Chauhan and Sharma [5] synthesized $[Et_3NH]Cl–AlCl_3$ for biodiesel production. Chloro aluminate ionic liquid was showed it is very capable for biodiesel production with high biodiesel yield 98.5% under the operating conditions: soybean oil 5 g, methanol 2.33 g, catalyst $[Et_3NH]Cl–AlCl_3(x(AlCl_3) = 0.7)$, reaction time 9 h, temperature 70 °C. Suppes et al. studied that catalyst used for the alcoholysis of soybean shows less activity as compared to the activities of faujasite NaX and ETS-10 zeolites. Conversion to methyl esters in excess of 90% were achieved at temperature of 150 and 120 °C with residence times of 24 h. At 100 °C, the ETS-10 provided a conversion of 92% in 3 h. Pretreating the ETS-10 catalyst at 500 °C for 4 h was instrumental in increasing the activity of the ET-10 catalyst [15]. Corma et al. experimented alcoholysis of triglycerides with using basic solid catalysts such as Cs-MCM-41, Cs-sepiolite and hydrotalcites. The reaction was carried out at 240 °C and 5 h of reaction time. Hydrotalcites gave a good conversion of 92% followed by Cs-sepiolite (45%) and Cs-MCM-41 (26%) [16].

2 Methodology

2.1 Materials and Methods

Mordenite, (SAR = 20) was obtained from the Qingdao Wish Chemicals Co., Ltd. China. NaOH and methanol were purchased of AR grade from Merck Specialties Pvt. Ltd. Karanja oil was obtained from local market. Table 1 shows the detail

Table 1 Composition of extracted oil for fatty acid [17]

Fatty acid	Molecular formula	Composition (%)
Oleic acid	$C_{18}H_{34}O_2$	51.61
Linolenic acid	$C_{18}H_{32}O_2$	16.66
Palmitic acid	$C_{16}H_{32}O_6$	11.64
Stearic acid	$C_{18}H_{36}O_2$	7.70
Dosocasnoic acid	$C_{22}H_{44}O_2$	4.46
Eicosanoic acid	$C_{20}H_{40}O_2$	1.33
Tetracosonaic acid	$C_{24}H_{48}O_2$	1.08

composition of Extracted oil. It was consisted of 94.48% pure triglyceride and rests were lipid associates free fatty acids. These will measure of unsaponifiable matter. The fatty acid profile of Karanja oil was recognized by gas chromatograph (GC). GC (Perkin-Elmer XL Auto system GC) was equipped with a flame ionization detector (FID) with a 14 ml carrier packed column. The temperature was raised from 60 to 240 °C with a 4 °C/min rise in temperature and then held for 5 min.

2.2 Catalyst Modification

The pure Mordenite was calcined at 600 °C for 2 h. Mordenite was modified by impregnation of various amount of Na loadings (5, 10, 15, 20, 25, and 30 wt%). Mordenite was mixed with NaOH solution for 24 h. Then, it was dried at 110 °C for 24 h before use as a catalyst in the reaction.

2.3 Catalyst Characterization

Parent Mordenite and modified mordenites were characterized by sophisticated instruments. FTIR spectrum of Mordenites was recorded on Agilent technologies in a range of 650–4000 cm^{-1}. Morphology of Mordenites were examined by Scanning Electron Microscope (SEM, JEOL/EO, Version 1.0, JSM-6390 operated at 10 kV. EDS analysis reported by the Instrument: 6390 (LA) with Detector Type: EX54175JMU.

2.4 Experimental Setup

Reaction flask with Large Capacity (Approx. 1 L capacity) and Three-Necked Morton-Type Round Bottom, separating funnel (500 mL), Bubble Condenser

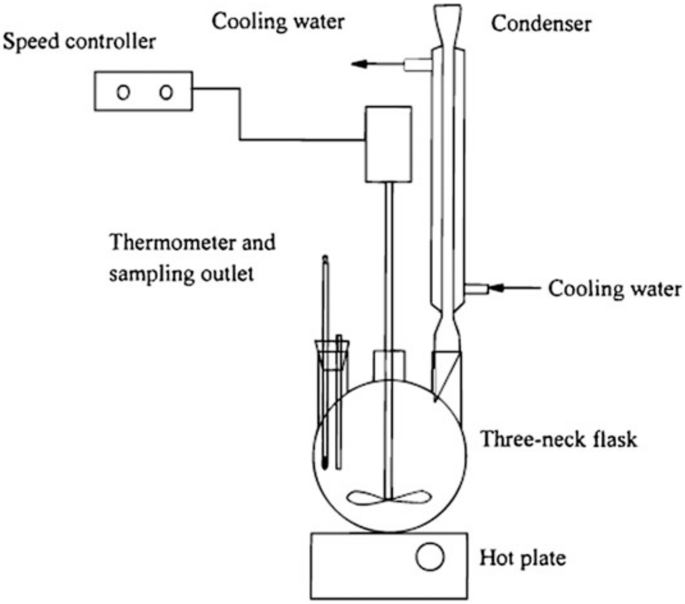


Fig. 1 Experimental setup for biodiesel production

(medium size), contact thermometer Hot plate with magnetic Stirrer and mechanical stirrer with electric motor were used for experimental set up as shown in Fig. 1 [17].

The Experimental reactions were carried out in a three-necked round bottom flask (capacity 1000 ml) having sampled outlet. The flask temperature was controlled by water bath within ±2 °C. One neck was equipped with a bubble condenser which will reduce alcohol loss through evaporation. Another neck is used to keep thermometer. Mechanical stirrer is arranged through the central neck of flask, which is connected to an electric motor along with speed controller. The reaction mixture is heated via water bath by a hot plate.

2.5 Preparation of Karanja Oil Methyl Ester

Karanja oil methyl ester (KOME) is produced by transesterification process of Karanja oil with methyl alcohol, with modified mordenite zeolite. The transesterification process was done for 60 min at reaction temperature 60 °C in a closed reactor vessel with alcohol to oil molar ratio (6:1) and mordenite 2% (by wt).

3 Results and Discussion

3.1 *Influence of NAOH Loading*

The SEM images reveal that the Mordenite and NaOH/Mordenite particles are irregular in shape. No significant difference in the morphology of the Mordenite and NaOH/Mordenite is observed. After being loaded with NaOH, the particles seem to agglomerate. Morphology of the 30 wt% NaOH/Mordenite changed to an amorphous structure due to the damaged structure of the Mordenite support. When loading NaOH to 20 wt%, the surface of the modified Mordenite still exhibits round shapes with crystallinity being almost the same as the unmodified Mordenite. An excess of Sodium at 30 wt% hide all the pores and surface of the Mordenite, which shows the growth of the particles.

FTIR spectra of the Mordenite support and the NaOH/Mordenite catalysts. The absorption peaks at 3614 and 3460 cm^{-1} are attributed to OH-stretching associated with terminal silanol groups and the H–O–H frequency of the H_2O molecule is located at a wave number of 1629–1646 cm^{-1} at a medium intensity. A set of strong intensity peaks at 1224 and 1046 cm^{-1} are ascribed to the vibration of external TO_4 (T = Al, Si) and anti-symmetrical stretching vibration of the tetrahedral (T–O bonds), respectively. The other absorption bands of 628–789 cm^{-1} correspond to the characteristic vibration of symmetrical stretching of Si(Al)–O bonds, and the bending of O–Si(Al)–O is interpreted at 437 cm^{-1}. These results confirmed the functional groups and the characteristics of the pure Mordenite support. For the fresh catalyst several absorption peaks are changed due to the Na loading. The reduction in intensity of the OH stretching vibration at 3600 cm^{-1} changes to a broadband. In addition, the set of high intensity absorption peaks at 1000–1250 cm^{-1} of the pure Mordenite support is converted into a broad peak at 800–1300 cm^{-1} for the NaOH/Mordenite catalysts. It could be inferred that the impregnation of NaOH affects the structure and composition of the Mordenite support, which shows of crystallinity loss, probably as a consequence of dealumination.

EDS analysis is recognized to the different Si/Al ratios of the mordenites as well as the amount and type of charge-balancing cations. Si/Al ratio on the NaOH/Mordenite catalyst decreased upon treatment suggesting that Si has been slightly extracted out of the Mordenite. Our results correspond with those of Guisnet et al., who noted that the decrease in crystallinity was probably due to the absence of extra frame work aluminum on the Mordenite which could be replaced by the silicon [18].

3.2 *Influence of Calcination Temperature*

Samples were calcined at different temperatures 400, 500, and 600 °C. The SEM results of the catalysts calcined at 400–600 °C is show that particles are agglomerated and irregular in shape, with a substantial variation in particle size. Inconsistency that it was observed between the effect of calcinations carried out on uncalcined and calcined catalysts is most likely attributed to a slight decrease in crystallinity of the calcined catalyst, particularly in samples calcined at a high temperature. After calcination, there was an increase in Si/Al ratio or decrease in Al atoms resulted (dealumination). Removal of framework Al after calcinations caused a change in morphology and an increase in particle size, while a decrease in surface area. Therefore, a high calcinations temperature altered the Si/Al value, which in turn changed the physical properties of the catalyst.

Effect of calcination temperature on the basic strength demonstrated that no difference in basic strength was found between the uncalcined and the calcined catalysts. However, the total basic sites of the calcined catalysts continuously decreased while the calcination temperature was increased. This could be due to the collapse of the pore structure.

3.3 Reusability of the Catalyst

The catalytic activity and reusability of the NaOH/mordenite were investigated. The spent catalysts were recovered by simple filtration and that was used to catalyze the next sample. A remarkable reduction in catalytic performance was observed yield 65.5 and 39.5 wt% of methyl ester content in the second and third runs for the NaOH/mordenite catalyst, respectively.

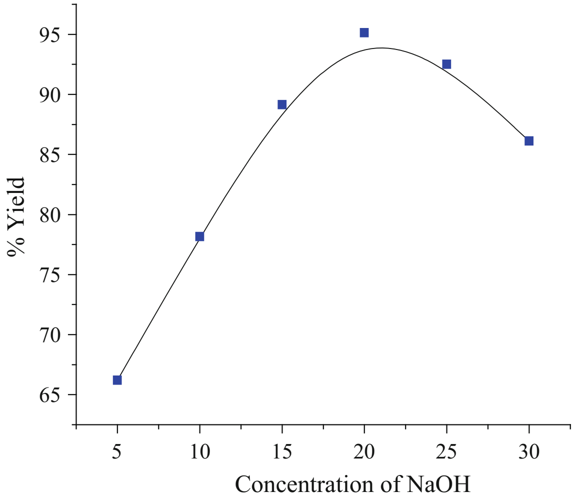
3.4 Results and Discussion

Table 2 and Fig. 2 show the effect of NaOH loading on Yield of KOME. The KOME yield was obtained higher for Mordenite catalyst with 20% NaOH than with 25% NaOH. 20% NaOH loading on Mordenite catalyzed process attained a maximum KOME content of 95.14% compared to 92.5% yield with 25% NaOH and 89.15% with 15% NaOH and followed by 86.12% with 30% NaOH. It was observed that the yield of Karanja Oil Methyl Ester increases with increase in the concentration of NaOH up to a certain value. After attaining the maximum value,

Table 2 Esterification of Karanja oil by modified zeolites

Run	NaOH loading (wt%)	Yield (%)
1	5	66.20
2	10	78.15
3	15	89.15
4	20	95.14
5	25	92.50
6	30	86.12

Fig. 2 Effect of NaOH loading on yield of KOME



the yield of KOME decreases with increase in concentration of NaOH. The reason behind this behavior is that the esterification process starts and the yield of KOME decreases. 66.2% yield was obtained with 5% NaOH and 78.15% yield was obtained with 10% NaOH. The maximum KOME conversion (yield 95.14%) is obtained with mordenite NaOH in 60 min at 60 °C.

Reaction conditions: Reaction time-3 h, Alcohol to Oil molar ratio-6:1, Catalyst amount (wt%) 2, Calcination Temperature-600 °C.

Table 3 lists the physico-chemical properties of the produced biodiesel in comparison with Karanja oil. The values of methyl ester flash point, viscosity, density, pour point, Cetane no. are close to the requirements of the ASTM standard. Owing to the absence of sulphur content in the biodiesel, the use of biodiesel can reduce emissions after combustion. Thus, the 20 wt% NaOH on mordenite catalyst can be a promising catalyst for the biodiesel industry.

Table 3 Physico-chemical properties of Karanja oil and KOME as per ASTM biodiesel standards

Properties	Karanja oil	KOME	ASTM biodiesel method
Kinematic viscosity (cst)	41.8	3.52	ASTM D445
Density @ 25 °C (kg/m^3)	926	891	ASTM D4052
Saponification value (mg KOH/g of oil)	184	116	ASTM D5558
FFA%	15.62	0.9	ASTM D5555
Pour point (°C)	−4	−7	ASTM D97
Flash point (°C)	208	97.1	ASTM D93
Cetane no.	40	52	ASTM D613
Colour	Dark brown	Golden yellow	–

4 Conclusion

20% NaOH/mordenite is an efficient catalyst for transesterification of Karanja oil with methanol, exhibiting the highest activity with methyl ester yield of 95.14 wt% among the tested catalysts. The activity of the uncalcined catalyst was higher than that of the calcined catalyst. At high calcinations temperatures, the pore structure of the mordenite collapsed and dealumination occurred. In addition, the basic sites decreased with increasing in calcination temperature. The leaching of the Na species was relatively low from the solid support during the reaction. Further studies need to be conducted to investigate the reusability of the catalyst after being treated with other solvents.

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A Review on Nano-catalyst from Waste for Production of Biofuel-Via-Bioenergy

Rajani Bharati and S. Suresh

Abstract The application of nanotechnology in production of biofuel by agriculture waste has been increased in recent years. Metal nano particles have been used as nanocatalyst in production of Biofuel, but impact of metal nanoparticles are not good on environment. So approach of green synthesis of nanocatalyst has attracted the focus of researchers. Synthesis of nanocatalyst by biomass is very eco-friendly and economic approach for making biofuels by agriculture waste. By the application of nanocatalyst the yield of production of biofuel has been increased. Biofuel production by conventional methods increase greenhouse gas emission in environment at some extent, production of biofuel by algae by nano-catalyzed reaction has solved the problem of greenhouse gas emission by production of biofuel. Nano-catalysts are used for converting methane into carbon and hydrogen. This approach can be used for anaerobic digestion to produce electricity from biogas fuelled electricity. Today the research has been increased on conversion of biomass into biofuels by nano-catalyzed reaction. The research have increased on application of nano-catalysts for production of biodiesel and glycerol from vegetable oils or animal fats, this application reduces many complicated steps from production of biodiesel by vegetable oils or animal fats in comparison of other conventional methods. In this processes nano-catalyst can be recovered and recycled which are not possible in conventional methods.

1 Introduction

Shortage of energy has become biggest problem in world. Shortage of energy is more serious issue in India than other developed countries because shortfall of conventional energy sources. So the emphasis of research has shifted on renewable

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energy resources than conventional resources [1, 2]. Renewable energy resources are ecologically sound, low-priced, easily available and rich in quantity. Renewable energy sources are wind energy, solar energy, Bioenergy etc. Bioenergy has immersed as alternative source of nonconventional energy source, it can be synthesized by waste materials so it is very good alternative to produce energy because it decreases disposal of waste on environment and convert waste as valuable product. Biodiesel is very good alternative fuel because lack of fossil fuel resources. Biodiesel are biodegradable, eco-friendly, low Sulphur content, high flammability and high cetane number. Due to urbanization demand of energy has increased. Fossil fuel consumption is not sufficient to fulfill this demand and it also creates pollution problems. Biomass is easily available and it has wide diversity in resources. Biodiesel is a eco-friendly renewable alternative fuel for conventional petroleum diesel [1, 2].

Application of nanocatalyst is the new and very effective technology to enhance efficiency of Bioenergy production processes. Biological sources are easily available and diversity in sources by which biomass can be getting to synthesis bioenergy [3]. Application of Catalyst to produce biofuel has increased. Nanocatalysts are very effective to improve product quality and achieving optimal operating conditions during production of biofuel. Nanocatalyst provides high specific surface area and increase rate of reaction which solve the most common problems during bio fuel production. During production of bio fuel application of heterogeneous catalysts have many problems such as high mass transfer resistance, time consuming process, fast deactivation and less efficiency. Due to these problems it is necessary to develop new types of nanocatalysts. By Biomass many types of biofuels have been produced among which biodiesel has attracted attention of researchers. Nanocatalytic conversion of biomass to biodiesel has been found more effective and efficient than other processes. By many research it has been found that application of nanocatalysts increases yield efficiency at relatively moderate operating conditions than the bulk catalysts.

2 Renewable Technologies for Synthesis of Biofuel by Biomass

To synthesis Biofuel by biomass first lignocellulose have been refined by biomass source to convert it in hydrocarbon biofuel. This conversion of biomass to biofuel has been dived in two these are: (1) Gasification and (2) Liquefaction. For this biomass is deconstructed to provide upgradeable gaseous or liquid products. This Synthesis is usually done by thermochemical processes to produce synthesis gas (by gasification) or bio-oils (by pyrolysis or liquefaction), or through the hydrolysis route to provide sugar monomers that then deoxygenated to make upgraded intermediates. Thermochemical conversion process is very effective technology in biomass upgradation for biofuels production [4–6].

3 Sources of Biomass

There are various sources of biomass which are easily available to synthesis biofuel by biomass which are carbohydrate-rich biomass while others are waste from agriculture and plant [1, 5, 6]. Biomass from agricultural waste material and plant is Cheap, easily available, rich in quantity and decrease the waste on environment [1, 5, 6]. There are many sources of Biomass some are wood, wood-based energy crops, corn Stover, grass, algae, wheat straw, rice straw, corn, miscanthus, nonedible oils, green and wood landfill waste, animal fats, waste frying oils, agricultural residues, municipal wastes, forest product wastes, paper, cardboard and food waste, plant wastes [1, 5, 6]. Non-edible vegetable oils (*Jatropha curcas*, tallow and neem oil) are very useful to synthesis biodiesel and it has been immerged as good alternative of diesel. Pongamia pinnata is easily available in all part of India and it can grow on any kind of soil. 30–40% of oil have been found in Pongamia pinnata kernel hence, research have been focused to produce biofuel by Pongamia pinnata kernel. There is potential to produce Bio energy by waste, now researchers are working to improving methods which can produce bio energy more efficiently and ecofriendly way at cheap cost by waste materials [1, 5, 6]. The transformation of biomass into fuel is very effective approach to replace petroleum feed stocks as fuel. Source for biomass is very cheap some are carbohydrate-rich biomass, renewable and rich in quantity; some are agricultural and plant waste [1, 5, 6].

4 Enhancement in Biomass Conversion Using Nanocatalysts

Used Waste edible oil is one of the sources of biomass research has been shifted on synthesis of biofuel by this biomass and its recycling to produce biofuel. Synthesis of biofuel by Waste vegetable oil is very effective and useful alternative in place of conventional fuel like diesel. Transesterification process is very effective technology synthesis biofuel by waste vegetable oil with methanol by nano sized zeolites catalyst with different quantity of Al_2O_3 content [3].

By using nanocatalyst biofuel can be produce at moderate operating conditions when compared to the bulk catalysts. Nanocatalyst has large surface to volume ratio of nanoparticles compared to bulk materials, makes them excellent potential catalysts [1, 7]. There are many factors which effect biofuel conversion from biomass some are effect of changes in acidic properties, type of metal content and porosity of catalysts. By many research it have been found that for increasing the products' quality, it is necessary to make new types catalysts [1, 8]. In applications of nanocatalyst to improve conversion of biofuel from biomass, increased surface area of nanocatalyst are very necessary candidates [1, 8].

Impregnation and precipitation processes are used to synthesis biofuel by biomass in presence of catalysts. This is the advantage of application of catalyst in biofuel synthesis that it improves biomass gasification methods to enhance the syngas production and reduce the tar formation [2]. Application of nanocatalyst has focuses on increase liquid yield and quality of products in biomass liquefaction. Nanocatalyst characteristics, such as high catalytic activities and high specific surface area have helped overcome some limitations on heterogeneous catalysts for their application in biodiesel production from biomass. This paper the review about application nanocatalytic in conversion of biomass to biofuel with improvement and solution of challenges which are faced in conventional technologies [1].

Application of heterogeneous nano catalysis reduces corrosion probles as well as neutralization of waste and catalyst recovery and reutilization [1]. Acid-functionalized paramagnetic nanoparticles are very effective for application in catalytic hydro conversion of biomass. Functionalized nanocatalyst are easily separated and recycled in the catalytic hydro conversion process. Nanocatalysts have many advantages which make them attractive for use in biomass to liquid (BTL) processes. Having the fluid solution characteristics, mono dispersed nanocatalysts have excellent accessibility to the oxygen atoms of the cellulose ether linkage [10]. Synthesis of biofuel by biomass such as liquid compounds such as paraffinic, naphtenic and aromatic hydrocarbons are alternative of the worldwide petrochemical demand. An application nanocatalyst in the catalytic synthesis of biofuel from biomass to liquid chemicals has had several advantages; most of the research attention has been paid to conversion of biomass to biodiesel [1]. Diesel fuel is in more demand in world. Application of nanocatalyst to synthesis of biofuel from biomass has imaged best approach for conversion of biomass to biodiesel in most efficient way [1, 5, 6].

The Application of homogeneous catalysts have many problems, such as need huge amounts of water, difficulties in product isolation, and environmental pollution caused by the liquid wastes [1]. The use of “a green” method based on heterogeneous nanocatalysts is a new technology for synthesis of biodiesel which has many advantages over other technologies [1]. Biodiesel making using solid nanocatalysts inplace of homogeneous have more potentially lead to cheaper production costs by reuse of the catalyst. Heterogeneous catalytic methods have some issue like high mass transfer resistant, more time consuming and inefficient this issue can be solve by application Nanocatalysts that have high specific surface and high catalysis activities [1, 7, 8].

5 Application of Nanocatalysts in Biofuel Production

Application of Biodiesel synthesis by biomass using nanocatalyst is one of the best technology alternatives of fossil fuel [1, 7, 8]. Iron nanocatalyst have been used as a nanocatalyst for the production of biodiesel using Pongamia pinnata oil with methanol [1]. In biomass gasification, reducing tar and char formation is an important issue. Nanocatalysts reduce the tar content; but also improve the quality of gas products and the conversion efficiency [1, 2]. For best result in gasification catalysts methods have some issue such as effective removal of tars, being resistant to deactivation as a result of carbon fouling or sintering, can easily be regenerated and are inexpensive [11]. Nanocatalysts for biomass gasification, nano-sized NiO (nano-NiO) is very effective for synthesis of biofuel [1]. Supported catalyst synthesized by loading nano particles of NiO on the surface alumina which are cheap [12].

Nanocatalysts of Ni and $Ni_3Cu(SiO_2)_6$ nanoalloy catalyst are very effective for biomass gasification to synthesis of biofuel [13]. It has been concluded by their research that nanoalloy catalyst increased biomass conversion efficiency at relatively low gasification temperatures [13]. Application of nano-ZnO and nano-SnO_2 have been found very effective catalyst for high-temperature for cellulose gasification during biomass conversion into biofuel [1]. It has been shown in Table 1, effect of nano-ZnO on cellulose conversion at 300 °C while nano-SnO_2 was an effective catalyst for the cellulose conversion at 400–500 °C. The data shown in Table 1 has been obtained cited by [14] (Table 2).

6 The Role of Nanocatalysts to Solve Some Problems in Biomass Conversion, Increasing the Products Quality

There are many challenges in biomass conversion which attract researcher's attraction for improving quality of products and solving its related environmental problems. In biomass liquefaction nanocatalysts have solved many environmental probles and also have increase the liquids yields and also enhance the value-added products [1, 3, 5–8]. Higher temperature is essential in the liquefaction process for increasing gaseous products, Nanocatalysts has solve this challenge in biofuel synthesis by biomass it has reduced reaction temperatures causing an increase in the liquids products which means an improvement in the liquefaction operation [1, 3, 6–8]. In pyrolysis of spent tea Co nanocatalysts decreased the operating temperature to 300 °C and increase the liquid product yield to 60%. Nanocatalysts for biodiesel synthesis have improved the yield of products and quality of products [1–8]. Magnetic nanoparticles loaded with different catalysts have been used in biodiesel

Table 1 Effect of catalyst during cellulose gasification on biomass conversion into biofuel [14]

Temperature (°C)	% Conversion of biomass			
	Nano-ZnO	Bulk-ZnO	Nano-SnO_2	Bulk SnO_2
300	92.0 ± 0.1	83.0 ± 0.1	71.0 ± 0.1	64.0 ± 0.1
400	83.0 ± 0.1	83.0 ± 0.1	88.2 ± 0.1	75.0 ± 0.1
500	89.0 ± 0.1	83.0 ± 0.1	88.4 ± 0.1	76.0 ± 0.1
600	86.0 ± 0.1	75.0 ± 0.1	84.0 ± 0.1	78.0 ± 0.1

Table 2 Nanocatalysts used for biodiesel synthesis by different biomass sources [1]

S. no.	Nano catalyst	Size (nm)	Biomass resource	References
1.	Cs/Al/Fe_3O_4	31–34	Sunflower oil	[10]
2.	(Mg–Al)	5–22	Pongamia oil	[15]
3.	MgO supported on titania	–	Soybean oil	[16]
4.	MgO	100	Sunflower oil	[17]
5.	ZrO_2 loaded with $C_4H_4O_6HK$	30	Soybean oil	[18]
6.	Lithium impregnated calcium oxide (Li-Cao)	40	Jatropha oil	[19]
7.	Magnetic solid base catalysts CaO/Fe_3O_4	49	Jatropha oil	[20]
8.	KF/CaO/Fe_3O_4	50	Chinese tallow seed oil	[21]
9.	Hydrotalcite-derived particles with Mg/Al molar ratio of 3:1	7.3	Jatropha oil	[22]
10.	Cao	20	Soybean oil	[23]
11.	Mgo	60	Soybean oil	[24]
12.	KF/CaO–Fe_3O_4	50	Stillingia oil	[25]
13.	TiO_2–ZnO	34.2	Palm oil	[26]
14.	ZnO	28.4	Palm oil	[26]
15.	KF/Al_2O_3	50	Canola oil	[3]
16.	CaO/MgO	–	Jatropha oil	[20]

synthesis; have advantage of catalyst recovery [1–8]. It is very big challenge to achieve high performances at relatively moderate operating conditions, it is necessary to increase the reaction time while at ordinary reaction time this problem has been solved by application of nanocatalyst, it is necessary to apply severe operating conditions. As a whole using moderate operating conditions reduces energy consumption requirements of the process which can be achieved by application of nanocatalysts [1].

The challenges of biodiesel synthesized by heterogeneous catalyst gives low yield of product and disposal problems on environment [1–3, 5–12]. It is very big issue to develop of new approaches to develop new technologies to achieve the efficient methods for biodiesel production [1–5]. Nanomaterial has imaged as effective catalyst for biodiesel synthesis, because it has large specific surface area, high catalytic activity, high resistance to saponification and good rigidity [1–8]. The transesterification process by homogeneous catalyst faces challenges that it requires additional downstream process to remove the homogeneous catalysts, it create problem of high cost of production [1–8]. Application of heterogeneous nanocatalysts such as zeolites solve this problem and it also shows advantages like this is non-corrosive, easy separation and require no washing of the ester [1–8].

7 Conclusion

Application of nanoparticles as catalyst has showed more advantage than the conventional catalyst and their counter parts bulk catalyst for the synthesis of biodiesel from biomass, because of its large specific surface area, high catalytic activity and high resistance to the saponification. It has been concluded by this review that synthesis of biodiesel by waste material as biomass is cheap and eco-friendly technology, so it is replace fossil fuel by biofuel. Source for biomass is waste materials and easily available in India so we found great potential of biofuel to replace conventional fuel. There are many non-conventional technologies available to synthesis energy among all available technologies bioenergy is best energy source. The energy released from biomass is renewable and eco-friendly. There are many methods are available for converting biomass to biofuel but application of nanocatalyst to synthesis of biofuel from bioenergy is best technology because it solve challenges create by other methods. Still research is necessary to develop new nanocatalsyt to solve changes which are not solved at moderate operating condition. Application of nanocatalyst has shown many advantages like it has increase reaction rate, low operating cost, mild optimum operating condition during biomass conversion into biofuel because their unique property of having high specific surface area.

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A Review on Application of Integrated Solar and Bioenergy Based Technology

Anshika Rani, S. Suresh and Anil Kumar

Abstract Water environment is encounter with increasingly heavier pollution trouble caused by economic development and population growth with unsafe water environmental policies, mainly in developing nations. Water pollution has been identified as a major contributing variable to the degradation and pollution of wetland biological communities. There are many commercial methods for treating of water pollutants from water, by Bioenergy and solar energy. Renewable energy made accessible from materials got from organic sources, is known as Bioenergy. Sun oriented vitality is the warmth and light transmitted from the sun that drives earth's climate and backings life. Solar Technologies make controlled utilization of this technology. The Solar desalination of saline water has been acknowledged as a standout amongst the most economical and new water asset substitute. It plays an important role in the socio-economic development for industrial sectors and many communities. This method is cost effective method among all the other commercial methods as there is no use of fuel so it also eco-friendly for treatment of wastewater. It produces quality of water for drinking and industrial purposes; there is no possibility of pollution and bacterial contamination and the active several effects units are more suitable for large scale applications. Solar energy could make accessible a supportable other option to drive the desalination plants, particularly in nations which lie on the solar belt such as China, India, the Middle East, and Africa. This review is focused on application of integrated Bioenergy and solar based technology.

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1 Introduction

The new energy producing technologies from renewable sources including solar energy, biofuels and wind energy have received considerable notice worldwide as use of fossil fuels must be replaced soon. Fossil fuels are known to have lower efficiency and higher emissions that add up to global warming with devastating consequences for the environment. Moreover, it is projected with a fuel scarcity for the next decades [1].

Renewable energy can be obtained from natural sources. It can be incessantly utilized and the sources include hydro, wind, wave, solar energy and geothermal heat. The distinguishing characteristics of solar energy are that it never runs out, any motion or combustion is desirable during the energy alteration process, there is no noise, and the energy capacities are variable. The setup to harness solar energy can be a stand-alone installation to be used in remote places such as on an island and in the back country [2].

Solar energy can be described as light and heat radiated from the Sun that is necessary to drive Earth's environment and support living on this planet. Solar technologies mark controlled use of this energy resource. Solar power is a name given to solar energy or denotes expressly to the transfer of light into electricity by use of photovoltaics, intent solar thermal devices and other different experimental technologies [3].

Solar radiations along with other secondary solar energy resources for example wave power and wind, biomass and hydroelectricity account for over 99.9% of the obtainable flow of renewable energy on Earth planet. The currents and reservoirs of solar energy in the environment are enormous as compared to present human energy requirements [4].

The measured use of solar energy is a key consideration in building design. Thermal mass is being used for conserving heat that solar radiations deliver to all buildings. Day lighting techniques optimize the usage of light in buildings. Solar water heaters are used to heat swimming pools and deliver household hot water [3].

Biomass has always been a significant energy source for the nation in view of the profit offered by it. Biomass is renewable, broadly obtainable, and carbon-neutral and also has the potential to offer substantial employment in countryside areas [5]. Biomass is competent of providing constant energy. About 32% of the total prime energy usage in the nation is still generated from biomass. Ministry of New and Renewable Energy has introduced a number of programs to encourage efficient technologies for its utilization in different fields to maximize the benefits [6].

Biomass power and cogeneration programme is executed with the main aim to promote technologies for optimal use of nation's biomass resources in captive power production and grid power generation. Biomass materials utilized for this purpose contain bagasse, straw, rice husk, cotton stalk, soya husk, de-oiled cakes, coconut shells, jute wastes, coffee waste, and saw dust so forth [7].

Biofuel (if cultivated, also known as agrofuel or agrifuel) can be described as gaseous, solid or liquid fuel comprising of or derived from newly lifeless biological material, such as plants. This differentiates it from fossil fuel, which is gotten from long inert natural material [8].

This paper provides information about solar energy Bioenergy and integrated solar and Bioenergy (Table 1).

2 Solar Energy

Earth uninterruptedly obtains 174 PW of solar radiation (insolation) at the upper atmosphere. Out of this around 30% is reflected back whereas the remaining 70% is immersed by the atmosphere, land mass and oceans. After fleeting through the atmosphere, the insolation spectrum is regularly split among visible and infrared ranges along with a small portion in the ultraviolet [3].

Water cycle and the winds are derived by the absorption of solar energy by climatic convection (sensible warmth transport), evaporation and buildup of water vapor (latent heat transport). Sunbeams captivated by the land masses and oceans helps in keeping the surface at an average temperature of 14 °C. The alteration of solar energy into chemical energy by plants through the course of photosynthesis yields wood, food and the biomass which is origin for fossil fuels [3] (Table 2).

Table 1 Top countries leading the world in renewable energy [9]

S. no.	Country	% of the world total
1	The United States	24.7
2	Germany	11.7
3	Spain	7.8
4	China	7.6
5	Brazil	5

Table 2 Top ten countries of total solar energy source [10]

Rank	Country	GWh/year
1	Russia	3.06×10^7
2	Antarctica	2.98×10^7
3	China	2.74×10^7
4	Australia	2.51×10^7
5	Brazil	2.50×10^7
6	United States	2.46×10^7
7	Canada	2.12×10^7
8	India	9.88×10^6
9	Sudan	8.70×10^6
10	Algeria	8.16×10^6

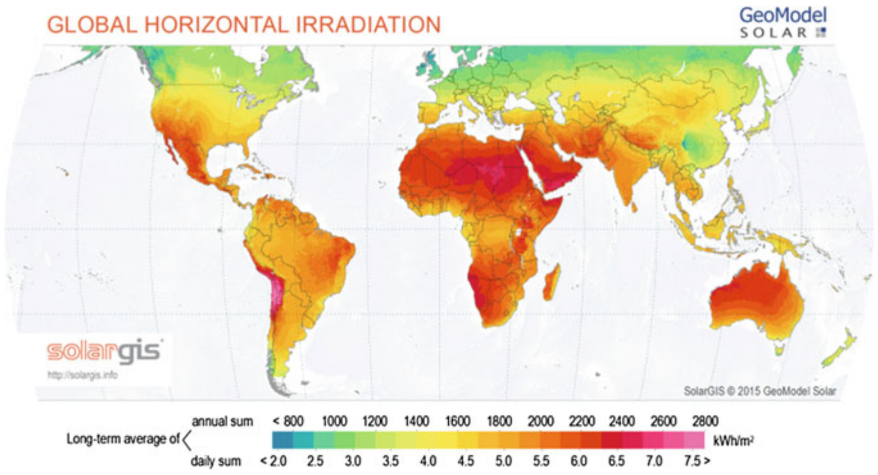

Fig. 1 Annual mean GHI of the earth [12]

Solar condensation and decontamination techniques harvest drinkable water for many of people around the world. Larger solar kitchens and Small-scale solar cookers utilized solar energy for drying, food preparation and pasteurization. More advanced focused technologies amplify the waves of the Sun for high temperature material testing, industrial chemical production and metal smelting. A variety of prototype solar vehicles provide ground, sea and air transportation [3].

The solar energy potential is governed by solar irradiation. The Global Horizontal Irradiance (GHI) is used as pointer of the irradiation level, and is an essential measure for solar potential valuation. GHI is direct normal irradiation (DNI) incorporated with diffuse horizontal irradiation (DHI) [11] (Fig. 1).

3 Bioenergy

Bioenergy is the form of chemical energy contained in biomass that can be transformed into energy forms that can be used directly, including heat, electricity and liquid fuel. Biomass is any organic mass of recently died living plant or animal origin. Dissimilar to coal, the biomass is not fossilized [13].

Biomass is available in many forms, for example: forestry products e.g. logs, sawmill residue, tree prunings, agricultural products e.g. sugarcane waste (bagasse), straw, manure crop stubble, poultry litter, nut shells, oilseeds and algae.

Woody biomass has conventionally been the major source of bioenergy but recent developments of technologies have extended the effective sources to include agricultural residues, oilseeds and algae etc.

These unconventional bioenergy technologies permit the bioenergy industry to improve sustainably without competing with the conventional agricultural industry for ground and further resources [14].

Renewable fuels produced from biomass can lower our dependency on fossil fuel resources furthermore, help in bringing down green house gas outflows [15]. First-generation biofuel formed from sugar and starch-based biomass is not sustainable due to its competition with food crops and insufficient land convenience [16]. Hence, lignocellulosic biomass, including devoted energy crops including switch grass, big blue stem, forest residues, and other agricultural residues which could economically complement biofuel production due to reduced necessity of production inputs and less competition with food production.

Amid change of biomass into vitality (through procedures including burning, gasification, pyrolysis, anaerobic assimilation or maturation), carbon dioxide created from the biomass courses through the biosphere and through photosynthesis, is reabsorbed in corresponding stores of new biomass.

4 Integrated Solar Energy and Bioenergy

Feroldi et al. [1] offered an energy managing approach for a sustainable hybrid system, which is built on solar–wind energy and bioethanol. Energy management for a stand-alone hybrid system which utilizes renewable energies (wind and solar) has been anticipated. The addition of a PEM fuel cell, which is fed with hydrogen using a bioethanol reformer, to the wind solar system provides a new concept to warrant a sustainable power supply for an extensive range of atmospheric conditions. First, a practice of optimum sizing using a GA approach was proposed. To accomplish this purpose, models of the wind turbines, the PV panels, the battery bank, the proton exchange membrane based fuel cell, along with bioethanol reformer (simplified model) were developed. Using these models, a method to achieve the optimal size of hybrid system was proposed. This developed approach is based on utilization of long-term data on wind speed, ambient temperature and solar radiation at a specific location and has been applied to design of a power system for supplying energy to a stand-alone house-hold. Once designed the hybrid power system, the EMS has-been developed.

Degliuomini et al. [17] produced hydrogen from bioethanol by utilizing solar energy. A innovative integrated system for obtaining power from bioethanol and solar energy sources was proposed. A fuel processor changes over the ethanol to H_2 rich synthesis gas, and feeds a fuel cell, which modifies the energy vector into useful power. The heat necessary for the plant is provided by electrical heating, by operation of photovoltaic arrays. The efficiency of the system is meaningfully improved, in terms of hydrogen production to ethanol consumption.

Nzihou et al. [18] proposed generation of synthetic fuels from biomass by gasification with weight on the application of supplementary high temperature solar energy. The background of this high temperature solar energy (solar concentrating) is deliberated, along with the proposed approaches of contact among solar radiation and biomass or steam reactants. The gasification of biomass for liquid fuel production is spoken in respects to biomass carbon content and hydrogen/oxygen ratio.

Morales et al. [19] examined orange-peel pyrolysis due to sun radiation that was utilized as a exceptional source of energy by way of a parabolic-trough solar concentrator. An optical analysis was directed by Monte Carlo ray-tracing method to give a comprehensive tridimensional description of the optical performance of the thermo-solar system.

Campo et al. reported [20] a scientific model that clarifies trailer scale biomass steam gasification system in coupling with a solar collector heat source and a micro gas turbine. This combined heat and power system is set to a recommended output of 20 kWe and several system conditions have been optimized in a parametric study to reduce resource consumption rates. Biomass feeding rates under optimal conditions were found to be between 23 and 63 kg/h dependent on the type of feedstock and other parameters. Water consumption is lowered through a condensation and recirculation practice which is a part of heat recovery unit. Also, solar energy requirements have been lowered by using a recuperator which extracts heat out from the combustion products. The overall system performance has been assessed by a utilization factor which was observed to range between 30 and 43%.

Tanaka et al. [21] proposed integration through heat exchanger network as a beneficial approach to attain the synergy among biomass and solar energy. In the process biomass is initially gasified in a bubbling fluidized bed (BFB) gasifier, and then syngas is utilized in a gas turbine. Excessive heat exists in this sub-system and concentrated solar thermal process while there is a necessity of steam for producing gasifying agent. Steam Rankine cycle exploits the heat made by these thermal streams to create power whereas fulfilling the steam demands.

Martín and Davis [22] optimized the amalgamation of biomass, solar and wind energy for the continual making of synthetic methane. Biomass is used for the era of power and/or hydrogen for further use. Photovoltaic wind and solar energy are utilized to gain power. Water is electrolyzed producing hydrogen and oxygen, further which is utilized to synthesize methane with CO_2.

Hertwich and Zhang [23] produced synfuel from biomass by using concentrating solar energy as its main energy source.

5 Concluding Remarks

From the above literature studies we concluded that when the combination of O_2 and steam was used as gasifying agent, greater overall efficiency of the developed system was attained at higher temperature and higher O_2 fraction in the gasifying agent.

Solar pyrolytic processes can become key methods for generating solar liquids fuels due to their possible for altering unrestricted amounts of solar energy into chemical energy. Moreover, replacing other processes with solar pyrolytic processes would decrease unsafe emissions and help moderate greenhouse gases.

The large area compulsory for the solar fields and the genuine environmental portion may shift from solar to wind.

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Optimization of Mass Flow Rate for N-Flat Plate Collector Integrated Biogas Plant for Winter Season at Srinagar, Kashmir (India) Location for Achieving Superior Performance

Jasleen Bhatti and G.N. Tiwari

Abstract Biogas is a sustainable form of renewable energy that can be harnessed from biomass and is freely available. Biomass is formed by the process of photosynthesis which can occur only in the presence of sunlight. Thus solar energy is the main driving force behind the production of bioenergy. A major concern that needs to be tackled especially in developing countries is energy poverty wherein 1.4 billion people in rural areas are still lacking access to electricity. This research work would be of great help in benefiting the rural masses that survive on burning of biomass. In this communication, the analysis has been done for Srinagar, Kashmir (India) which has harsh and cold climatic conditions. A detailed parametric analysis has been performed. The calculations were performed by using MATLAB 2014a. In this paper the effect of mass flow rate of the slurry $(\dot{m}_f)$ a sensitive parameter has been presented to design an active system. Further, the mass flow rate of the slurry $(\dot{m}_f)$ for an active N-flat plate collector integrated biogas (N-FPCIB) plant has been optimised for the winter season that is for the months of October to February for Srinagar, Kashmir (India) location by using IMD, Pune data. The N-FPCIB plant would show superior performance if made to function at optimized mass flow rate.

Nomenclature

A	Area (m^2)
A_h	Horizontal area of the gas holder exposed to solar radiation (m^2)
A_m	Module area (m^2)
A_v	Vertical area of the gas holder which is exposed to solar radiation (m^2)
A_t	Area of the top (m^2)

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A'_h	Slurry vertical Area (m^2)
A'_v	Vertical area of the gas holder which is submerged in the slurry (m^2)
C_f	Specific heat capacity of fluid (anti-freezing liquid) (J/kg °C)
C_s	Specific heat capacity of slurry (J/kg °C)
FPC	Flat plate collector
F_R	Flow rate factor (dimensionless)
h	Heat transfer coefficient (W/m^2 °C)
h_{rps}	Radiative heat transfer coefficient (W/m^2 °C)
h_1	Heat transfer coefficient from gas holder plate to gas (W/m^2 °C)
h_2	Convective heat transfer coefficient from gas holder plate to ambient (W/m^2 °C)
h_3	Heat transfer coefficient from gas to slurry (W/m^2 °C)
h_4	Heat transfer coefficient from slurry to ground (W/m^2 °C)
h_c	Heat transfer coefficient from gas holder to slurry (W/m^2 °C)
h_s	Heat transfer coefficient inside the tube from tube to slurry (W/m^2 °C)
h_w	Heat transfer coefficient inside the tube from water to tube (W/m^2 °C)
h_{sa}	Heat transfer coefficient from slurry to air (W/m^2 °C)
I(t)	Incident solar intensity (W/m^2)
$I(t)_v$	Incident solar intensity on vertical section of dome (W/m^2)
K	Thermal conductivity (W/m K)
m	Number of photovoltaic thermal flat plate collectors connected in parallel
$\dot{m}_f$	Mass flow rate of flowing fluid (kg/s)
L	Length of the heat exchanger (m)
M_S	Mass of slurry (kg)
N	Number of photovoltaic thermal flat plate collector connected in series
NN	Number of clear days
N_o	Number of sunshine hours (h)
$\dot{Q}_{U,N}$	Rate of useful energy transfer (kW)
r_1	Inner radii of the tube (m)
r_2	Outer radii of the tube (m)
t	Time (s)
T	Temperature (°C)
T_a	Ambient temperature (°C)
T_{foN}	Outlet temperature of fluid of the Nth photovoltaic thermal flat plate collector (°C)
T_{fi}	Inlet temperature of fluid in the photovoltaic thermal flat plate collector (°C)
T_g	Gas holder temperature (°C)
T_p	Absorber plate of dome temperature (°C)
T_s	Slurry temperature (°C)
T_w	Fluid temperature (°C)
U	Overall heat transfer coefficient of the system (W/m^2 °C)

Subscripts

a	Ambient air
eff	Effective
ele	Electrical
g	Glass
s	Slurry
w	Water

Greek letters

α	Absorptivity of solar cell
α'	Absorptivity of dome
$(\alpha\tau)_{eff}$	Product of effective absorptivity and transmissivity
τ	Transmissivity
η_m	Module efficiency

1 Introduction

Biogas is produced by the controlled decomposition of biomass like animal manure, agricultural residues and by-products, digestible organic wastes from food and agro industries, dedicated energy crops like maize, sorghum, clover etc. A number of scientists have studied the various feedstocks that can be used for biogas production and the chemical composition of biogas [1–5]. They suggested that biogas is formed via the process of photosynthesis where biomass (a living store of solar energy) undergoes anaerobic decomposition in the absence of oxygen at temperatures suitable for naturally occurring mesophilic or thermophilic anaerobic bacteria. In this process the input is converted into biogas and whole digestate. They have also stated that biogas primarily comprises of methane (CH_4) and carbon dioxide (CO_2) and it may also have small amounts of nitrogen (N_2), hydrogen sulphide (H_2S) and hydrogen (H_2). The digestate produced is a rich source of nutrient for the soil and hence serves as an excellent fertilizer for the crops. It has been suggested by many authors [6–13] that the rate of biogas production and retention period were functions of slurry temperature. Moreover, an optimum temperature of 37 °C ensured maximum biogas yield. However, in northern India particularly in Srinagar, Kashmir (India) the maximum ambient temperature observed during the winter season is around 23 °C. Thus, if a biogas plant is made to function during the winter season in northern India or if it has to be installed at Srinagar, Kashmir (India) a significant drop in ambient temperature would either result in reduction or inhibition in the production of biogas. Hence, in order to enhance the biogas production, increase in slurry temperature inside the digester was recommended [14–27]. An active method was suggested by Tiwari et al. [28] by which the slurry could be heated through a heat exchanger connected to flat plate collectors in series under forced mode of operation. In this paper an attempt has been made to achieve maximum slurry temperature (T_{smax}, °C) that coincides with the optimum temperature of 32–37 °C required for maximum biogas production. The optimization has been carried out for the winter season mainly for the months of October to February wherein the mass flow rate ($\dot{m}_f$, kg/s) which is a very vital parameter is varied over a range of 0.001–0.002 kg/s. The N-FPCIBP system is more effective for harsh cold climatic conditions.

2 General Specifications

A cylindrical digester made up of re-enforced concrete and cement (RCC) having 2500 l capacity has been designed. A floating biogas plant having a metallic cylindrical dome installed over the digester has been considered for this study. There was a support system for the dome present inside the digester. A spiral heat exchanger with effective length of 10 m made up of copper coil was placed inside the digester. The top of the heat exchanger was connected to the outlet of N-flat plate collector's (N-FPC's) which were connected in series combination as shown in Fig. 1.

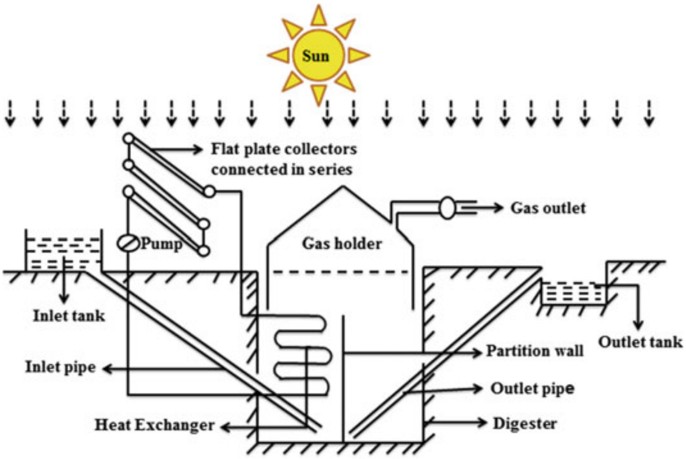

Fig. 1 Schematic view of a vertical floating type biogas plant integrated with flat plate collectors connected in series

3 Thermal Modelling

In order to write down the energy balance equations for each component of an active N-flat plate collector's integrated biogas plant we have considered the following assumptions:

- Each component of the system is in quasi-steady state condition
- There is no stratification along the depth of the slurry and the gas column
- Thermal capacity of the biogas is neglected
- The connecting pipe is perfectly insulated
- Average working fluid temperature is approximately equal to the flat plate collector outlet temperature.

The energy balance equations for each component of an active N-flat plate collector's integrated biogas plant are given as follows:

For Gas holder: (dome, absorber Plate.)

$$\alpha'\left[A_h I(t) + I(t)_v \frac{A_v}{2}\right] = h_1 A_t\left(T_p - T_g\right) + A'_v h_c\left(T_p - T_s\right) + (hA)\left(T_p - T_a\right) \quad (1)$$

$$(hA) = h_{rps} A_h + h_2(t) A_t \quad (2)$$

For Biogas:

$$h_1 A_t\left(T_p - T_g\right) = h_3 A_h\left(T_g - T_s\right) \quad (3)$$

For Slurry:

$$(M_s C_s)\frac{dT_s}{dt} = h_3 A_h\left(T_g - T_s\right) + (Ah)_s\left(T_p - T_s\right) - (Ah)_\infty (T_s - T_a) + \dot{Q}_{u,N} \quad (4)$$

where $(Ah)_s = A_h h_{rps} + A'_v h_c$; $(Ah)_\infty = h_4 A_h + h_{sa} A'_h$

The hourly outlet fluid temperature (T_{foN}) at Nth flat plate collector for the given N-FCPIB system has been calculated by using (5) given by Tiwari et al. [29] and by applying I(t) and T_a data taken from IMD, Pune.

$$T_{foN} = \left(\frac{\dot{q}_{ab}}{U_L} + T_a\right)\left\{1 - \exp\left\{-\frac{NA_c U_L F'}{\dot{m} C_f}\right\}\right\} + T_{fi}\exp\left\{\frac{NA_c U_L F'}{\dot{m} C_f}\right\} \quad (5)$$

4 Results and Discussion

As shown in Figs. 2, 3, 4, 5 and 6, the I(t) and T_a data taken from IMD Pune for the months of October to February have been used for carrying out the calculations. In Fig. 7 the mass flow rate ($\dot{m}_f$) has been optimized in order to achieve optimum

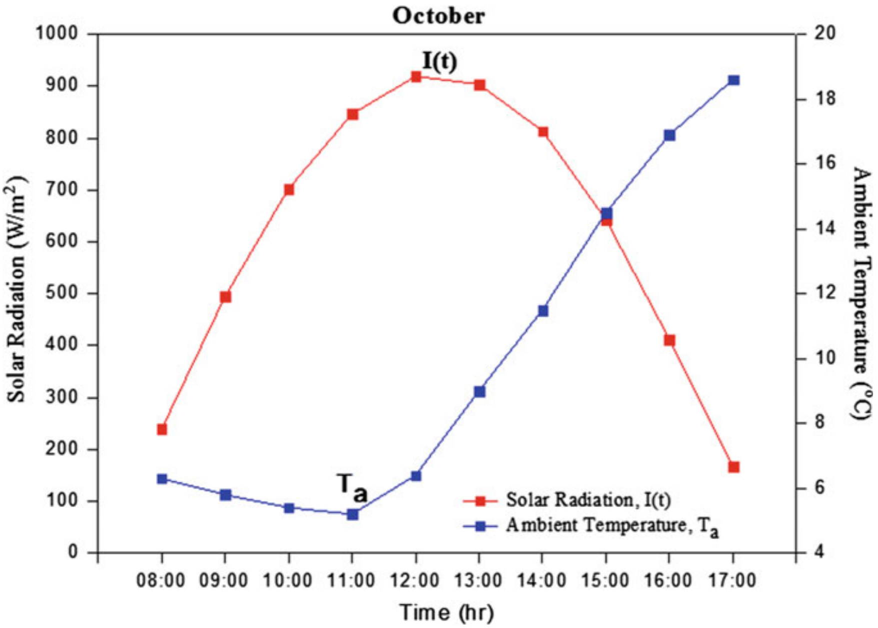

Fig. 2 Variation in solar radiation I(t) and ambient temperature T_a with time for the month of October (IMD Pune data for Srinagar)

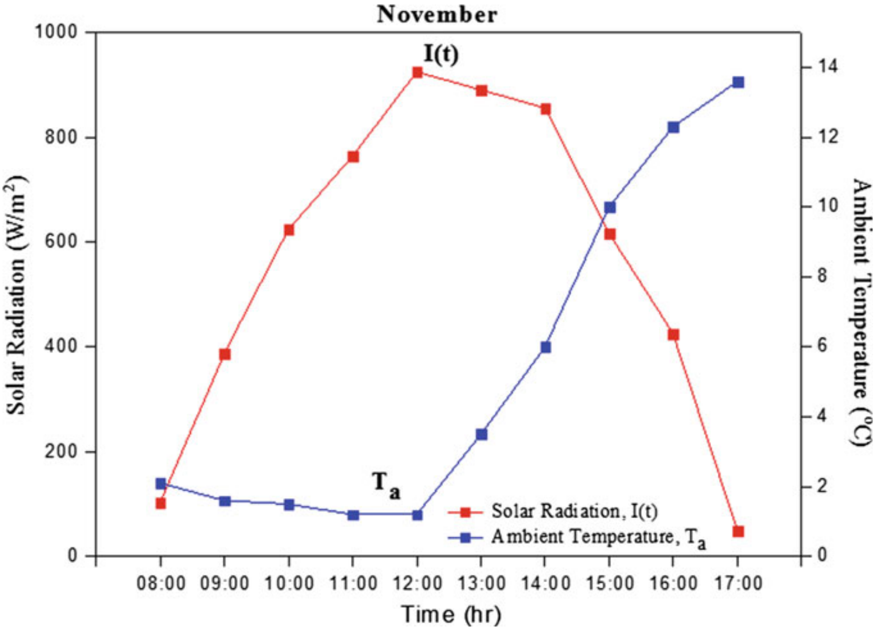

Fig. 3 Variation in solar radiation I(t) and ambient temperature T_a with time for the month of November (IMD Pune data for Srinagar)

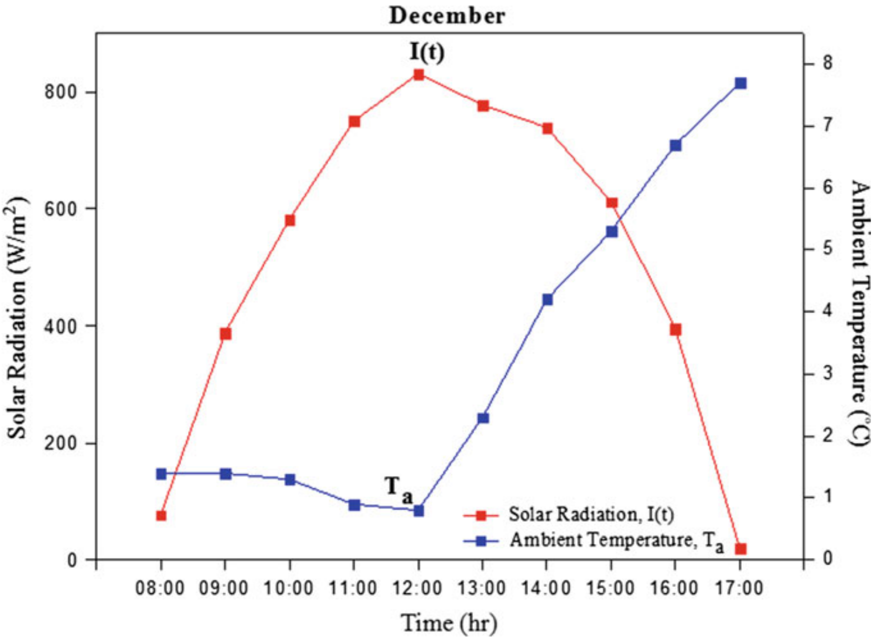

Fig. 4 Variation in solar radiation I(t) and ambient temperature T_a with time for the month of December (IMD Pune data for Srinagar)

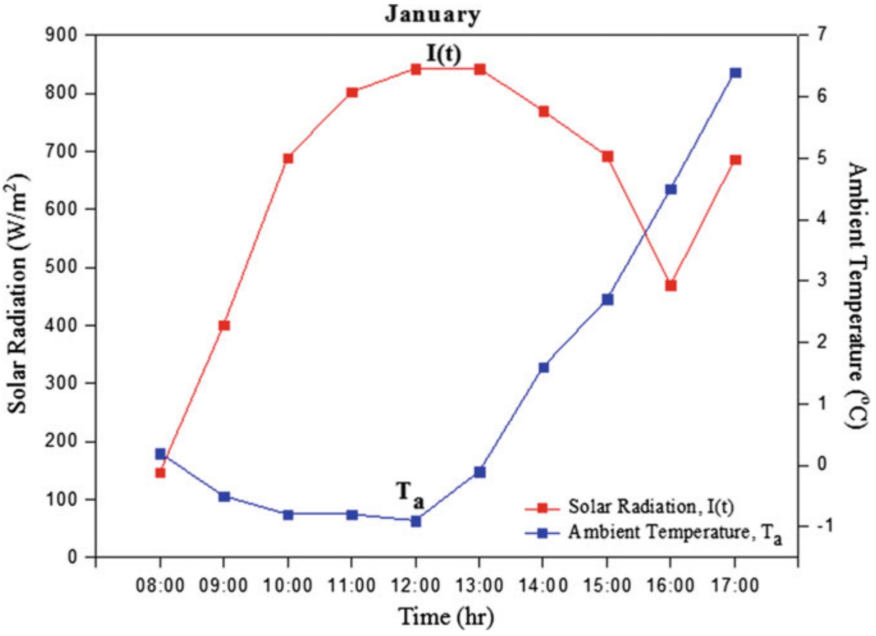

Fig. 5 Variation in solar radiation I(t) and ambient temperature T_a with time for the month of January (IMD Pune data for Srinagar)

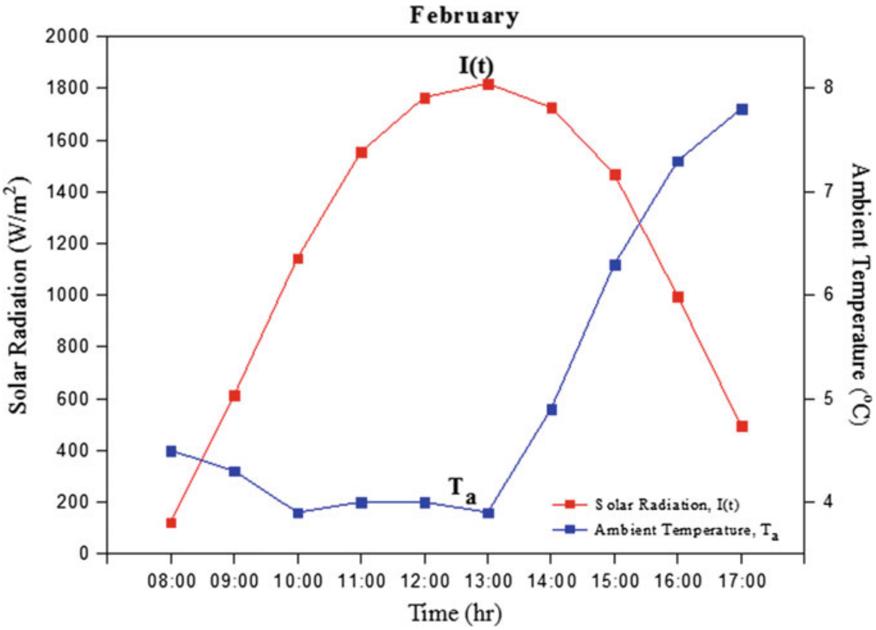

Fig. 6 Variation in solar radiation I(t) and ambient temperature T_a with time for the month of February (IMD Pune data for Srinagar)

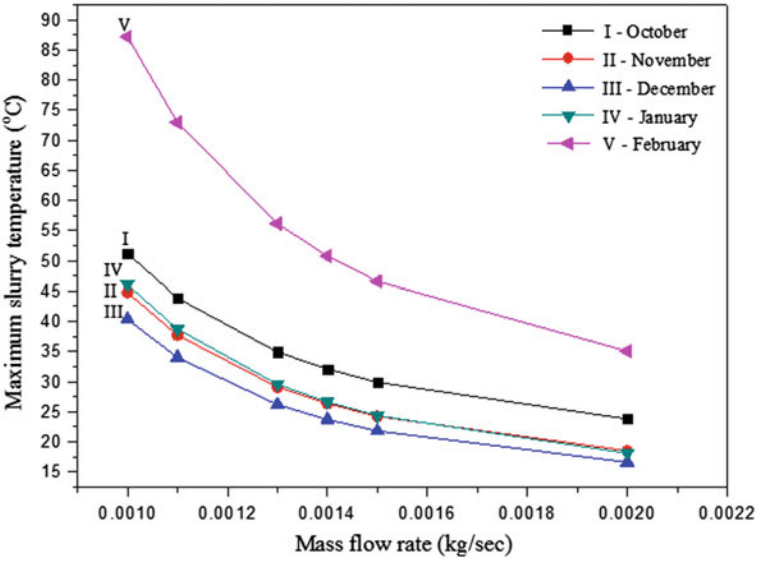

Fig. 7 Variation in T_{smax} (maximum slurry temperature, °C) with mass flow rate (other parameters M_s = 2500 kg, L = 5 m and N = 5 kept constant). NN stands for number of clear days for a specific month

slurry temperature of 32–37 °C for each month starting from October till February. For each month T_{smax} values have been plotted against the mass flow rate $(\dot{m}_f)$ which has been varied from 0.001 to 0.002 kg/s by keeping the other parameters constant (M_s = 2500 kg, L = 5 m, N = 7). Where M_s is the mass of the slurry (kg), L is the length of the heat exchanger (m) and N is the number of clear days. It can be clearly seen from Fig. 7 that all the five curves (I, II, III and IV and V) show a decreasing trend with an increase in the value of $\dot{m}_f$ (kg/s). On the basis of the above discussion the mass flow rate which is a very critical parameter has been optimized for the months of October to February for Srinagar, Kashmir (India). The optimised mass flow rate of slurry $(\dot{m}_f)$ for the month of October is 0.0014 kg/s, November is 0.0011 kg/s, December is 0.0011 kg/s, January is 0.0011 kg/s and February is 0.002 kg/s.

5 Recommendations

The above study has been carried out for the winter season that is for the months of October till February. In a similar manner the mass flow rate of the slurry $(\dot{m}_f)$ can be optimised for the remaining months of the year for Srinagar as well as for other regions in the country.

6 Conclusions

The study has been done for the months of October to February by using IMD Pune data for Srinagar. It was found that the new design of N-FCPIB system showed much better thermal performance than a simple biogas plant.

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Synthesis and Characterization of Biodiesel from *Simarouba glauca*

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Abstract B*iofuel* is produced from biological resources such as plants and animal origin, rather than a fuel produced by geological processes. It is involved in the formation of fossil fuels, such as coal and petroleum which is from prehistoric biological matter. Many researchers are working in the area of synthesis and characterization of biodiesels using non edible oils in the globe. In the present work an attempt is made to prepare the biodiesel from *Simarouba glauca* non-edible oil and its properties have been presented in this paper. Simarouba seeds contain 23% of oil with seed to kernel ratio of about 3:1. The oil containing FFA 7.85% was converted into biodiesel by two stage process. The first step, acid catalyzed esterification process to reduce FFA below 3%. In the second stage, transesterification process was carried out using NaOH and Methanol. During this experiment the maximum yield of biodiesel was obtained 6:1 molar ratio of methanol to the oil. The acid value of the biodiesel was found to be 0.28. The oxidation stability of the Simarouba biodiesel (SBD) was evaluated using Rancimat method EN 14112 was to be 3.5 h, cloud point of SBD was found to be 19 °C which may be due to the higher saturated fatty acids in the bio diesel. SBD obtained was found to be comparable with the ASTM and BIS specifications.

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1 Introduction

Biodiesel is an alternative fuel which encourages rural employment and economic development of rural sector, to develop long term replacement of fossil fuels, to reduce the petroleum import and to increase the energy security [1]. The higher production charges of biodiesel is the main barrier for the commercialization, even though it has a lot of advantages [2]. The cost of feed stock accounts for 70–95% of total biodiesel production cost [3–6]. The non edible oils can be alternative source to improve the economy of biodiesel production commercial scale.

Simarouba (*Simarouba glauca*), commonly known as paradise tree belongs to family Simaroubaceae. It is also known as Simaba, Maruba, Lakshmitaru, Dysentry bark, Pitomba etc., in different part of the country. Simarouba is being promoted in the country as the latest wonder tree which is a source of edible oil that has wide utility [7]. Simarouba is a medium sized evergreen tree (height 7–15 m). It is well adapted up to 1000 m altitude in all types of well drained soils (pH 5.5–8). It grows well in the regions with 250–2500 mm annual rainfall and temperatures up to 45 °C [8]. This tree starts bearing fruits from four years of age, but it attains full production at six years of age. The flowers during December and bears fruits in January–February. The fruits are normally harvested during May. The economic yields of about 20 kg fruits per tree can be harvested after about 10 years of planting. The average yield of fruit from a 10 year old plantation of simarouba will be about 6000–8000 kg/ha [9]. The simarouba fruitlets are collected and dried to reduce the moisture content. Simarouba seeds comprising of 60% shell and 40% kernel are preferably decorticated before oil extraction. After decortification, oil is extracted from the kernels by using conventional oil expellers [7]. Since it contains high percentage of oil it may be used in the biodiesel production by transesterification process. Transesterification is process in which triglycerides react with methanol in the presence of catalyst to obtain fatty acid methyl esters (biodiesel) and glycerol.

2 Materials and Methods

Simarouba seed were collected and sun dried to attain constant weight.

Physical Characterization of seeds: 100 seed weight, seed to kernel ratio, seed diameter and length were determined.

Oil estimation: The seed oil and kernel oil content was determined by soxtherm apparatus (Gerhardt, Germany) by means of petroleum ether as solvent. The percent oil content was calculated on weight basis.

Physico-chemical properties of oil: Acid value, saponification value and iodine value were determined as per standard procedure [10]. The density (pycnometer), viscosity (Cannon-Fenske viscometer) of the oil was determined. The fatty acid profile of simarouba oil was done using GC-FID (Agilent 7890 A) using SP2560 fused silica capillary column, 100 m × 0.25 mm × 0.2 μm.

2.1 Biodiesel Production

The seed were collected from different sources and decorticated using seed decorticator the partially decorticated seeds were crushed mechanically by screw press oil expeller (Sardar, India) and oil was filtered. Biodiesel production was carried out by two stage acid-base process using H_2SO_4 as acid catalyst for pre-treatment (acid esterification) and NaOH as base catalyst for transesterification process with methanol.

In the first step, the FFA present in the oil was reduced below 3% by acid esterification process. Conc. H_2SO_4 at a ratio of 5% of FFA (0.05 g H_2SO_4 for every 1.0 g of FFA) was added to methanol in methanol to FFA molar ratio of 40:1. The reaction was carried out in laboratory setup. The pretreated oil was then taken for transesterification process.

2.2 Transesterification of Crude Oil of Simarouba Glauca

Transesterification reaction carried out in a laboratory biodiesel system consisting of 2000 ml three necked flask with a reflux condenser, catalyst dozer and temperature control unit. First, calculated amount of oil was taken in the flask and was heated to essential temperature of 60 °C on a magnetic stirrer with heating controller. Sodium Methoxide was prepared using methanol in the ratio of 1:6 (oil: methanol) and sodium hydroxide (NaOH for neutralization of FFA present in pretreated oil + 3.5 g for catalysis) [11] and was added to the pre-heated oil with continuous stirring. The mixture was briskly stirred and refluxed; the transesterification reaction was carried out for 2 h. After completion of the reaction the mixture was allowed to settle down in a settling tank for overnight, which results in formation of two layers out of which one is said to be as biodiesel layer and the other is glycerin layer. Glycerin formed in the reaction was drained out and the biodiesel was separated washed twice with equal quantity of water and acetic acid to remove the soluble contaminants. Biodiesel was recovered and then heated up to 110 °C until the moisture content was removed completely. It was cooled and filtered, then subjected for further analysis.

2.3 Quality Analysis of Biodiesel

The quality analysis of simarouba was done as per the American society for testing and materials (ASTM) methods: kinematic viscosity by viscometer (ASTM D445), flash point and fire point using Pensky-Martens closed cup apparatus (ASTM D93), copper strip corrosion test using copper strip corrosion apparatus (ASTM D130), cloud and pour point (ASTM D2500 and ASTM D97), and water and sediments using centrifuge method (ASTM D2709), Fatty acid methyl ester content (EN14103) test method. The oxidation stability was tested as per EN14112 test method, density by pycnometer and calorific value by Bomb calorimeter.

3 Results and Discussion

The ripen simarouba seeds were harvested and washed in water to remove the outer pulp. The sundried seeds were taken for further analysis. The seeds were elongated with diameter 8.65 ± 0.5–10.54 ± 0.3 and length 18.15 ± 0.6–21.3 ± 0.7. The hundred seed weighed between 89.88 ± 4.2 and 108.4 ± 5.2. The kernel to seed ratio was found to be 0.42 which indicated that the kernel accounts for 42% that contains oil and husk counts for 58% which does not contain oil. But the husk is required for crushing. It was observed that in the absence of husk, kernel forms into paste during oil extraction by screw expeller. The simarouba kernel contains 59.11% oil whereas whole seed along with the husk contain 23.08% oil.

The property of simarouba oil is specified in Table 1. The acid value of simarouba oil was far above the ground due to presence of free fatty acids (7.85%). The viscosity was also high (49 cSt) which is mainly because of high molecular weight fatty acids. The higher viscosity of oil makes its use in engine limited. Hence transesterification process is carried out to enhance the fuel properties of the oil. It was observed that the oil was in solid state in room temperature (27 °C). This may be because of higher content of saturated fatty acids such as Palmitic (12.3%) and Stearic acid (27.3%) (Table 2). The Gas chromatogram of Simarouba oil is given in Fig. 1.

3.1 Simarouba Biodiesel and Its Quality Parameters

Vegetable oils are made of triglycerides, also known as glyceryl esters of fatty acids. The triglycerides are oxidized into free fatty acids (FFA) during storage. These free fatty acids form soap during transesterification process. If the FFA is more than 3% the recovery of biodiesel is reduced drastically. Hence, an acid pre-treatment is given during which FFAs are converted into biodiesel by

Table 1 The physico-chemical properties of *Simarouba glauca oil*

Properties	Values
Kinematic viscosity at 40 °C (CSt)	49
Density (kg/m^3)	914
Saponification value (mg KOH/g)	184
Iodine value (g/100 g)	54
Acid value (mg KOH/g)	15.7

Table 2 Fatty acid composition of Simarouba oil

Fatty acid	Percentage (%)
Stearic acid ($C_{18:0}$)	27.3
Oleic acid ($C_{18:1}$)	54.6
Palmitic acid ($C_{16:0}$)	12.3
Linoleic acid ($C_{18:2}$)	2.3
Arachidic acid ($C_{20:2}$)	1.2
Erucic acid ($C_{22:2}$)	0.4
Linolenic acid ($C_{18:3}$)	0.2
Saturated fatty acids	39.6
Unsaturated fatty acids	60.4

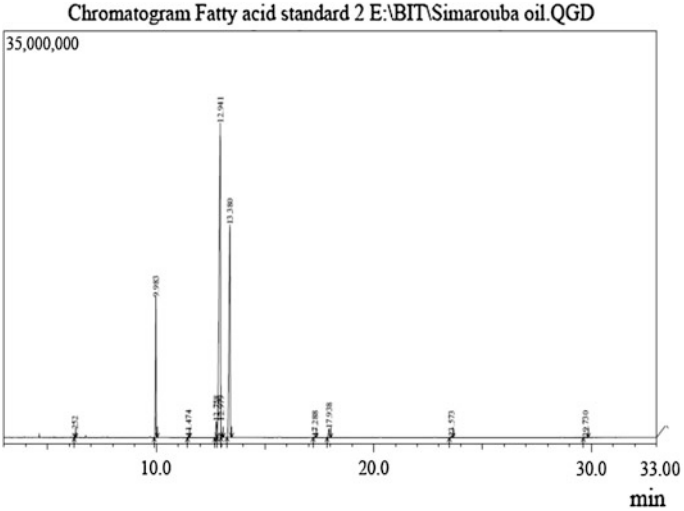
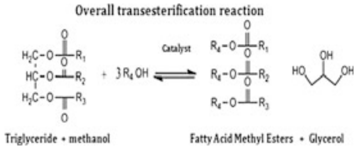


Fig. 1 Gas chromatogram of fatty acid profile in simarouba oil

acid-esterification. Vegetable oils having low FFA content (below 3%) can be converted into biodiesel by direct transesterification.

In transesterification process there is sequence of three consecutive reversible reactions which includes conversion of triglycerides to diglycerides followed by diglycerides to monoglycerides. Finally the glycerides were converted into glycerol and one ester molecule (biodiesel) at each step. The overall reaction is represented below.



As simarouba oil consist FFA 7.85%, acid pretreatment was given prior to transesterification process. By Transesterification process the fuel property of simarouba oil was enhanced. The density and viscosity were reduced from 914 to 871 kg/m^3 and 49 to 5.1 cSt. All among the parameters of biodiesel the viscosity is the one which controls the uniqueness of the injection from the injector in diesel engines because high viscosity leads to unfavorable pumping; inefficient mixing of fuel with air contributes to incomplete combustion which results in increased carbon deposit formation [12].

A comparative account of the properties of simarouba biodiesel with Pongamia and Jatropha is given in Table 3.

Flash point is defined as when a tiny flame is brought near the oil, it gives off enough vapors that ignite for that moment which takes place at low temperature that point is said to be as Flash point. Simarouba oil and SOME having flash point were determined 225 and 165 °C respectively and is compared with diesel. Biodiesel is safe to transport when compared to diesel because the flash point of biodiesel is higher than diesel. Temperature below which biodiesels form a cloudy appearance is referred as Cloud point. The presence of the higher saturated fatty acids like Stearic Acid ($C_{18:0}$) and Palmitic Acid ($C_{16:0}$) may be the reason where Simarouba oil results in having very high Cloud point i.e.19 °C.

Biodiesel fuels are unstable due to natural oxidation process. The oxidation stability of *Simarouba* biodiesels was 3.5 h. The biodiesel failed in oxidation stability test, the reason being biodiesel obtained from the oil are easily attacked by the enzymes and degrade easily whereas, petroleum fuels exhibit extremely long storage stability periods the oxidative stability decrease with increase in poly-unsaturated fatty acids. Giwa et al. [15] reported that the oxidation stability of biodiesel decreases due to increase in unsaturated fatty acids such as Linoleic acid and Linolenic acid esters. Simarouba oil methyl ester which is rich in unsaturated

Table 3 Fuel properties of Simarouba oil methyl esters (SOME) with comparisons of other non edible biodiesel

Properties	SOME	POME [13]	JOME [14]
Kinematic viscosity at 40 °C (cSt)	5.1	9.6	4.32
Density at 15 °C (kg/m^3)	871	876	880.3
Calorific value (kJ/kg)	40	36.12	39.6
Flash point (°C)	165	187	>130
Fire point (°C)	180	–	–
Pour point (°C)	14	7	−1
Cloud point (°C)	19	–	–
Copper strip corrosion test	1a	–	–
Water and sediments	0.02		
Iodine value (g/100 g)	74	–	62
Acid value (mg KOH/g)	0.30	0.31	0.27
Oxidation stability (h)	3.5	3.4	–
% of FAME	96.6	–	98.6

fatty acids this has leaded to lower oxidative stability. However, the oxidation stability of the fuel possibly will be superior by adding antioxidants.

4 Conclusions

Biodiesel play a significant role to restore the fossil fuels. The rural development in India can be improved by huge production of biodiesel by potentially edible tree like Simarouba which could offer opportunity for upcoming generation. The production process is based on the alkaline catalyzed transesterification and can be further improved to get high yield and good fuel quality Biodiesel.

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Preparation of Bio-diesel from Jatropha Curcas Oil and Testing of Its Blends with Diesel on a CI Engine

Abhijeet Dubey, Apurv Pant, Savita Dixit and G. Dixit

Abstract Depletion of oil reserves because of its increased demand led to the search of substitute fuels that had to be environmentally friendly, energy efficient as well as frugal. This is where biodiesel plays an important role. Out of the several other crude oils we chose jatropha because being nontoxic, it delivers a high oil content in its category i.e. non-edible, one of the major limitations of the globe, having such a population increase. Out of several catalysts with their concentration ranges, a number of experiments were accomplished for the suitable catalyst with its optimized concentration and several other reaction parameters for a two-step transesterification process were fixed. The blends of jatropha methyl ester and diesel blended in different volumetric ratios and was analysed with diesel fuel by testing on a single cylinder 4-stroke Kirloskar CI Engine. Engine parameters and emission characteristics were obtained using software Engine Test Express V5.0 by Legion Brothers and AVL DITEST 1000 XDS Gas Analyser respectively. As the fuel was tested on the engine, blends of biodiesel gave better outcomes in terms of exhaust emission and several engine parameters. The decrement in the brake specific fuel consumption was noted while at that position was an appreciable increase in terms of indicated power, mechanical efficiency, heat dissipated rate etc. as compared with diesel fuel. In terms of emissions, HC and CO emissions are found to be similar with a minor increase in NOx emissions as compared to diesel. Fuel properties and results obtained from diesel engine showed that B20 blend of jatropha methyl ester in diesel can be an alternative for diesel fuel without changing the engine setup. Good quality at a low price is difficult, but the most desired combination seems to be achieved by the results obtained.

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1 Introduction

Keeping global ecosystem as the main concern for sustainability, it urges to propose fuels with characteristics similar to petroleum fuels. These alternatives are very much similar to diesel in their properties so the prepared fuel is termed as bio-diesel and to be tested on CI engine.

2 Problem Identification and Basic Principle

The major problem of using non-edible oils in crude form is their high viscosity when compared to diesel. This leads to problem such as choking of diesel injector nozzle, gel formation which leads to sticking on piston oil ring. Therefore two methods are used: trans-esterification with methanol or ethanol and cracking process for their conversion into bio-diesel fuels (Fig. 1).

3 Methodology [1]

The oil is extracted from the vegetable oils through the trans-esterification process in which one form of ester is converted into another form. This reaction may or may not employ a catalyst in the conversion process. In this reaction the glycerol based triesters are converted into monoesters thereby generating free glycerol as a by-product.

$$\text{Triglycerides} + \text{Monohydric alcohol} \rightarrow \text{Mono-alkyl esters} + \text{Glycerol}$$

Fig. 1 Jatropha oil and diesel

It is evident from the above reaction that bio-diesel fuels consist of a mixture of trans-esterified free fatty acids of high molecular weight. Typical chemical syntheses of bio-fuels are reported in the literature based on the distribution of the fatty acids in their corresponding vegetable oils.

This reaction is done through two-step transesterification process…

1. **Double-step transesterification process**: In this process crude oil is first processed through acid catalysed transesterification and then by base catalysed transesterification. So this process is better suited for the oils having high content of fatty acids, like in our case, jatropha crude oil.

In this process the crude oil is at first treated with acid catalysed reaction, for reduction in fatty acid content and then is further processed with base catalysed reaction.

- **Acid catalysed transesterification** [2]: Acid catalysed reaction is used for the crude oils containing high amount of fatty acids. In this reaction process, methanol is added to the preheated crude oil along with catalyst like H_2SO_4 (98% pure).
- **Base catalysed transesterification** [3]: Base catalysed reaction is used very often commercially for bio-diesel production. This reaction is best suited for low fatty acid oils, thus methanol is added to the reacted mixture obtained after acid catalysed reaction along with the catalyst such as strong base NaOH/KOH. The reaction of oil with methanol with the help of catalyst is termed as alcoholysis. This reaction is faster than the previous one (Fig. 2).

4 Reaction Process

At first we were with the range of composition in case of acid and base catalyzed reaction. It took months to find:

I. Correct ratio of methanol with acid and base.
II. Reaction time.
III. Rpm required.
IV. It's settling time.

Thus the following procedure we obtained:

- 1st Step acid catalyzed reaction process:
    1. Preheat the selected amount of oil in a round bottom flask at 65 °C for 10 min to remove moisture content.
    2. Now prepare a mixture of 20% methanol (v/v) and 2% H_2SO_4 (v/v).
    3. Mix it slowly with the heated oil.

Fig. 2 Glassware Jatropha oil production set-up

4. Start the reaction on a heater with magnetic stirrer at 500 rpm with temperature 55 °C below the boiling point of methanol.
5. Apply the condenser over the round bottom flask so as to condense evaporated methanol.
6. The reaction time will be 90 min.
7. Now allow the reaction mixture to cool.
8. Let the mixture separate in a separating funnel overnight.

- 2nd Step base catalysed reaction process:

9. Now drain the free fatty acids in the form of glycerol the other day.
10. Now weigh about 0.5% (w/v) NaOH flakes using weigh balance.
11. Mix it with 25% (v/v) methanol.
12. Add it to the obtained treated oil and heat it for 90 min at 500 rpm and 55 °C.
13. Apply the condenser.
14. Now let the mixture separate for 24 h.
15. Separate the remaining amount of fatty acids.

Fig. 3 Bio-diesel production unit MANIT

- **Washing** [3]:

16. Now washing needs to be done for the removal of small amount of gums or fatty acids if present.
17. Go for repeated washing until clear water is obtained.
18. Now heat the mixture.
19. Thus obtain jatropha methyl ester (Fig. 3).

The testing of bio-diesel is in process and the results are expected to suggest jatropha bio-diesel might be a good alternative for diesel with lower emission values.

5 Results and Discussions

The viscosity of crude oil is then decreased near to conventional diesel to make it preferable for use in diesel engine and thus determine the performance of engine with proposed fuels. In this study, viscosity was decreased by (i) preheating oil (Jatropha oil) and (ii) by blending Jatropha methyl ester with diesel.

The performance and emissions tests are performed with diesel, and blends of Jatropha methyl ester at different loads and constant speed (1500 rpm). Number of

Table 1 Physical properties

Properties	Unit	Jatropha oil	Jatropha methyl ester	Diesel
Density (300 K)	kg/m^3	918	901	840
Viscosity (313 K)	mPa	42.4	5.73	3.29
Flash point	K	468	445	333
Fire point	K	484	463	356
Calorific value	MJ/kg	33.2	37.8	42

tests are to be done and results to be analysed for the emissions, in order to compare the blend with the diesel.

As the results depicted, blend of jatropha methyl ester with diesel is obtained to be an alternative fuel for diesel engines. It can be used as straight vegetable oil for alternative of diesel fuel and may not reflect need for any modification in the engine (Table 1).

6 Conclusions

Jatropha methyl ester and diesel were characterized for their vast physiochemical properties and were found resembling. Viscous property of jatropha methyl ester blends (till 30%) was found near to diesel. Emission parameters for smoke opacity, CO_2, CO, and HC increases with rising proportion of jatropha methyl ester blends compared to diesel.

Therefore, blends of jatropha methyl ester can be used in diesel engines and thus it can be used as an alternative for diesel villages for farming and water supply at first. Timed servicing may be required to control carbon deposits on usage of jatropha methyl ester blends.

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Indian Energy Sector and Analysis of Potential of Bioenergy in India

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Abstract India faced serious challenges in achievement of energy security, because it is not able to provide adequate energy in a sustainable manner to its rising population. India needs energy for maintaining 8% GDP growth for next 25 years which is necessary for eradication of poverty and achievement of its human development goals. But in reality the energy reserves in India are not sufficient to meet the rising energy demand specifically for oil. In 2014–15, India imported 189 MT of crude oil which is 80% of its oil requirement. The gap will be widening in future because of high growth rate and limited scope in expansion of domestic oil production. Continuous increase in consumption of petroleum products has been a matter of great concern because out go of foreign reserves and rising GHGs emmisions. Liquid biofuels may be an option for replacement of oil in transport sector. Bio-ethanol is used a substitute of gasoline could also be produced from lignocellulosic biomass has significant importance for India. Because in India, more than half of the geographical area is under agricultural cultivation, and nearly 22% area is covered with forest. It is the biomass inventory for supply of feedstock and may use in the production of bio-ethanol. The Objective of the present study is to calculate the surplus quantity of biomass from various sources and their respective energy potential. It is calculated that agriculture and industrial wood production totally generated around 1011 MT of residues per annum. After meeting the competing uses the remaining surplus has the energy potential of nearly 5.6 EJ. The information generated in this paper might be useful for the understanding the current and future energy consumption pattern and help in deriving the suitable policy for energy independency.

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Abbreviation

CAGR	Compound annual growth rate
EJ	Exa joule
GW	Gigawatt
LC	Lignocellulose
MT	Million ton
MW	Megawatt
Mha	Million hectares
Mtoe	Million ton oil equivalent

1 Introduction

1.1 Energy Status of India

India recognizes as the fastest growing economy with consumption of the (872 Mtoe) or (37 EJ) of energy which is third largest in the world [1]. The demand for energy is very high due to fast growth in GDP and population. Migration from rural to urban area is primary cause of changing in consumption pattern and make contribution in rising energy demand. In a year 2014 the energy consumption is 7.1% more than the previous year. It is the largest ever increase in consumption which is recorded previously and it leads India to the point where it accounts for the 34.7% of global consumption increment [2]. The large difference in per capita energy consumption in India (0.58 toe) from OECD region (4.8 toe) and world average (1.8 toe) show that there is immense scope for increase in energy demand [3]. Energy is very needed for sustaining the growth and development process continue and India needs to maintain 8–10% GDP growth rate over the next 25 years for eradication of poverty and to achieve its human development goals but the task is seems to very difficult because of huge reliance on the imported energy. India must be increase its primary energy supply by 3–4 fold to 2030–31 from 2003 to 04 level for achievement of its growth objective and fulfilling the energy needs of rising population [4].

2 Major Supply Sources

2.1 Coal

Coal is the primary electricity generation source in India. India produces nearly 8% of world's coal [5]. The estimated reserves of coal in India are 302 billion tones [6]. India is self-dependent for satisfying domestic coal requirement for power generation. 78% of domestic coal is directed towards the electricity generation and 50% of commercial energy requirement is met by the coal [4]. Coal using thermal power plants accounts 57% of total power generation capacity in India. The consumption of coal is on the rise from years and it is reaches up to 791 MT in 2013 from 140 MT in 1984. Increase in India's coal consumption was largest in world (+35.9 Mtoe) in 2014 and makes it world's third largest market for coal [2]. The metallurgical coal is imported and in 2013 it is 178 MT [5]. This import is likely to rise in the future because in metallurgical coal India is not self sufficient due to high ash content and low calorific value [4].

2.2 Oil

Oil is the primary fuel for transportation sector but India is short in oil supply. The demand for oil is around 3727 thousand barrel per day but the domestic production is limited to nearly 894 thousand barrel per day [7]. The domestic production of oil is declining from five consecutive years and in 2014 it is lowest and count only to the 23.2% of its current oil requirement [2]. The production of crude oil is declining from years but the consumption is going on rise with the CAGR of 6.14% during 2005–06 to 2013–14 [6]. For meeting its growing oil needs India heavily relied on the imported crude oil which is currently 189 MT which make up the 80% of total demand and costs 112.75 USD [8]. The share of India in global oil demand will be rose up to 8% in 2035, and the Oil imports will be increase up to 161% more than the present level which has the share of 61% in total imports [9] as country expands its transportation sector and logistics (Fig. 1).

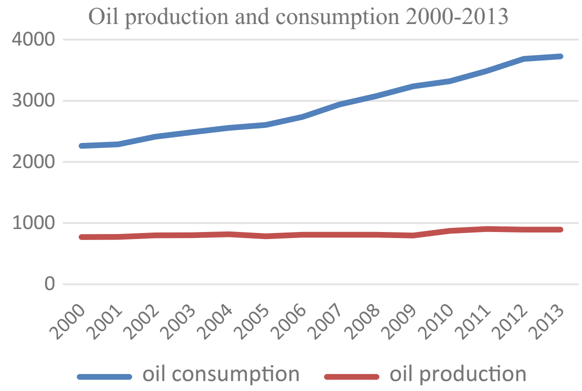

Fig. 1 India's oil production and consumption 2000–2013 (Thousand barrels per day). *Source* BP

2.3 Natural Gas

Natural gas is the fossil fuel which may use in fueling vehicles, cooking food and power generation. In India the maximum use of Natural Gas occurs in fertilizer industry (32.56%) followed by power generation (31.02%) and (8.60%) as used for domestic fuel. India's natural gas production is at peak in 2011 but declined after by 20.3% in 2014 [2]. However this fall is not pretty alarming due to its low CAGR which is 1.12% over the period of 2005–06 to 2013–14. There is very huge reserves of natural gas are found in India (1427.15 BCM) on the eastern offshore [6]. In 2035 the demand for natural gas will be increase and rose up to +145% for the current level and replace the coal and oil in power and transpiration sectors but dominancy of both is maintained [10].

2.4 Renewable Energy

Renewable energy is the very important source of energy for India as it helps in diversification of energy resources and also eco-friendly in nature. India has the separate ministry for the renewable energy which is engaged in executing the several projects and planning of renewable based energy production. The total installed capacity of renewables in India is 31,692 MW out of which wind has the largest share of 66% and biomass has 12% share. In 2014 the potential of biomass is 17,538 and 5000 MW from bagasse based cogeneration in sugar mills represents the 15% share of total renewable potential for power generation [6].

2.5 Future Energy Demand and Supply Scenario

India's population is 1.24 billion in 2011 and it is projected that it can take over china in 2025 [11]. India's share in global energy demand rose up to 8% in 2035. Population growth and increases in income per person are the key drivers behind growing demand for energy. Demand is increased for all type of fuels but the gas is at the top by +145% increase, oil demand rose by +117% but demand for coal is slightly behind them and raise up to +112% from the current level this is because of penetration of gas and renewable in power sector. The production to consumption share of India's energy declined by 59–56% and created the gap in supply and demand. The gap is primarily filled by the imports which are rise to 143% from the current level. The energy mix of India evolves very slowly over decades with dominancy of fossil fuels. The fossil fuel met 87% of energy demand which is higher than the global average but it is 5% less from the today's level. The oil dominates in the transportation sector while coal is dominated in power sector but the demand is increased for renewable energy (+564%) [10].

2.6 *What the Big Picture Says?*

The rising energy demand with limited reserves, rising population, global oil politics, wars, increasing energy imports and environmental concerns generate the motivation for shifting towards the renewable resources. It is very needed for India to maximally developed there domestic supply option as the need of diversification of energy resources for energy security is very high. It is clear by the overview of India's energy mix, that coal is in sufficient quantity and, the less CAGR of natural gas and its newly discovered proven reserves in India is sufficient for meeting its demand in future but, the overview of oil sector tells that India has huge dependency on imported oil for their transport sector requirement. It imports 80% of the currently required crude oil in 2014–15 which is 189 MT in quantity and cost USD 112.78 billion [8]. The situation is get critical due to granting of subsidy by the government which is necessary for keeping oil price low for providing cheap transportation to public and industrial sector. Subsidy creates the heavy burden on the government and they are unsustainable in the long run. The situation will be worsened in future because the gap in demand and supply is tending to increase more. For the avoidance this situation and reduce its impact there is an option for India in the form of biomass because it is a country with ample quantity of biomass due to its vast agriculture and forest cover. Biomass resources can be diverted to the liquid biofuels production which is a good source for cutting the fuel subsidy, slowing down the carbon emission and ensuring the energy supply. So the focus is in this paper is on the potential of biomass energy for production of LC-ethanol.

3 Biomass as an Alternate Source of Energy

Biomass is an organic matter produced by plants and animals. Plant is the only organisms which is capable in trapping the solar energy and convert it into the material. Being a product of natural resources biomass is renewable in nature. Plant captures CO_2 from the atmosphere and converts into sugars by photosynthesis. After combustion of biomass it release $CO_{2,}$ it is closed carbon cycle and in very short time the cycle is completed [12]. Biomass contributes 14% of the total energy supply worldwide and 38% of this energy is consumed in developing countries, mainly in the rural and traditional sectors [13].

3.1 *Biomass Uses in India*

3.1.1 Traditional Use

69% population in India is lived in rural areas [14] and out of this 86% is dependent on the traditional fuels (Table 1) 62.5% on firewood, 12.3% crop residue, and

Table 1 India households by primary fuel used for cooking [16]

Fuel type	Total	Rural	Urban
Firewood	49.0	62.5	20.1
Crop residue	8.9	12.3	1.4
Cow dung cake	7.9	10.9	1.7
Coal, lignite, charcoal	1.4	0.8	2.9
Kerosene	2.9	0.7	7.5
L.P.G/piped natural gas	28.5	11.4	65
Electricity	0.1	0.1	0.1
Bio-gas	0.4	0.4	0.4
Any other	0.5	0.6	0.2
No cooking	0.3	0.2	0.5

10.9% use dung as primary fuel but on the other hand only 3% urban households use crop residue or dung and only 20% use firewood as primary energy for cooking fuel. 5% of the households in rural areas and 44% in the urban areas have access to the LPG. Other source of energy is kerosene used by 22% urban households and only 2.7% of rural households [15].

3.1.2 Modern Uses of Biomass

The biomass may be used in the power generation and for the production of liquid biofuels. India has 3.8 GW utility based installed capacity in biomass sector and bagasse-based cogeneration in mid-2014. According to MNRE there are 18 GW electricity generation capacities in biomass and additional 5 GW comes from the biomass bagasse [16]. The lignocellulosic biomass from plants can be converted into ethanol which can be used in blending with the gasoline [17]. The feedstock for production process is can be a residue from crop, wood and dedicated energy crops like Miscanthus, crysanthium etc. [18].

3.2 Potential of Biomass for Lignocellulosic Ethanol

Despite the dominant traditional use of biomass in the form of wood fuel for heat generation, the liquid biofuel production has shown rapid growth since last decade with 45% per annum in OECD regions [19]. Liquid biofuel consumption is fairly low in India and mostly generated by the states that mandated the 5% blending of ethanol in gasoline [16]. The rising demand of liquid biofuels discover important role of biomass for energy production and, its importance for the transport sector.

Table 2 Land use in India[a]

Total geographic area	328.73	% of total
Reporting area for land utilization	305.57	100.0
Forests	69.97	22.9
Not available for cultivation	41.98	13.74
Permanent pasture and grazing land	10.48	3.43
Land under miscellaneous tree crops and groves	3.38	1.11
Cultivable wasteland	13.24	4.33
Other fallow land	11.31	3.70
Current fallows	14.49	4.74
Net area sown	140.71	46.05

Source [21]

[a] Land use area in million hectares percentage

3.2.1 Natural Conditions for Biofuel Feedstock Production

India is very diverse country; geographically it has the large area of mountains, dessert, plains and myriad river systems which means a large portion of the land is good for agriculture. The climatic condition is varied from region to region; temperature is high all over the country except at the higher altitude and diversified land like alluvial soil which covers almost a quarter of total land area founded in northern region. Black soil found in Deccan plateau and is good for cotton, red soil of southern peninsula is well suited for rice production [20]. So India can support the wide range of varieties of agriculture production. More than half of the geographical area is under cultivation (Table 2) with reported forest cover of 22% the net sown area is 46% land under miscellaneous tree and crops is 1% and cultivable waste land is 4%. The statistics [21] show that, the wheat straw, rice straw, sugarcane bagasse etc. and residue from corn, sorghum and millets other crops is primary potential feedstocks for the production of lignocellulosic ethanol.

4 Methodology

The statistics on crop production is available on the Ministry of Agriculture website. It is the primary government website which gives the precise and accurate data on the crop production. The average of five years production quantity is taken in this study for minimizing the yearly fluctuation. The data of the production of industrial wood is taken from the FAO. The process of calculation of energy potential is break in four steps.

- The first step is selection of biomass which is taken in account for the study.
- The second step is calculating the gross residue generation from the RPR (Residue to Production Ratio). RPR gives the amount of residue generated for per kg of crop produce.
- The third step is about the calculation of the surplus residue from the gross residue.
- In fourth step the energy potential is calculated by multiplying combustion heat of selected material with the surplus residue.

The detailed procedure is discussed in the further related steps.

4.1 Selection of Biomass

The biomass selected for the study is belonging from the two broad categories named as crop residues and wood residues. Crop residue is the by-product of cropping system and wood residue is a residue which is left after manufacturing of industrial wood. There is limited data for complete biomass availability but the data on the agricultural output and industrial wood production is available. The selected biomass for this study is grouped into the seven categories named as:

Cereal: *Wheat, Rice, Ragi, Small Millets, Jowar, Bajra Barley and Maize*.
Pulses: *Arhar, Gram, Massor, Moong, Urad*.
Oilseeds: *Mustard and Rapeseed, Niger, Groundnut, Til, Soybean, sunflower, safflower*.
Horticulture and spices: *Arecanut, Banana, Coconut, Cardamom, Coriander, Cumin, Onion, Potato, Tapioca and turmeric*.
Other: *Cotton, Jute and Mesta* (Tables 3 and 4).
Sugarcane.
Wood: *Residue left after industrial manufacturing*.

4.2 Estimation of Quantity

4.2.1 Gross Residue

Gross residue potential is the total amount of residue produced. For calculating the quantity of gross residue the 2 parameter is taken in the study, first is the total production of the *crop (α)* and second is *RPR (α)* which may be same or different for each crop. In the (1) the *CR (α)* is the quantity of crop residue generated by the *crop (α)*, *RPR (α)* is the residue to production ratio of the *crop (α)* and *P (α)* is the quantity of production of the *crop (α)*. The estimation of biomass of fronds bearing crops like coconut and other is taken as the fronds generated in ton per hectare.

Table 3 Agricultural Residues and their Energy Potentials

Crops	Residue	RPR	Area (Mha)	Crop production (MT/year)	Biomass generation (MT)	Biomass surplus (MT/year)	Heating value MJ/kg	Power potential in Joule in a year
Arecanut	Fronds	3	0.43	0.57	1.72	0.60	18.10	1.09142E+16
Arecanut	Husk	0.8	0.43	0.57	0.46	0.16	17.90	2.87828E+15
Banana	Residue	3	0.79	27.49	82.46	28.85	12.31	3.55142E+17
Cardamom	Stalks	0.64	0.09	0.02	0.06	0.05	12.32	5.68616E+14
Coriander	Stalks	1.15	0.48	0.40	0.46	0.05	12.34	5.71673E+14
Cumin seed	Stalks	1.55	0.59	0.34	0.53	0.43	11.34	4.82134E+15
Dry chilly	Stalks	1.5	0.79	1.26	1.88	0.20	12.30	2.49573E+15
Onion	Stalks	0.05	0.96	15.02	0.75	0.08	13.20	1.0586E+15
Potato	Leaves	0.76	1.89	40.03	30.42	6.07	13.28	8.06015E+16
Potato	Stalks	0.05	1.89	40.03	2.00	0.54	12.33	6.70803E+15
Tapioca	Stalks	0.75	0.22	7.98	5.98	4.19	12.31	5.1525E+16
Turmeric	Stalks	0.3	0.19	0.95	0.28	0.14	12.27	1.75255E+15
Coconut	Fronds	4	21.37	15.60	85.48	42.66	10.00	4.26631E+17
Coconut	Husk and pith	0.53	21.37	70.52	37.38	18.69	19.40	3.62548E+17
Coconut	Shell	0.22	21.37	70.52	15.51	11.02	19.40	2.13728E+17
Total potential from spice and horticulture					**265.39**	**113.73**		**1.52194E+18**
Castor	Husk	0.10	NA	1.67	0.17	0.08	14.40	1.20081E+15
Castor	Stalks	4		1.67	6.68	3.34	14.40	4.80672E+16
Groundnut	Stalks	2	5.50	7.04	14.08	2.21	14.40	3.18727E+16
Groundnut	Shell	0.3	5.50	7.04	2.11	1.29	15.56	1.99989E+16
Linseed	Stalks	1.47	NA	0.15	0.22	0.02	14.35	3.19522E+14

(continued)

Table 3 (continued)

Crops	Residue	RPR	Area (Mha)	Crop production (MT/year)	Biomass generation (MT)	Biomass surplus (MT/year)	Heating value MJ/kg	Power potential in Joule in a year
Mustard and rapeseed	Stalks	1.8	6.21	7.43	13.37	6.06	17.00	1.03102E+17
Niger seed	Stalks	1	NA	0.10	0.10	0.01	14.35	1.04328E+14
Safflower	Stalks	3	NA	0.15	0.44	0.35	13.90	4.90347E+15
Soyabean	Stalks	1.7	9.96	11.90	20.23	6.68	16.99	1.13566E+17
Sunflower	Stalks	3	1.16	0.71	2.13	0.31	17.53	5.50672E+15
Til (Sesamum)	Stalks	1.2	NA	0.72	0.86	0.20	14.35	2.88004E+15
Total oil potential					**60.40**	**20.57**		**3.31522E+17**
Sugarcane	Tops and leaves	0.05	4.70	337.80	16.89	3.17	20.00	6.33307E+16
Sugarcane	Bagasse	0.33	4.70	337.80	111.47	56.14	20.00	1.12277E+18
Sugarcane potential					**128.36**	**59.30**		**1.1861E+18**
Bajra	Stalks	2	8.67	9.03	18.06	2.88	18.16	5.22784E+16
Bajra	Cobs	0.33	8.67	9.03	2.98	1.41	17.39	2.45163E+16
Bajra	Husk	2	8.67	9.03	18.06	4.31	17.48	7.53865E+16
Barley	Stalks	1.3	0.23	1.64	2.13	0.22	18.16	3.95784E+15
Jowar	Cobs	0.5	7.03	6.10	3.05	1.14	17.39	1.98315E+16
Jowar	Stalks	1.7	7.03	6.10	10.37	1.24	18.16	2.24288E+16
Jowar	Husk	0.2	7.03	6.10	1.22	0.58	17.48	1.01467E+16
Maize	Stalks	2	8.49	21.35	42.69	8.29	17.39	1.44177E+17
Maize	Cobs	0.3	8.49	21.35	6.40	2.39	17.39	4.15603E+16
Paddy	Straw	1.5	43.42	100.45	150.68	30.74	15.54	4.77673E+17
Paddy	Husk	0.2	43.42	100.45	20.09	13.00	15.54	2.0209E+17

(continued)

Table 3 (continued)

Crops	Residue	RPR	Area (Mha)	Crop production (MT/year)	Biomass generation (MT)	Biomass surplus (MT/year)	Heating value MJ/kg	Power potential in Joule in a year
Ragi	Straw	1.3	1.49	1.91	2.49	2.09	18.16	3.79163E+16
Small millets	Stalks	1.2	0.84	0.43	0.51	0.05	18.16	9.32698E+14
Wheat	Stalks	1.5	29.04	90.33	135.49	23.48	17.15	4.02695E+17
Wheat	Pod	0.3	29.04	90.33	27.10	12.16	17.39	2.1154E+17
Total grain					**441.33**	**103.98**		**1.72713E+18**
Arhar	Stalks	2.5	3.82	2.83	7.08	1.14	18.58	2.10983E+16
Arhar	Husk	0.3	3.82	2.83	0.85	0.42	18.58	7.8667E+15
Gram	Stalks	1.1	8.41	8.35	9.19	1.71	16.02	2.74276E+16
Masoor (lentil)	Stalks	1.8	1.49	1.02	1.84	0.28	14.65	4.08303E+15
Moong	Stalks	1.1	1.35	1.38	1.52	0.15	14.65	2.22387E+15
Moong	Husk	0.15	1.35	1.38	0.21	0.06	14.65	8.55179E+14
Urad	Stalks	1.1	1.52	1.67	1.84	0.20	15.00	2.94287E+15
Urad	Husk	0.2	1.52	1.67	0.33	0.16	15.00	2.38025E+15
Total pulse potential					**22.84**	**4.11**		**6.88778E+16**
Cotton	Stalks	3.8	11.10	4.51	42.18	26.03	17.40	4.52836E+17
Cotton	Husk	1.1	11.10	4.51	4.96	3.06	16.70	5.11176E+16
Cotton	Bollshell	1.1	11.10	4.51	4.96	3.06	18.30	5.60151E+16
jute	Stalks	2	0.89	1.92	3.84	0.48	19.70	9.46585E+15
Meshta	Stalks	2	0.89	0.11	1.61	0.16	12.33	1.97881E+15
Meshta	Leaves	0.05	0.89	0.11	0.04	0.00	11.33	4.54861E+13
Total others					57.59	32.79		5.71459E+17
Total crop residue potential					**975.91**	**334.48**		**5.407E+18**

Table 4 Residue left after industrial manufacturing

Wood use in India in MT	Wood residue MT	Energy density by volume MJ/kg	Energy in joule
35.24	**14.098**	**18.6**	**2.11E+17**

$$CR(\alpha) = RPR(\alpha) \times P(\alpha) \tag{1}$$

The wood residue quantity is calculated by the general assumption is that 40% of all industrial wood is waste as residue [22]. For calculation of wood residue only industrial wood taken in consideration which is available in volumetric terms. The density of wood residue which is considered for calculating its weight is taken 380 kg/m^3.

$$WR = IW \times (40 \div 100) \tag{2}$$

4.2.2 Surplus Residue

The surplus residue is the residue left after meeting the competing use of gross residues. Surplus residue is only available for the bioenergy production. In this study the data available from the BRAI [23] (biomass resource atlas of India) which is the project of MNRE and executed by the CGPL (Combustion, Gasification and Propulsion Laboratory) of IISc. Bangalore is used to calculate the fraction of residues. There is limited literature is available on competing uses of the crop residues so, for calculating the availability of surplus the percentage availability is calculated by BRAI database by assuming that there is no significant change in pattern of competing uses of residues since 2004 and the present production of surplus residue is in the same ratio to the gross ratio as in 2004. The θ(α) is the % of surplus of Crop(α) to gross residue.

$$SR(\alpha) = \theta(\alpha) \times CR?(\alpha) \tag{3}$$

4.2.3 Energy Potential

The energy potential of biomass is calculated by the combustion heat HV (α) of the biomass which is taken from the sources like BRAI and USDOE [24]. The combustion heat data which is obtain from the BRAI is in mega electric watt (MWe) and converted into the joule by multiplying with appropriate conversion factor.

$$E(\alpha) = SR(\alpha) \times HV(\alpha) \tag{4}$$

5 Results and Discussion

In India (1011 MT) of total biomass residue is generated on an annual basis by the 35 crops and wood which is taken for this study. The (976 MT) residue is generated by the crop production system. 34% of the gross crop residue is available for the energy production at national level and amount is (334.5 MT). The residue of industrial wood processing is (35.24 MT). In quantity terms the highest gross residue is generated by cereal crops which amount to the (441 MT), out of this the surplus residue is available for the energy generation is (104 MT) and have the energy potential of (1.73 EJ). In the cereal the highest residue is come from the paddy (170 MT) out of which (44 MT) is available for the energy generation with the potential of (0.7 EJ). The second highest residue (265 MT) is come from the spice and horticulture crops and in this section the highest contribution is by the coconut (138 MT) out of which (72 MT) is surplus residue with energy contribution of (1 EJ) secondly the residue generated by banana which is (82 MT) with the surplus residue of (28.8 MT) and has the energy potential of (0.4 EJ). The sugarcane crop is contributed the (128 MT) residue out of which (60 MT) is surplus with the energy potential of (1.19 EJ) the largest potential among the all individual biomass. The gross residue generated by the oil crops is (60.3 MT) with surplus availability of (20.5 MT) and has the bioenergy potential of (0.33 EJ). The residue generated from other crops is (57 MT) with the surplus residue of (32.8 MT) and has the bioenergy potential of (0.57 EJ) of energy. Pulses generated the (23 MT) with only (4 MT) availability and has minimum potential among all only (0.07 EJ). The total industrial wood consumption in India is (35.24 MT) out which (14 MT) is residue which is generated in the manufacturing of industrial wood and has the energy potential of (0.23 EJ).

The finding of the present study may not be in conscience with the other study like Hiloidhari which, calculate the crop residue amount of 686 MT [25] Ravindranath et al. [26] who reported the gross crop residue of 626.5 MT, IREDA [27] who projected the total crop residue is only 350 MT. MNRE tells about only 120–150 MT of crop residue and forestry residue are available for energy generation in India which is equivalent to 18 GW of potential [20]. The variations in estimations could be due differences in consideration of crop types, selection of crops for the study like Ravindranath et al. [26] and Hiliodhari [25] did not include ginger, cardamom, coriander, garlic, cumin, dry chilly residues and the other things may be RPR, heating values, and surplus residue fraction [25]. Sukumaran [28] reported that precise estimate of biomass availability in India is non-existent and the only statistics that available are on crop production and of forest coverage. The total bioenergy potential from the surplus portion of residue in the country would be (5.67 EJ) per annum. This is approx. 15% of primary energy consumption in India; total primary energy consumption in India is about 37 EJ.

5.1 *Major Issues Associated with the Uses of Residue Biomass*

There are several reasons which are stated by the removal of wood residue like adversely impact on the fertility of soil because of not completing of the nutrition cycle, erosion of soil and degradation in the organic matter of soil [29]. The other issues are the logistic problem of biomass like moisture content in biomass makes its transportation costly. Because, the biomass transportation cost is a function of the quantity of available biomass in a region and the transportation distance [30]. The huge resource of biomass is dispersed over large areas leading to high collection and transportation cost. The moisture in the biomass is create further complexity in the logistics system because when the green biomass is loaded on the truck it has the 50% of moisture content which reduced the quantity of dry matter and increase the transportation cost per unit of energy [31]. Therefore, it is desirable to ensure availability of adequate biomass in the vicinity of power plant location. The conversion process of biomass into liquid is depend upon the moisture content in general the, thermal conversion requires low moisture content (less 50%) while bio-conversion can utilize high moisture feedstock [32]. Moisture in biomass fuel reduces the heating value, thus if too much moisture is present, the fuel will not spontaneously react [33].

6 Conclusions

The present study is analyze current energy mix of India and try to find out what is the demand of energy in future and what is the probable supply sources. The dependency on the fossil fuels is increased in future if the present trend of energy consumption by conventional sources is continued. India's dependent on coal for meeting its power generation needs and oil and natural gas for its transportation sector requirements. In the matter of coal India is self-sufficient as, it has the 302 billion ton of coal reserves but in oil sector the situation is just opposite. The huge dependency on imports is increasing day by day. In 2014 India imports its 80% of the total crude oil requirement and it is estimated to reach up to 161% in 2035. The oil demand is rising with CAGR of 6.14% and after combining with the decline in oil production from five years steepens a gap in supply and demand of oil. Bioenergy is a sustainable alternative for overcoming this dependency because it is the only large scale renewable energy source which is converted into the liquid fuels. Biomass is work as the feed stock for the generation of liquid fuels primarily LC-ethanol because of its ability to work as an additive with gasoline or solely work as fuel. LC-ethanol is the most promising technology for India's transport sector because it is produced from the cheap feedstock which is amply available has high octane number with less carbon emission which is help in decarbonizes its transport sector and achieve its GHG mitigation goals [34]. It is very clear from the study that India have the ample bioenergy untapped in the form of biomass which is not consider till date as important it is. The analyses of 35 crops on the national level and production of industrial wood results that, there is (976 MT) of gross crop residue and (87.8) million m^3 or (35.24 MT) of industrial round wood is produced in India. The 35% of crop residue and 40% of industrial wood which is waste as residue in manufacturing process is available for the bioenergy generation. The total energy untapped in the mentioned biomass is (5.8 EJ) which is 15% of the total energy consumption of India. The oil used in India contained (7.97 EJ) of energy, if the available biomass is directed towards the LC-ethanol production which can replace 73% of oil and ultimately leads to the reduction in import bill and GHG mitigation.

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Thermochemical Conversion of Biomass into Gaseous Fuel for Electricity Generation

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Abstract Bio energy is accepted most trusted source of renewable energy that could be relied upon for providing the energy in the upcoming future. There are majorly three different methods of producing these bio fuels-biological conversion, physical conversion, chemical conversion. Our research constitutes mainly converting the biomass into bio fuel by using thermochemical reaction. Lot of primary and secondary products can be derived such as gases, liquids, solid fuels and electricity as well as considerable number of chemical by products. Here we take the biomass and mix it thoroughly in the presence of an acid and a base. As we know this is an highly exothermic reaction and generates large amount of heat. This heat decomposes the Bio mass and the hot vapours obtained by the decomposition of this organic matter as well as vapours from the neutralisation reaction combinedly are obtained and are used to turn the turbine blade and to generate the electricity. This method increases the efficiency as compared to a pyrolysis reaction and we can also use a thermocouple to enhance the heat and convert it into electricity so we have a two way advantage.

1 Introduction

Since there are growing concerns over energy insecurity and fossil fuel depletion. We could concentrate on developing alternate forms of energy such as bio energy (i.e. a form of solar energy stored in biomass) as a viable option for sustainable development. Generally we produce bio-fuel in two stages, first, production of biomass and second, (pre-)treatment of biomass and conversion of it into different

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energy products, e.g. heat, electricity, gaseous and liquid fuels like methane, ethanol and biodiesel. The conversion is basically done through three principal routes: (1) thermochemical conversion (combustion, gasification, pyrolysis and heat of neutralization), (2) biochemical (anaerobic digestion and fermentation) and (3) physicochemical (mechanical and chemical extractions), of which the first two are commonly used [1]. Energy production is limited by the amount of fossil fuels available and the availability of their sources. E.g. coal, oil, natural gas, the net amount of energy obtained depends on how are we relying on these sources, since with the increasing need of energy the fossil fuels are rapidly depleting.

Biomass can be used as renewable source of energy, as a fuels, and by subjecting it to different thermal, biological, and physical processes we could obtain sufficient amount of energy [2].

Thermo-chemical conversion is the most commonly employed method for converting biomass into fuels with high calorific values. Major thermo-chemical conversion processes are by direct combustion, gasification, liquefaction, hydrogenation, and pyrolysis. The selection of the conversion of different process depends on the type and amount of biomass feedstock, the required energy form, environmental standards, economic conditions, and project-specific factors [3]. Various types of biomass feedstocks have been tested for the production of biofuels. Their treatment methods also influence the amount and calorific value of bio fuel obtained. From the results obtained, microalgae have shown great promise due to their high lipid content, high growth rate. Thermo-chemical conversion, which includes pyrolysis, hydrothermal liquefaction (HTL), and alcoholysis is one of the practical method followed for the conversion of microalgae into liquid products (e.g., bio-oil). In our study we have also taken up the concept of heat of neutralization as a part of thermochemical reaction which is the major source of heat input for biomass to degrade into its several forms. Further more our study lead us to know how much of energy can be produced with this reaction with reference to various types of biomass available. With all the conditions we have researched about the remaining residue and have derived its applications accordingly.

2 Problem Identification and Basic Principle

Though biomass is attractive renewable low-sulfur fuel, utilization of biomass as an energy resource is not without potential environmental impacts. Since no process is ideal the adverse affect of this on environment is negligible. Biomass production mainly depends on the availability of bio mass for which we require some land, providing land just for production of bio mass has become a problem. Soil disturbance, nutrient depletion and impaired water quality are also some important environmental effects from biomass feedstock production and utilization of agricultural and forest residues for energy. The severity of these impacts is highly site-dependent and must be assessed monthly, based on nature of land. Biochemical processes for converting biomass materials to fuel may produce air pollutants, solid wastes and wastewater, which may adversely impact the environment [4]. In our study we have used the concept of heat of neutralization as a part of thermochemical conversion.

$$\text{Acid} + \text{Base} - - - \text{Salt} + \text{Water}$$

This heat of neutralization is made as a major source for biomass degradation. The heat liberated when a strong acid is mixed up with a strong base which gives us 58 kJ/mole of enthalpy. This is rather used in place of a acid which can also degrade the biomass in a harmful way by using only the acid. Here a strong acid and a strong base is recommended as the heat produces is much higher than the weak once (11.7 kJ/mole) and is sufficient for the biomass to degrade. These acid and bases are taken in equal ratios and these enthalpies vary from different type of acid base combinations. This method used in very cost effective when compared to processes like pyrolysis [5].

The acid used in this process can be regenerated by doing the hydrolysis of the remaining salt. One of the major advantages of this process is we don't use external heating as the heat is liberated by neutralization, hence by which we save resources and reduce environmental flaws. Moreover this process is easy to simulate and handle with respect to other processes. All products and reactions in this process are less harmful or toxic and hence can be used in all environmental aspects [5, 6].

3 Methodology

Biomass is available to us in basically two forms with respect to its physical state. Wet biomass and dry biomass. They vary with the ratio of moisture content with them. In our study we have taken up dry biomass in which wood (stems of trees) and dry leafs play as major components. This matter is collected and weighed using a digital weight balance machine. These particles are cut-down into small pieces for effective combustion.

In our study we have taken up the strong acid i.e. H_2SO_4 and strong base as NaOH (Fig. 1). As per table we have taken calculated amount of acid and base for the reaction to occur. Initially the biomass is taken into a beaker with appropriate weight and the base is added to it. Equal calculated amount of acid is poured slowly into the beaker along the sides and at the opening a thermometer is put up to calculate the temperatures of the liberated gases. These gases are carefully passed through a compressor. In this compressor these gasses are compressed to their standard pressures respectively and their enthalpies are noted. This is then connected to a condenser where the gases are condensed and then are weighed. We have taken up the values by varying the amount of biomass at the initial stage and have tabulated it accordingly with respect to the two types as-well.

Mean while when the temperatures are raised in the beaker due to heat of neutralization, thermocouple of type-E are put up into the setup which are used

Fig. 1 Acid and base; thermocouple

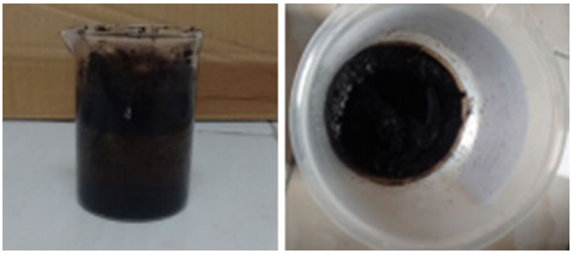


Fig. 2 Residue after neutralization

throughout the flow of gas i.e. tubes etc. This device converts the hear liberated into voltage (mV). A number of thermocouples can placed in such a way in order to obtain higher voltages. This can be also taken as different way to increase efficiency from this process.

The compressed vapors from the compressor have high energy content in them along with high pressures. This can be taken as an advantage as these vapors can be sent to run a turbine in order to produce power output which can be used for various purposes. In order to ensure complete combustion the amount of acid and base in calculated quantities have been increased and have tabulated the variations of temperatures and quantity of residue obtained (Fig. 2).

In order to test this residue this compound is taken under the test of Thin layer chromatography, or TLC, for analyzing mixtures by separating the compounds in the mixture. TLC can be used to help determine the number of components in a mixture, the identity of compounds, and the purity of a compound. By observing the product formation or the disappearance of a reactant, it can also be used to understand and study the progress of a reaction.

The sample is dissolved in a easily evaporated solvent to produce a very dilute (about 1%) solution. Spotting is using a capillaries to transfer a small amount of this dilute solution to one end of a TLC plate, in this case a thin layer of powdered silica gel that has been coated onto a plastic sheet. The spotting solvent evaporates swiftly and leaves behind a small spot of the material.

Fig. 3 Development of TLC

Development is done by placing the bottom of the TLC plate into a shallow pool of a development solvent, which then travels up the plate by capillary action. As the solvent travels up the plate, it moves over the original spot. A competition is between the silica gel plate and the development solvent for the spotted material. Initially a ratio of 50%:50% is taken between hexene and ethyl acetate. But if this could not give appropriate results, in order to retest the polarity was changed to 70–30% (Fig. 3).

After the run down the silica gel on the TLC plate is seen with a fluorescent material that glows under ultraviolet (UV) light. A spot will interfere with the fluorescence and appear as a dark spot on a glowing background. While under the UV light, the spots is outlined with a pencil to mark their locations. Here we get to see that the spots did not raise in the TLC place. Which indicates that the component is not organic and non-polar in nature (Fig. 4).

4 Results and Discussions

A better understanding on the house hold based bio energy use and we need to decrease the amount of wood usage in the house holds due to wood scarcity. Instead we could use bioenergy from bio fuels which are majorly eco friendly and save our planet from becoming extinct due to global warming. Sample households consumed

Fig. 4 Florescent light; spots on TLC

multiple fuels that are either complementary or substitutes, particularly low-quality agricultural fuels are typically used as a backup for fuelwood for residential cooking or heating needs. The amount of substitution between energy sources relies on cultural preferences, lifestyle, of the energy used.

We need to understand the ecological problem very carefully and take the necessary steps. In this scenario our experiment becomes important.

Here we have taken only small amount of biomass and by varying their weights initially, we have found out the temperature obtained and the mass of residue etc.

We have also made our study on how the variations in energy were obtained when different amount of biomass are taken, as we understood by conducting trials and made a primary observation that when we increase the amount of biomass and introduce proportional quantities of acid and base we see a rise in temperature and enthalpy rise. This can be understood as the amount of fuel(biomass) is increased with increase in the combustion volumes and the transfer of energy is more as a result we have higher temperatures, if there is an increase the amount of biomass. Care is taken that we have introduced only a single type of biomass namely leaves or stem as we know the heat obtained also depends upon the type of biomass used (Table 1).

Wood is taken instead of leaves but now complete combustion of the fuel is given priority. A standard mass of wood is taken and proportional quantities of acid and base are added until the complete combustion of the biomass is ensured. The amount of residue and its nature (Fig. 5) is also given importance and those values are also tabulated (Table 2) and T.

Table 1 Performance factors

Leafs	Trial 1	Trial 2	Trial 3
Amount of biomass (mg)	1.03	2.01	3.06
Amount of acid (mg)	11.04	27.6	46
Amount of base (mg)	1.01	2.45	3.4
Temperature evolved (°C)	131.1	162	178
Mass of residue (mg)	11.53	27.15	45.08

Fig. 5 Amount of biomass

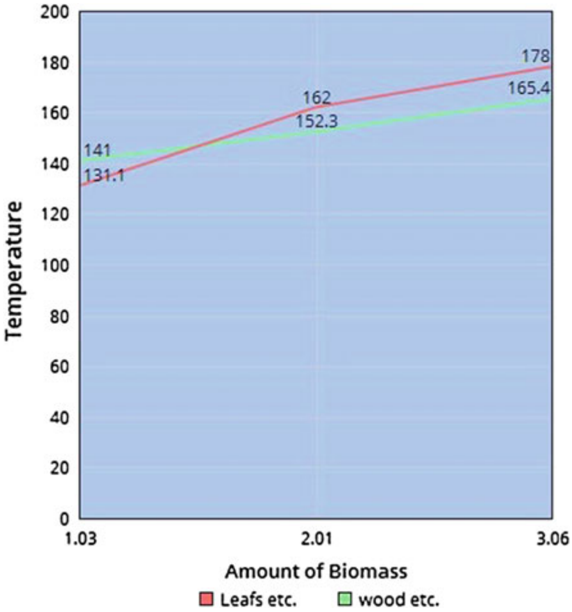


Table 2 Amount of biomass and its nature in different trials

Wood	Trial 1	Trial 2	Trial 3
Amount of biomass (mg)	3.06	3.06	3.06
Amount of acid (mg)	46	55.2	64.4
Amount of base (mg)	3.4	4	5.02
Temperature evolved (°C)	141	152.3	165.4
Mass of residue (mg)	49.01	58.24	67.45

Furthermore as we have placed E-type of thermocouples, in the passage lines of the obtained gases and calculated the amount of voltage outputs obtained. Here we can increase the amount of thermocouples to increase the amount of voltage obtained. We have also added the seeback coefficient values and calculated the errors in temperatures as exact values of temperatures cannot be obtained (Fig. 6 and Table 3).

This method is also an alternative source for energy production and here voltage is generated from the gases produced (Table 4).

In our study, the gases produced are at atmospheric pressure. Furthermore in order to produce high enthalpies these gases were compressed to their standard pressures as shown above and their enthalpies are calculated (Figs. 7 and 8).

$$\text{Total Enthalpy obtained} = \text{Enthalpy} * \text{Mass of gas obtained}$$

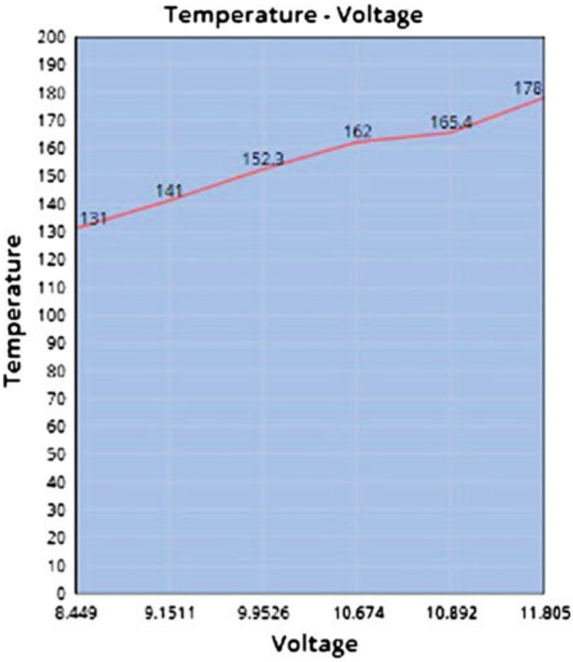


Fig. 6 Temperature voltage variations

Table 3 Seeback coefficient for different thermocouple voltage

Temperature (°C)	Thermo couple voltage (mV)	Seeback coefficient dv/dt	Standard limits of errors (±°C)	Special limits of errors (±°C)
131(w)	8.449	0.0698	1.7	1.0
141(l)	9.1511	0.0705	1.7	1.0
152.3(l)	9.9526	0.0712	1.7	1.0
162(l)	10.674	0.0719	1.7	1.0
165.4(w)	10.892	0.0721	1.7	1.0
178(w)	11.805	0.0728	1.7	1.0

w wood, *1* leafs

Table 4 Enthalpy obtained

Weight (gas) (mg)	Standard pressure (bar)	Temperature (°C)	Enthalpy obtained (kJ/kg)	Total enthalpy (kJ)
1.55(l)	3.26	131	2718.2	4.213
4.91(l)	7.42	162.4	2758.08	13.59
7.32(l)	10.795	178	2772.65	20.29
3.45(w)	4.086	141	2733.81	9.43
4.02(w)	5.253	152.3	2748.64	11.049
5.03(w)	8.078	165.4	2760.88	13.8

Fig. 7 Total enthalpy for mass of gas (w)

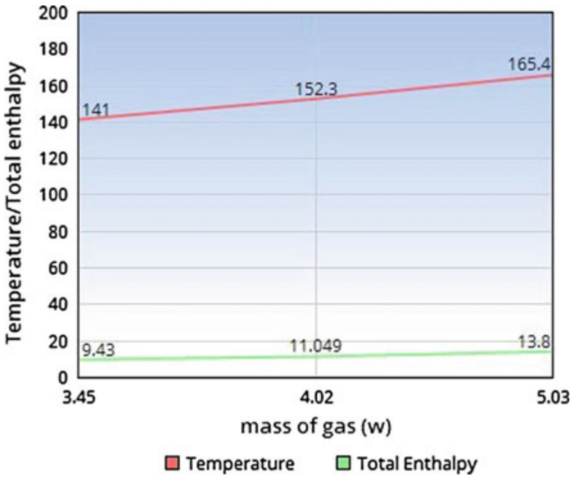
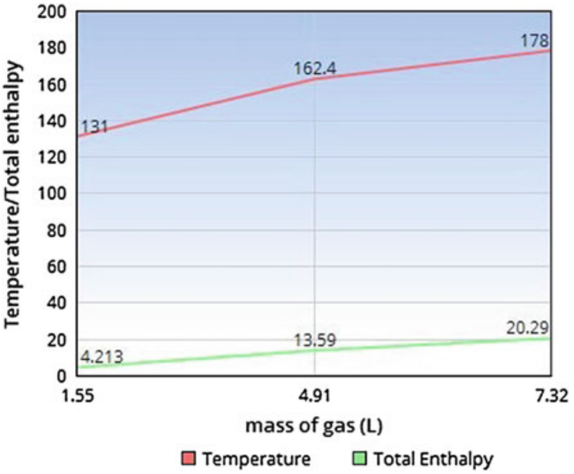


Fig. 8 Total enthalpy for mass of gas (l)



5 Discussions

As per the results of this experiment the major end products derive from the residue and the gases are carbon and salt crystals in the form of mixture with the residue. The carbon obtained is in wet state which is easy to collect and carbon ink can be primarily derived from it. The resultant can be used for various purposes like in the construction mixtures, laying of the roads and by various construction companies in their construction works like in making of bricks etc.

We can also regenerate the reactants by separating the salt and it should undergo the hydrolysis. This results in the formation of original reactants. This process is very eco-friendly and easy to perform. The energies obtained for a small amount of biomass are also pretty good so can be used for power generation and other energy utilities. This gives us an additional advantage of degrading biomass over conventional methods, as no additional heat input is supplied and the end products are more useful.

6 Conclusions

The energy and environmental crises which the modern world is experiencing is forcing it to re-think on its way of using these perishable natural resources. The efficient utilization or finding alternative uses for natural, renewable resources, using clean technologies are important solutions before us which are to be strictly followed. In this regard, heat of neutralization on biomass holds considerable potential to meet the current energy demand of the modern world. This is also essential in order to overcome the excessive dependence on petroleum for liquid fuels. Further advanced biotechnologies are crucial for discovery, characterization of new enzymes, and production in homologous or heterologous systems and ultimately lead to low-cost conversion of biomasses into bio-fuels and bio-chemicals. In current scenario future trends are being directed to biotechnology and genetic engineering for improved processes and products. To overcome the current energy problems it is thought that use of heat of neutralization to degrade biomass in addition of green biotechnology will be the main focus of the future research.

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Enrichment of Biogas from Biodegradable Solid Waste—A Review

Hemant Kumar Balsora, Pratibha Gautam and Monoj Kumar Mondal

Abstract Due to rapid increase in population and explosive evolution of life standards, there is tremendous increase in solid waste generation in the last few decades. Furthermore, most of the countries are going to be industrialized; hence more amount of energy will be required in upcoming decades. Today's more than 85% of the world demanded energy is supplied by fossil fuels. Fossil fuels are finite source of energy and therefore it is necessary to find out other alternatives for energy generation. Improper management of solid waste (MSW, waste biomass, etc.) is responsible for climate change, water and soil and local air pollution. These wastes have a high value with respect to energy recovery. The energy generation from the biological waste materials has been identified as alternative to the fossil fuels due to it's dual benefit of resource generation and waste minimization. Anaerobic conversion of solid waste biomass is a matured technology for environmental protection and waste management. The end products are biogas (a mixture of methane and carbon dioxide), which is a useful, renewable energy source and organic manure slurry which can be used as fertilizer for agricultural purposes. Anaerobic digestion is a simple process, used to convert organic material (from a wide range of solid waste) into methane. This paper is mainly focused on the anaerobic digestion of solid waste biomass to produce methane, technologies related to pre-treatment of feed materials and post treatment of product gas to enrich the methane composition and the value addition of product fractions are also discussed.

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1 Introduction

A remarkable rise in solid waste generation has been observed in the last few decades owing to explosive growth of population with comfortable life standards. Sustainable management of this huge quantity of solid waste has become one of the biggest challenges for mankind [1]. Unplanned dumping or dumping solid waste in engineered landfills is a common practice today, specifically in developing countries. With increasing population, land availability is decreasing day by day and such unsustainable methods of waste disposal not only occupy and deplete the land resources but also lead to anaesthetic and unpleasant environment. Another challenge faced by the whole world today is exponential increase in energy demand against its production and availability [2, 3]. At present around 88% requirement of electrical and thermal energy is met by non-renewable sources [4]. It is well known that these non-renewable resources of energy are going to exist for a finite time, therefore number of researches are going on to explore new renewable sources and to establish such technologies which can utilize existing renewable sources to its optimum extent.

There are different methods available to treat the various solid wastes. For biodegradable waste also, there are number of treatment methods available such as aerobic composting, anaerobic digestion, anaerobic fermentation, pyrolysis, incineration with or without energy recovery, etc. [5]. Out of these methods, anaerobic digestion is one of the most promising technologies to address both of the above mentioned issues. In this method, putrescible wastes are biologically degraded in absence of oxygen with the help of anaerobic bacteria in order to produce compost and biogas [6]. Biogas produced from this process majorly consists of methane (CH_4), carbon dioxide (CO_2) with some impurities of moisture, hydrogen sulfide (H_2S), ammonia (NH_3), siloxane, particulate matter, etc. Biogas can be converted to energy directly by combustion or it can be cleaned and enriched in terms of methane to increase its calorific value and to make it as a clean fuel [7].

2 Process of Waste Degradation and Biogas Generation

Degradation of putrescible fraction of the waste in an anaerobic digester takes place in four stages, namely: hydrolysis by hydrolysing bacteria, acidogenesis by acidifying bacteria, acetogenesis by acetogenic bacteria and methanogenesis by methanogenic bacteria [4, 7].

2.1 Hydrolysis

This is considered to be the first stage of anaerobic digestion in which hydrolyzing bacteria transforms complex compounds such as protein, carbohydrates and fats into simpler compounds such as amino acids, monosaccharides, soluble fatty acids and other monomers [4]. Hydrolysis can also be considered as pre-treatment of solid waste for further reactions such as acidogenesis. This step is considered to be the rate limiting step of whole process of anaerobic digestion [7, 8]. Various kinds of enzymes such as proteases, lipases and cellulases are also involved in the process of degradation of proteins, lipids or fats, and cellulose, respectively. Rate of this process depends on various parameters such as pH of the medium, enzyme production, particle size, etc.

2.2 Acidogenesis

Products of hydrolysis such as fatty acids, amino acids, sugars and other water soluble chemical substances are then undergo acidogenesis where monomers are converted into volatile fatty acids (acetic acid, butyric acid, propionic acid, formic acid), aldehydes, alcohols and gases (carbon dioxide and hydrogen). Anaerobic microorganisms use amino acids and peptides as source of energy which is derived from decomposition of proteins [4].

2.3 Acetogenesis

The acetates and hydrogen to be used by methanogenic bacteria in methanogenesis phase are produced in this phase by the acetate bacteria. It is stated in literature that the microorganisms which carry out this process, gets affected by toxic effects of hydrogen produced in this phase. Therefore a syntropy exist between acetate bacteria (producing hydrogen gas) and autotrophic methane bacteria (require hydrogen to produce methane gas). Acetogenesis is considered to be a very important phase of the process of biogas generation, as the methane produced from the acetate reduction accounts for 70% (approximately) of total methane generated in the process [4].

2.4 Methanogenesis

In this phase, products of previous phase (acetic acid, hydrogen, carbon disulphide and methanol, etc.) are converted into methane by methanogenic bacteria. Heterotrophic methane bacteria are responsible for conversion of acetic acid into methane whereas autotrophic methane bacteria are responsible for CO_2 reduction into methane [4].

3 Feedstock for Anaerobic Digestion

There are variety of feedstocks which has shown the potential to generate biogas by anaerobic digestion such as waste from the dairy, food and feed industries, sludge from municipal wastewater treatment plants, wastes from slaughterhouses, kitchen (food) waste, garden waste, animal waste, crop waste from agriculture, etc. The amount and the composition of the biogas produced depend on the operating conditions as well as the type of substrates used. While selecting feedstock for anaerobic digestion it should be well ensured that it is able to fulfil all nutritional requirements of microorganisms. Usually organic material fed to the digester is of varying composition, therefore the composition and quantity of biogas produced also varies. Organic material fed to the digester majorly composed of carbohydrates, fat and protein. All these components provide different quantity of biogas with different composition when undergo anaerobic digestion. With support of previous researches, Schnurer [9] has reported that carbohydrates produce 0.38 m^3 of biogas/kg VS with ratio of CH_4:CO_2 reaching approximately 50:50. Similarly fats are reported to produce 1 m^3 of biogas/kg VS with 70:30 ratio of CH_4:CO_2, and Proteins are reported to produce 0.53 m^3 of biogas/kg VS with CH_4:CO_2 ratio approximately 60:40 where VS stands for volatile solids. These data can be used for theoretical calculation of biogas production but there are several factors which affects the process and thus amount of biogas produced. Schnurer [9] has also reported approximate methane yield (m^3 CH_4/ton VS) by various substrate such as for food waste it varies from 400 to 600, for slaughterhouse waste it is 700 approximately, from sugar beets it ranges from 300 to 800 and for municipal sludge it shows in the range of 160–350, etc. To get better results, codigestion of different (mixed) substrate should be done instead of a single type of waste.

Results can be further improved by pre-treatment of substrate [10, 11]. Type of pre-treatment depends on type of waste; certain pre-treatment such as size reduction can be used to increase the efficiency of process when size of the substrate is bigger. There are other pre-treatments also such as chemical treatment of cellulosic material can be done to break its crystalline structure and increase the rate of degradation. Pre-treatment of saturated fats with heat is also in practice to increase their digestibility. Other Pre-treatment methods such as chemical solubilisation, thermo-chemical liquidization, wet oxidation and mechanical disruption are also used to increase the decomposition of VS, destruction of pathogens and production of methane [1].

4 Parameters Influencing the Process

The quantity and composition of biogas produced through digestion process largely depends on the operating parameters such as pH, temperature, loading rate, retention time, moisture content, degree of digestion, mixing and C/N ratio [9, 12].

(i) **pH**: pH of the system varies during different stages of anaerobic digestion, such as during acidogenesis, pH of the system falls in acidic category whereas methanogenic activities requires pH to be in the range of 6.5–7. Therefore it is very much necessary to regulate and maintain the pH at desired range at various stages in the entire digestion process.

(ii) **Temperature**: All the physical and chemical processes are very sensitive to temperature. The optimum temperature or temperature range is therefore very necessary for a process/reaction to occur for maximum product yield. The progress of anaerobic digestion is strongly influenced by the activities of various microorganisms. It is reported in [12] that the optimum temperatures for psychrophilic microorganisms is 10 °C, for mesophilic microorganisms this range is 20–45 °C and for thermophilic microorganisms it is even greater than 50 °C.

(iii) **Loading rate**: Loading rate in a digester defines food availability for microorganisms. A very high loading rate can create an imbalance in system, as much of substrate will remain undecomposed because microorganisms will not be able to decompose all substrate provided.

(iv) **Retention time**: Retention time is very much dependent on feedstock. Complex compound such as fibre and cellulosic material need more time for hydrolyses to get converted into simpler compound, thus overall retention time increases, on the other hand, easily degradable feedstock such as sugar, does not require hydrolysis therefore retention time decreases. Usually it varies from 10 to 30 days. In colder atmosphere retention time may go as high as 100 days.

(v) **Degree of digestion**: For same retention time degree of digestion is usually much more for easily degradable material such as sugar as comparative to complex material such as fibre. More retention time is an indicator of high degree of digestion.

(vi) **Mixing**: Mixing is the essential part of an anaerobic digester. A gentle mixing serves number of purposes in an anaerobic digester such as:

- It provides uniform temperature throughout the process.
- It facilitates contact between the nutrients, substrate and microorganisms.
- Material accumulation at the bottom of digestion tank is also prevented by proper mixing and thus risk of foaming is also reduced.
- Transfer of hydrogen between microorganisms responsible to carry out anaerobic oxidation and methane producers is also facilitated by mixing.
- Gentle mixing helps in aggregates formation and thus helps in preventing the washing out of methane producers.
- Uneven loading in the digestion tank can also be avoided by continuous mixing which avoids sedimentation and thus utilizes the existing digestion tank volume.

(vii) **C/N ratio**: The substrate act as a source of energy for microorganisms, it must be able to meet the nutritional requirements (C and N) of the microorganisms. Microorganisms consume carbon (C) as their energy sources and nitrogen (N) as to build new cells. Therefore, It is important that the C/N ratio neither should be too low (too much nitrogen relative to carbon) nor should be too high (too much carbon relative to nitrogen). Too low C/N ratio means that carbon will get exhausted very fast as compared to nitrogen. This ultimately will lead to ammonia formation (undesirable because of ammonia inhibition). Too high C/N ratio means that significant amount of carbon remains undecomposed which ultimately leads to poor performance of digester [12].

5 Enrichment of Biogas

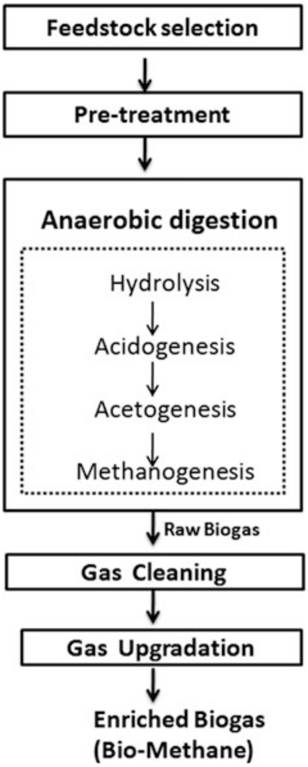
As discussed earlier, Biogas produced from anaerobic digestion mainly consists of methane (CH_4) and carbon dioxide (CO_2). The types of substrate used, fermentation technology and collection method can all affect the production and composition of raw biogas. Besides CH_4 and CO_2, raw biogas also contains some trace amounts of ammonia (NH_3), hydrogen sulphide (H_2S), hydrogen (H_2), oxygen (O_2), nitrogen (N_2), water vapour, carbon monoxide (CO), and Siloxanes [13, 14]. Raw biogas contains about 50–65% CH_4, 30–45% CO_2 and traces of other impurities. The biogas gas having 50% of methane has the heating value of 21 MJ/m^3, while upgraded biogas with 100% methane has a heating value of 33.41 MJ/m^3, which indicates that upgraded biogas be utilized as a renewable energy source in combined heat and power plants, as a vehicle fuel, or as a substitute for natural gas [13–16]. The overall process for production of upgraded biogas (bio-methane) can be easily understood with the help of Fig. 1.

6 Effect of Impurities

Presence of impurities in biogas (as mentioned in previous section) not only reduces the heating value but can also cause corrosion and mechanical wear of the equipment. CO_2 in biogas reduces the heating value. It takes up space when biogas is compressed and stored in cylinder. It can cause freezing problems at valves and metering points where the compressed gas undergoes expansion during engine running. It also causes corrosion (low concentrated carbonic acid) if the gas is wet. It damages the alkali fuel if biogas is used as a fuel in internal combustion engine [15].

The traces of H_2S which is hazardous in nature, it produces H_2SO_4 which corrodes the internals of pipes, fittings, etc. It emits sulphur dioxide after burning [13, 15]. Water vapour in the biogas will lead corrosion in equipment and piping systems, this water vapours may condense and responsible for damage in instruments used in the plants. It may also lead the risk of freezing of piping system and nozzles [15, 16].

Fig. 1 Production of bio-methane by anaerobic digestion



The presence of nitrogen is also lower the heating value of biogas. Traces of dust can block nozzles and fuel cells [13, 15, 16]. Siloxanes are compounds containing a silicon-oxygen bond. While burning siloxanes, silicon oxide, a white powder, is formed which can create a problem in gas engines. It acts like an abrasive and can damage engines [15, 16].

7 Bio Gas Cleaning and Upgrading Technologies

Biogas cleaning and upgrading can be referred to as biogas enrichment. Biogas cleaning is removal of corrosive products, mainly H_2S, H_2O, and particles while the upgrading involves removal of CO_2 to increase heating value of the biogas [15, 17]. The technology used for the CO_2 separation, can also remove other acidic gases, H_2S and trace of nitrogen from biogas. Nevertheless, pre separation of some of these components like H_2S, if present in higher amount, is necessary before the up-gradation step since these components can cause operational problems in upgrading process [17].

7.1 Biogas Cleaning

7.1.1 Removal of Hydrogen Sulphide

a. **Sulphide precipitation**

Hydrogen sulphide is formed during microbiological reduction of sulphur containing compounds (sulphates, peptides, amino acids). The hydrogen sulphide removal can be start from the digesting tank with help of various metal salts. When Fe^{2+} or Fe^{3+} ions are added in the forms of $FeCl_2$, $FeCl_3$, or $FeSO_4$, to the digester, the sulphur content of the substrate is precipitated in the form of insoluble iron sulphide. This method is primarily used for high sulphur content in the biogas [13, 14, 16]. Several technologies are also available to remove H_2S from the biogas like adsorption, absorption and biological scrubbing.

b. **Adsorption on metal oxides**

H_2S can be removed by the selective adsorption onto the metal oxides like iron oxide, zinc oxide, copper oxide or on the activated carbon. During the adsorption of H_2S on the metal oxides, sulphur is adhered as metal sulphide and water vapour is released [14–16]. The adsorption on activated carbon is usually carried out with the addition of small amount of oxygen, this oxygen helps to oxidise H_2S into sulphur that binds to the surface. The rate of reaction can be enhanced by the doping or impregnating the pores of the activated carbon with potassium iodide, potassium carbonate or zinc oxide [15, 16]. Although, zinc oxide doping is expensive, it is still most preferable due to its ability to remove H_2S to less than 1 ppm in biogas [16]. This technique is useful when either H_2S content is very low in the raw biogas or the technology is used for final desulphurisation [14].

c. **Biological desulphurisation**

The H_2S can also be removed through oxidation by chemoautotrophic microorganisms. Most of the sulphide oxidising micro-organisms belong to the family of Thiobacillus or sulfolobus. For the microbiological oxidation of sulphide it is essential to add stoichiometric amounts of oxygen to the biogas. The degradation can occur inside the digester and can be facilitated by immobilizing the microorganisms occurring naturally in the digestate [14, 16, 18]. Depending on the temperature, reaction time, amount and place of the air/oxygen added, the hydrogen sulphide concentration can be reduced to less than 150 ppm [18]. This method seems to be a cost effective and environment friendly solution, since it can proceed at lower temperatures and pressures, and with limited or no reagent consumption [14, 19].

d. **Chemical-oxidative scrubbing**

Chemical absorption is also one of the ways to remove H_2S, as H_2S is acidic in nature; it can easily be absorbed in the alkali solutions. Absorption in caustic solutions is one of the oldest methods for gas desulphurization. Nowadays NaOH is used as caustic and by controlling the pH selective separation may occur. Iron-chelated solution catalysed by ferric ethylenediamine tetraacetic acid (Fe/EDTA) has also been used for removal of hydrogen sulphide from raw biogas [20]. Chemical absorption of H_2S in the iron chelated solutions offers a high efficiency and selectivity with low consumption of chemical [15, 21]. The conversion of hydrogen sulphide into elemental sulphur is catalysed by Fe/EDTA, The elemental sulphur is then easily removed from the slurry by sedimentation or by filtration operations. The entire process can be performed at ambient temperature [15].

7.1.2 Removal of Water

Water vapour in raw biogas can be removed by condensation achieved by either increasing pressure or by reducing the temperature. It can also be removed by the adsorption in which raw gas is passed over silicon dioxide or activated carbon packed bed [16, 22].

7.1.3 Removal of Siloxanes

There are several methods available for siloxanes removal from bio gas. Adsorption on the adsorbent (like activated carbon, activated alumina, silica gel, etc.) is one of the well-established technologies for siloxanes removal. Other existing methods include gas-liquid absorption and separation by refrigeration and condensation. Recently, membrane separation and biological degradation have been tested for siloxanes removal [15, 16]. Siloxanes can also be separated during the H_2S removal.

7.1.4 Removal of Ammonia

Ammonia is formed during the degradation of proteins. Its concentration depends on the type of digested substrate. The concentration of ammonia in biogas is usually very low and no separate system is required for its removal. It can be removed during gas drying in the process of biogas up-gradation [15, 16].

7.1.5 Removal of Particulates

Presence of particulate in biogas can cause wear in gas and turbine engines. Particulates can be removed by passing biogas over mechanical filters [15].

7.2 Biogas Upgrading Techniques

A number of different methods available for biogas up-gradation to bio-methane are discussed in this section.

7.2.1 Absorption

In this method, separation is achieved based on the difference in the solubility of the gaseous components in an absorbent. During the up-gradation, raw biogas is contacted in counter current manner with absorbent over a packed bed filled with suitable packing material. Packing materials is used to increase the interfacial contact area and therefore increases the rate of absorption [13–16].

Water Scrubbing

In water scrubbing, water is used as absorbing solvent. The solubility of methane is much lower than the solubility of carbon dioxide in water especially at lower temperature. Literature reveals that the solubility of carbon dioxide is approximately 26 times higher than that of methane at 25 °C [15, 22, 23]. In packed column carbon dioxide is absorbed in the water while the gas stream gets enriched with methane. In principle, H_2S can also be removed along with CO_2, Since the H_2S is more soluble than CO_2 in water. As H_2S is poisonous and dissolved H_2S is responsible for corrosion problems. Therefore, H_2S separation is necessary before the up-gradation of biogas. CH_4 purity can be achieved to 80–99% by water scrubbing (depending upon the presence of non-condensable gases) [13, 15].

Physical Absorption

In principle, physical absorption is very similar to the water scrubbing. In place of water, organic solvent such as methanol, polyethylene glycol-dimethyl ether (PEG-DME), rectisol, selexol, etc. are used as absorbents [13–15, 24]. CO_2 is more soluble in these organic solvents than in water. Hence, less scrubbing liquid circulation and smaller apparatuses are required for the same capacity [14].

Chemical Absorption

Chemical absorption process is accomplished with a reaction occurs between CO_2 and a suitable chemical absorbent or a mixture of absorbents. Chemical absorption is more advantageous over physical and water scrubbing in its capacity to absorb more CO_2 [25]. Chemical absorbents such as monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), and di-2-propanolamine (DIPA) are commonly used. Other absorbents such as, diglycolamine (DGA), 2-(2-aminoethylamino) ethanol (AEE), 2-amino 2-methyl 1-propanol (AMP), N-2-aminoethyl 1,3-propanediamine (AEPDNH2), triethanolamine (TEA), triethylene tetra amine (TETA), piperazine (PZ), glucosamine (GA), NaOH, NH_3, K_2CO_3, KOH, Na_2CO_3, etc. were also tested for CO_2 removal, however their individual limitations make them less suitable for large scale operation. Nowadays concept of blending, in which two or more absorbents mixed in varying concentrations are used. A blend of MDEA and PZ are used industrially for biogas up-gradation. Chemical absorption with amines solution is a well established and mature technology, complete CO_2 removal is achievable by this [15, 25, 26].

7.2.2 Pressure Swing Adsorption

Selective retention of a solute molecule on a solid surface is known as adsorption. Significant intermolecular forces between gases (including CO_2) and the solid surfaces are mainly responsible for selective separation. Depending on the temperature, partial pressure, surface force and adsorbent pore sizes, single or multiple layers of gases can be adsorbed [24]. In pressure swing adsorption (PSA), carbon dioxide is separated from the biogas by adsorption on a surface under elevated pressure. The adsorbing material, usually activated carbon or zeolite, is regenerated by a sequential decrease in pressure. During the CO_2 adsorption, H_2S is also adsorbed irreversibly and thus H_2S considered toxic to PSA. Therefore, H_2S removal is necessary prior to PSA. Methane purity about 96–98% can be achieved by PSA [13, 15, 16].

7.2.3 Membrane Technology

Membranes are consists of semi-permeable barriers that separate specific component(s) from gas stream by various mechanisms (solution/diffusion, adsorption/diffusion, molecular sieve and ionic transport). In biogas upgrading, the carbon dioxide is diffused through membrane while methane is retained on it. Commercially feasible membranes for biogas upgrading are made of polymeric materials like cellulose acetate, polycarbonate, polyetherimide, polysulfone, polyimide or polydimethylsiloxane [14, 15, 23, 24]. The presence of H_2S, leads softening/plasticization of membrane and thus it limits the use of membrane. Hence, H_2S should be removed before up-gradation of biogas by membrane [27].

7.2.4 Cryogenic Techniques

This process involves compression and cooling of the gas mixtures in several stages to induce phase change. The cryogenic technique is based on the difference in the condensing temperature of various components contained in a biogas stream. The separation of gas components is achieved through condensation and distillation [13, 15]. The process starts with compression of raw biogas to 17–26 bar and then cooling to −26 °C for removal of H_2S, SO_2, and siloxane [15]. Further cooling of biogas reaches a temperature where CO_2 gas is liquefied and separated by several condensers. The water content in biogas should be minimal in order to avoid freezing in the cooling units by dry ice or unacceptably high rise in pressure drop during operation. Therefore, water traces from the bio gas need to be pre-separated. In view of these limitations and high cost of refrigeration, this process can be used only for special circumstances as an adjunct to other processes [13, 24].

7.2.5 Hydrate Based Separation

Gas hydrate is a promising way to separate gas component(s) from a gas mixture (biogas). The difference in hydrate formation tendency of various species at specified conditions is main responsible to separate a gas component. The basic mechanism is the selective partition of the target component between the hydrate phase and the gaseous phase [13, 24]. This technology has been successfully used to remove CO_2 from contaminated natural gas, for a CH_4 to CO_2 ratio of 3:1 and the concentration of CO_2 can be reduced to 16%. However, the amount of associated CH_4 removed with CO_2 is still relatively high [13].

7.2.6 Biological Separation

Recently, the enzymatic based CO_2 separation has also been used to enrich biogas. This is based on the naturally occurring reactions of CO_2 in living organism. Carbonic anhydrases (CA) rapidly and selectively catalyse the hydration of CO_2 to bicarbonate. This selective movement of CO_2 in to the liquid phase is helpful for biogas enrichment. Currently, these enzymes are also being used with some chemical solvents for CO_2 absorption. It is reported that absorption of CO_2 in alkanolamines can be catalysed very fast at ambient condition using small amount of enzymes (such as carbonic anhydrate). Addition of CA enzyme to solution enhances the CO_2 dissolution and forms carbonic acid, the production of carbonic acid adds value to this process. The rate of CO_2 dissolution in water in this technology is limited by aqueous CO_2 hydration and CO_2 carrying capacity is limited by buffering capacity. Apart from this, production of enzymes can be costly due the difficulties of cell culture and enzyme purification and extraction from cellular materials [24, 28–30].

8 Conclusion

The biogas produced from putrescible fraction of waste has the potential to be used as fuel. The digestion process is mainly completed in four different stages as hydrolysis, acidogenesis, acetogenesis and methanogenesis by activity of specific microorganisms in each of these steps. The amount and composition of raw biogas is strongly dependent on the type of substrate, pre-treatment method, process and operating parameters. The temperature and pH are the two key parameters which affect the yield of biogas. The presence of impurities on raw biogas limits its use as vehicular fuel. The CO_2 is responsible for low heating while other traces of impurities are responsible for operational issues. Among the all available technologies, amine based chemical absorption for upgradation of biogas is well established and mature technology. Through this technology, complete CO_2 and H_2S removal can be achieved.

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Investigation of Waste Frying Oil as a Green Alternative Fuel: An Approach to Reduce NO_x Emission

Shrivastava Nitin

Abstract The rapid depletion of fossil fuels and environmental degradation has led search for an alternative fuel. Biodiesel is renewable and environment friendly fuel. Waste frying oil methyl ester is a biodiesel prepared from waste frying oil. It is less expensive than fresh vegetable oil and moreover, it helps solving the environmental problems coupled with disposal of the waste frying oils. Majority of the literature reported comparable performance and considerable reduction in emission except oxides of nitrogen (NO_x) from the engine fuelled with Biodiesel. NO_x emission needs to be control to make Biodiesel more viable alternative fuel. Exhaust gas recirculation (EGR) is a method, involves the re-circulation of the exhaust gases back to the combustion chamber, it reduces the NO_x emission by reducing the in-cylinder temperature. The present study involves the use of cooled EGR in a Diesel engine with waste frying oil methyl ester as fuel. The result showed use of waste frying oil methyl ester with cooled EGR reduces the NO_x emission considerably.

Abbreviations

BMEP	Brake mean effective pressure
BSEC	Brake specific energy consumption
BTE	Brake thermal efficiency
CO	Carbon monoxide
EGR	Exhaust gas recirculation
HC	Unburned hydrocarbon
NO_x	Nitrogen oxides
WFOME	Waste frying oil methyl ester

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1 Introduction

The fast depleting oil resources, increasing rate of vehicle rise and stringent emission norms is a global issue. So the search is of an alternative fuel which is renewable in nature and meets stringent emission norms. Biodiesel is an alternative renewable fuel produced from resources like vegetable oils, including animal fats. It consists of short chain esters of methanol or ethanol widely known as methyl ester or ethyl ester, and is produced by transesterification process. Neat biodiesel or blends of biodiesel with diesel fuel can be used directly in a Diesel engine.

Biodiesel is non-toxic, contains no sulfur, less pollutant to water and soil, has higher biodegradability than fossil fuel, and does not contain aromatics. It is safe to handle in the neat form and shows reduced oral and dermal toxicity, mutagenic and carcinogenic compounds. It is suitable for areas where working conditions must meet high environmental standards like underground mines etc. or in environmentally sensitive areas like national parks, rivers, lakes. Currently, the 84% share of world biodiesel production is met by rapeseed, 13% sunflower, 1% palm, and 2% soybean and others. More than 95% biodiesel is made from edible oils [1]. Continuous and large-scale production of biodiesel from edible oil without proper planning may raise food versus fuel issue in near future. A possible solution to overcome these problems is to use non edible oils or waste frying oil for biodiesel production. Since the cost of biodiesel production mainly depends on the cost of feedstock, use of waste frying oil can minimize the production cost.

The frying oil when heated for extended time degrades by forming oxides. The presence of substances like hydro peroxide, epoxide and polymer etc. has adverse health effects which includes increase in kidney, and liver size. Bulk of waste frying oil is available throughout the world. Estimates of waste frying oil collected every year in the US range from 1.2 to 3 billion gallons a year, and 4–6 lakh tones annually in Japan [2]. Management of waste frying oil is also a big challenge due to the disposal problem and the possible contamination with water. With the increase in number of food centers chains globally it is expected that considerable amount of waste frying oil will be discarded into drains. So the use of waste frying oil to produce biodiesel offers significant advantages because of the reduction in environmental pollution.

Studies on the performance and emission of the biodiesel fuelled engine showed almost similar performance as that of diesel fuel. The carbon monoxide, unburned Hydrocarbon and particulate emission found with the biodiesel fuelled engine are less than the Diesel fuel. The NO_x emission is found to be higher for the Biodiesel fuel [3–6]. The increase in NO_x emission is a significant barrier in the market expansion of the biodiesel fuel. Hence there is a need for reduction of engine-out NO_x.

Recirculation of the exhaust gases back into the combustion chamber is a popular method of reducing NO_x emission popularly known as exhaust gas recirculation (EGR). EGR is most used and studied technology as regards the in-cylinder strategies aiming at reducing NO_x emissions [7–9]. The objective of this study is to evaluate the effect of using Exhaust gas recirculation in diesel engine fuelled with biodiesel prepared from waste frying oil.

2 Production of Biodiesel from Waste Frying Oil

The waste frying oil collected from various restaurants is used in the present study. The sample oil collected was allowed to settle down the impurities by standing the oil for 2 days. The oil was filtered to remove impurities like food residue and solid precipitates. The formation of methyl ester or biodiesel by transesterification of waste frying oil requires the reaction of oil with methanol in a reactor. Optimum reaction conditions for the maximum yield of methyl esters were found to be 1% potassium hydroxide catalyst and 40% methanol at 65° temperature for 2.5 h. It than allowed to settle the two distinct layers of waste frying oil Methyl ester (WFOME) and Glycerol in reactor for 24 h. Once the heavy black glycerol layer was settled down, the methyl ester layer formed at the upper part of the reactor. Glycerol followed by WFOME separated from the bottom part of the reactor through a valve. The prepared biodiesel contains water soluble impurities like un-reacted KOH, leftover methanol, and some free glycerin. Washing the fuel with water remove these undesired impurities. The other benefit of washing is it stops slow reaction that sometimes occurs. Washed fuel look cloudy or hazy, shows the presence of water. A heating process at about 60 °C was applied for removing water contained in the waste frying oil methyl ester and finally, left to cool down.

3 Fuel Properties

The fuel properties were determined and are listed in Table 1, for waste frying oil methyl ester Biodiesel and diesel fuel.

Table 1 Fuel properties of diesel and WFOME

Properties	Test method	Diesel	WFOME
Kinematic viscosity @ 40 °C, cSt	D445	2.4	4.8
Density @15 °C, kg/m^3	D1298	822.4	882.5
Flash point, °C	D93	67	171
Net calorific value, MJ/kg	D240	42.7	38.4
Water and sediments % volume	D2709	0.01	0.02
Sulfer, %wt	D4294	0.28	Nil

4 Experimental Setup and Test Procedure

The experimental setup consists of a Diesel engine, an engine test bed, a gas analyzer and a smoke meter. The main specifications of the Diesel engine are given in Table 2. The setup contains instruments for measuring various parameters such as brake load, gas temperatures, and air flow. The schematic of the experimental setup is shown in Fig. 1.

For recirculation of the exhaust gas, an external EGR pipe line was created and part of exhaust gases was fed back to the cylinder by a control valve. No insulation on the pipe line was provided therefore allowing the re-circulated exhaust gases to partially cool down, further cooling was provided through a EGR cooler. An air damping box was placed in this route to dampen the fluctuations of the pulsating exhaust. The re-circulated gases before entering the engine cylinder were then passed to particulate filter to reduce the particulates entering into the combustion chamber. The percentage of EGR is calculated based on the following equation.

$$\text{EGR rate} = 100 \times (Q_{\text{without EGR}} - Q_{\text{EGR}})/Q_{\text{without EGR}}\%$$

where $Q_{\text{without EGR}}$ is air flow rate before EGR where as Q_{EGR} is the air flow rate using EGR.

Table 2 Test engine specification

Make	Force motors
Cylinder number and type	Four, four stroke
Bore (mm)	78
Stroke (mm)	95
Compression ratio	18.65:1
Rated power (H.P.)	27
Rated speed	2200 rpm

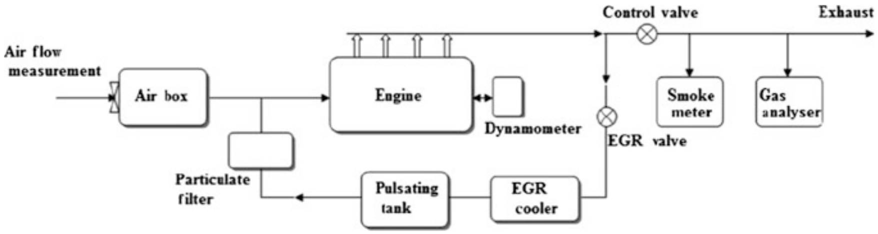

Fig. 1 Experimental setup

5 Result and Discussion

The test was carried out at a constant rpm of 2000 with 10% EGR, and by varying the load. Each test was repeated thrice to ensure that the results are repeatable within the experimental uncertainties.

The performance parameters tested was brake specific energy consumption, brake thermal efficiency, carbon monoxide, hydrocarbon, NO_x and smoke emissions. The base line data was prepared by using diesel as fuel.

5.1 Brake Specific Energy Consumption

Brake specific energy consumption (BSEC) is the product of brake specific fuel consumption with the calorific value. The BSEC is more reliable parameter for comparing the two fuels of different calorific values. The variation of Brake specific energy consumption (BSEC) of WFOME with the Brake mean effective pressure on different loading conditions is shown in Fig. 2. The values of BSEC were decreased with the increase in load, possibly due to reduction in losses at higher loads. BSEC of waste frying oil methyl ester was found to higher at all the loads. It may be due to the combined effect of higher viscosity and lower calorific value of the blend than those of diesel fuel. Use of EGR showed almost same BSEC as that of without EGR. A slight increase in BSEC was observed at highest load.

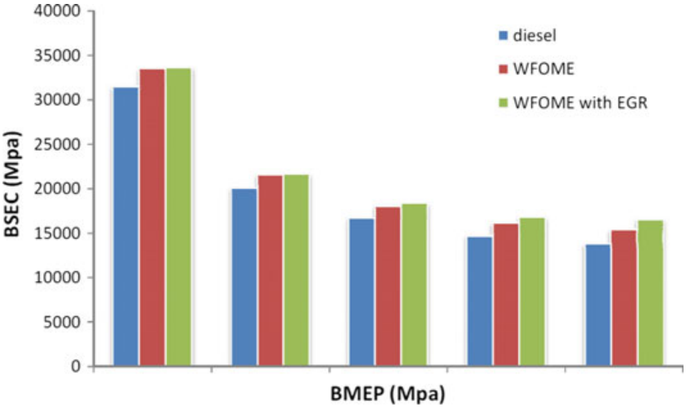

Fig. 2 Variation in BSEC with BMEP

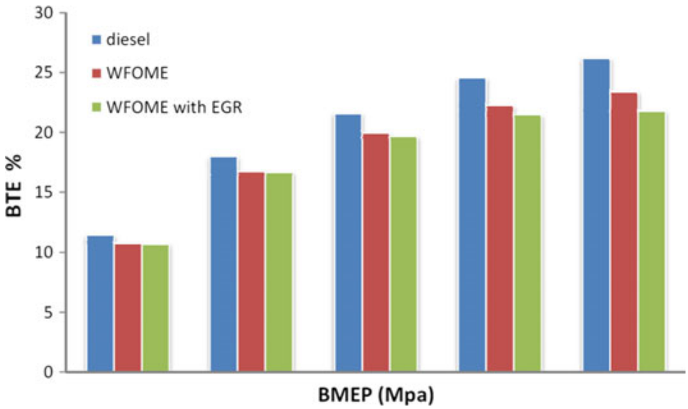

Fig. 3 Variation in BTE with BMEP

5.2 Brake Thermal Efficiency

Figure 3 shows the variation of Brake Thermal efficiency (BTE) with the BMEP. Thermal efficiency is the ratio of engine brake power to the energy of fuel. Energy of fuel is the product of mass flow rate of fuel and calorific value which is the BSEC and hence Brake thermal efficiency indicates the inverse of BSEC. BTE increases with increase in load due to reduction in heat losses at higher load.

WFOME showed lower efficiency than the diesel fuel. WFOME showed an average 8% reduction in BTE. This can be attributed to the lower calorific value of the WFOME which leads to increase in the fuel consumption. Use of EGR showed almost same BTE except a slight drop at peak load, it may be attributed to the admission of diluents affecting the combustion.

5.3 CO Emission

The variation of the carbon monoxide (CO) emission with the BMEP is shown in Fig. 4 CO emission was found to be reduced with increase in load. This trend is different from the most of the researcher [10, 11], but the similar trend was observed by few [12].

CO emission of diesel fuel was from 433 to 174 ppm. Waste frying oil methyl ester showed an average reduction of 13%. The reduction in Carbon monoxide emission may be due to the presence of oxygen molecules in WFOME, which promotes the conversion of CO into CO_2.

Use of EGR found to aggravates the carbon monoxide emission. An average increase of 8% was observed with the use of EGR compared to WFOME without EGR. The possible reasons could be attributed to the diluents admission. The effect

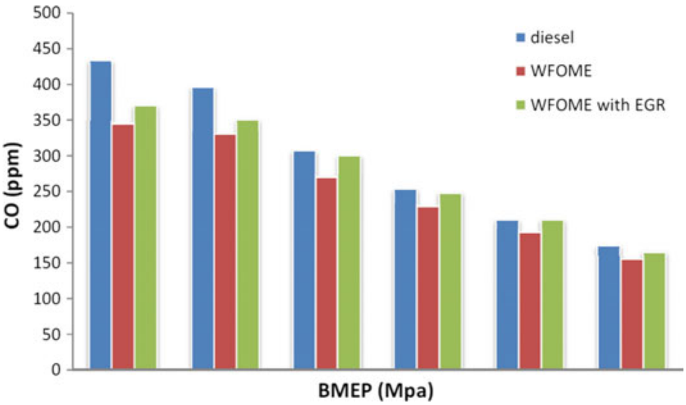

Fig. 4 Variation in CO emission with BMEP

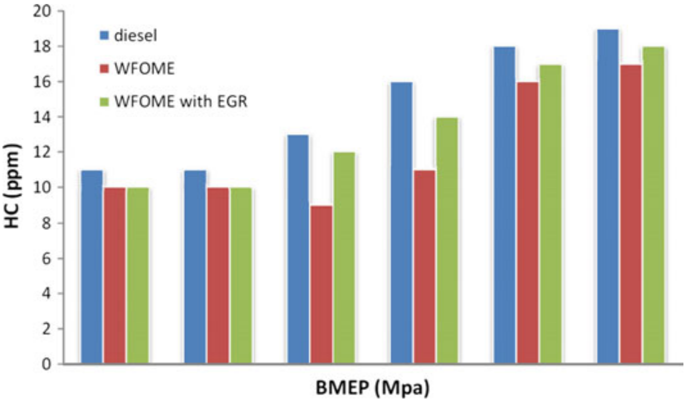

Fig. 5 Variation in HC emission with BMEP

of diluents admission is to lower the concentration of oxygen, which results in the retarded combustion.

5.4 HC Emission

The variation of unburned Hydrocarbon (HC) emission with BMEP is shown in Fig. 5. Graph shows that the increasing the load increases the hydrocarbon emission. WFOME showed an average 17% reduction in HC emission compared to diesel fuel, it is indicative of cleaner combustion which could be due to the presence of oxygen molecules in the WFOME fuel and higher temperature makes the HC oxidation easier.

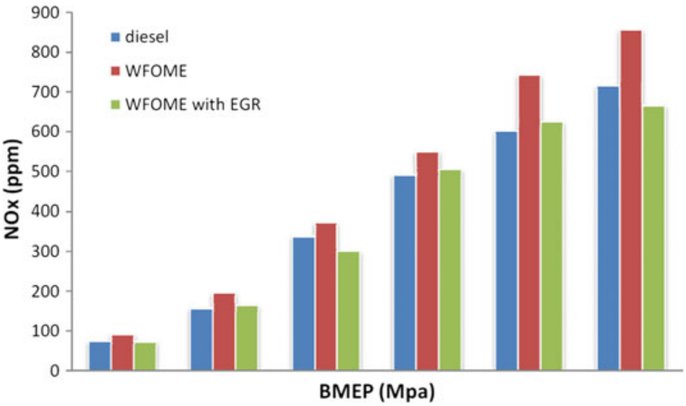

Fig. 6 Variation in NO_x emission with BMEP

Engine when operated with EGR, hydrocarbon emission increases. Applying EGR in an engine reduces the concentration of oxygen in the combustion chamber and hence the oxidation rate reduces, which in turn increase the Hydrocarbon emission. Effect of EGR was comparatively found to be higher at medium load. EGR showed an average 12% increase in HC emission. This may be attributed to the reduction in excess oxygen in combustion due to EGR.

5.5 NO_x Emission

Figure 6 shows the graph of variation of NO_x emission with the BMEP. The graph indicates that the increasing the load increases the NO_x emission. WFOME showed higher NO_x emission when compared to diesel fuel. WFOME showed 19% increase in NO_x emission compared to diesel fuel. Since NO_x formation depends upon the in-cylinder temperature, use of WFOME increases the oxygen contents and which in turn increases the temperature so NO_x formation increases.

NO_x emission was found to be decreased when establishes the EGR. The use of EGR results in 17% reduction compared to without EGR. The reason could be the replacement of in-cylinder oxygen molecules by the water and carbon dioxide, which results in the reduction of in cylinder temperature.

5.6 Smoke Emission

Figure 7 shows the graph of variation of Smoke emission with the BMEP. The graph showed raise in smoke emission with the increase in load. WFOME showed slight reduction in smoke emission due to oxygen enrichment. An average 13% reduction in smoke emission was observed with WFOME.

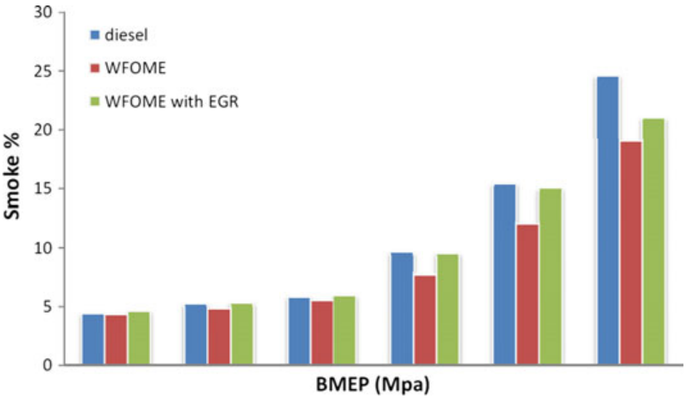

Fig. 7 Variation in smoke emission with BMEP

Use of EGR showed increase in smoke emission. Result showed an average increase of 14% compared to without EGR. The possible reason could be the reduction in the availability of fresh oxygen, inside the combustion chamber to oxidize the formed soot and outside the chamber to premix with the injected fuel.

6 Conclusion

In the present study, experiments were conducted with a diesel engine to investigate the performance and emission parameters of the biodiesel prepared from waste frying oil. The effect of cooled exhaust gas recirculation on the biodiesel was compared with the diesel fuel. The major conclusion was as follows.

- The WFOME showed reduction in carbon monoxide, hydrocarbon, and smoke emission and increase in NO_x emission, brake specific energy consumption and reduction in brake thermal efficiency.
- The recirculation of the cooled EGR showed reduction in NO_x emission with a slight increase in unburned hydrocarbon, CO, and smoke emissions.
- WFOME with EGR showed average reduction in CO, HC, NO_x and smoke emission if compared with diesel fuel with slight penalty in Brake specific energy consumption and brake thermal efficiency.

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Utilization of Waste Biomass into Useful Forms of Energy

Arunabha Sarkar and Ghodke Praveen

Abstract The rising cost of fossil fuel and environmental concern has motivated the scientific committee to research on alternative sustainable solution for energy and economic development. One of such sustainable energy resource is biomass, which is abundant, clean and carbon neutral. Agricultural residue which is abundant and causing problems of storage being wasted without using in any form energy source. The present study highlights utilization of residue biomass to useful form of energy using different thermochemical conversion technologies. This study is presented as a technical review cum analysis study which has been done on various common agricultural wastes for their Thermochemical conversion technologies which includes combustion, gasification, pyrolysis, torrefaction and liquefaction. The common agricultural wastes that are being taken for study are coconut shell, rice husk, corn cobs, cotton stalk, groundnut shell, cotton, sugarcane (bagasse). In Combustion process, the yield of gaseous product is around 50%, which can be utilized for combined heat and power production. In the combustion process, drawbacks are discussed and specified. It was observed that suitable combustor can be implemented for improving its oxidative characteristics so that the product gas yield can be increased for high quality steam production. In Gasification process, the biomass is partially oxidized to give a raw product gas or syngas which can be used in IC engines and for running gas turbines to produce electricity. It was observed that product gas or syngas obtained is around 85–90% pure compared to the gases obtained from coal gasification. Suggestions are made to improve the yield of syngas by suitable designs for specially downdraft gasifiers. Finally, Pyrolysis process of biomass is discussed, and focuses on improving the yield of liquid content by varying the operating conditions. Bio-oil production from pyrolysis can be varied from 65 to 75% by varying operating temperatures

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(500–650 °C) and heating rate. Finally, in this study we suggest the design of pyrolyser with different operating conditions for maximum yield of liquid, an attempt was made to increase the liquid product and reduce the char/gas content.

1 Introduction

The power and electricity consumption has been rising owing to increasing population. This has increased the pressure on fossil fuel resources such as coal, petroleum and natural gas. With these resources being gradually depleted in course of time the need for alternative, renewable energy resources has been realized and much of the work has already been progressed in renewable over the past decade. The oldest and the cleanest renewable technology that is being used is the Biomass conversion technology. It is the cleanest, abundant source energy that is being available in the environment. The available abundant sources such as agricultural residues, food wastes, energy crops, of biomass present in the environment makes it most popular in energy usage. The carbon neutrality of biomass fuels, makes it environment friendly, does not cause CO_2 emission thus preventing global warming and greenhouse effect. The term carbon neutral signifies no net release of carbon emissions into the atmosphere. This happens due to balancing a measured amount of carbon released with an equivalent amount of carbon sequestered or offset, or buying enough carbon credits to make up the difference [1]. In India, the biomass energy potential is estimated to be one-third of the total energy consumption in the country. The fuel wood estimates in India is around to be 218.5 million tons (dry), crop residue 96 million tons, cowdung or gobar for biogas production is around 37 million tons [2]. The production of biomass power generation in India is now carried out through on grid connected megawatt scale power generation with multiple biomass materials being the source raw materials such as rice straw, rice husk, bagasse, wood waste, wild bushes and paper mill waste [3]. Nearly 55 MW of grid connected biomass power is commissioned and around 90 MW is under construction, till date [4].

2 Basic Principle and Understanding

The Biomass feedstock that has been studied are some of the common agricultural or food wastes are coconut shells, corn cobs, rice husk, cotton stalks, groundnut seed and sugarcane (bagasse). The characteristics of each and every biomass be it the agricultural crop wastes or forest wastes or wood or energy crops is always determined by some of the characteristic properties present in it [5]. The property of a biomass material capable of use as a fuel depends on the following properties such as: moisture content, calorific value, proportions of fixed carbon and volatiles, ash or residue content, alkali metal content, cellulose/lignin ratio, carbohydrate content, protein content, lipid/fat content, pH level [6].

The type of biomass to be used decides the most likely form of the energy conversion process to be used. The moisture content is the main characteristic that has to be taken into account when considered in some situations, especially to those biomasses that lies between that of ‘wet’ and ‘dry’ variety. For wet biomass, the cellulose/lignin ratio determines the conversion process, while for dry biomass the calorific value, the proportions of fixed carbon and volatile matter, ash/residue content and alkali metal content are important factors. Therefore, some biomasses can be used for nearly all of the technological processes while others can be used just for a few processes [7].

3 Methodologies Used

We have considered thermochemical conversion processes for various biomass feedstock conversion processes. The various thermochemical processes for conversion technologies that are being implemented are combustion, gasification, pyrolysis and liquefaction [8] (Fig. 1).

In expanding the conversion routes to include the kind of biomass wastes and the specific energy product generated, we represent this in the following chart [9] (Table 1).

3.1 Combustion

Combustion is one of the oldest and still the most common method of thermochemical conversion process to convert biomass into energy. The usefulness of

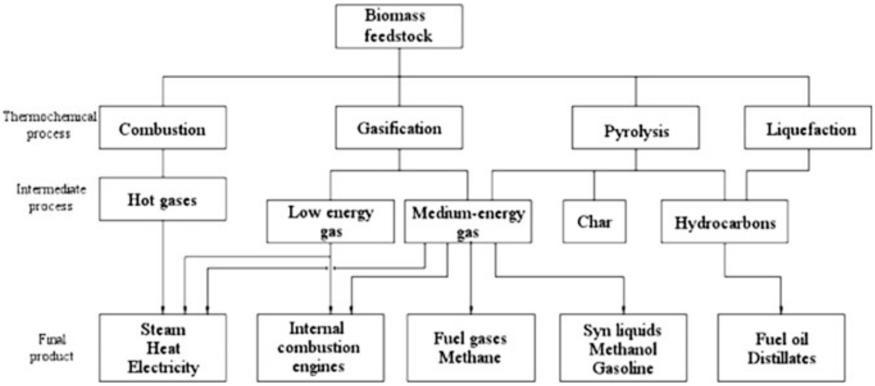

Fig. 1 Depicting main thermochemical conversion processes, their classification and their final energy products [8]

Table 1 Biomass conversion technologies used

Technology	Conversion process type	Biomass waste	Energy/fuel produced
Biodiesel production	Chemical	Rapeseed Soyabean Waste vegetable oil	Biodiesel
Direct combustion	Thermochemical	Agricultural waste Mixed waste	Heat Steam Electricity
Ethanol production	Biochemical	Sugar or starch Wood waste Pulp sludge Rice and corn straw	Ethanol
Gasification	Thermochemical	Agricultural waste	Low/medium producer gas
Methanol production	Thermochemical	Agricultural Mixed waste	Methanol
Pyrolysis	Thermochemical	Agricultural waste Municipal solid waste	Synthetic fuel Oil or biocrude Charcoal

combustion is largely seen in heat production. In power production the smallest commercial technologies are about 50 kW. However, combustion is not an effective way to generate electricity compared to gasification and even unfavorable in purpose for liquid and gaseous fuel production [10]. The different types of combustors used mainly for biomass agricultural wastes are fluidised bed, cyclonic, rotary kiln and liquid and gaseous incinerators are some of the examples.

The analysis of biomass combustion is preferably carried out in Fluidized bed Boilers, either Bubbling Fluidized Bed or Circulating Fluidized Bed. The major factors affecting combustion efficiency are:

1. Fuel characteristics.
2. Operational parameters.
3. Design parameters.

Biomass is a renewable fuel source and is considered greenhouse gas-neutral [11].

These fuels are generally more reactive than fossil fuels such as the type of coals such as anthracite and lignite. As a result, combustion is not such a major issue but problems like bed sintering, slagging, fouling and corrosion are there. The first three problems occurs due to relatively high alkali content of biomass fuels, while corrosion occurs due to the chlorine content [12].

Another characteristic of biomass fuels is its relatively high volatile content (60–80%). This makes any type of common combustion processes particularly unsuitable because combustion efficiency becomes relatively low. The simplest method of combustion seemed suitable for study of agricultural biomass waste combustion is

Table 2 Effect of biomass fuel properties on boiler performance

Fuel properties	Effect
Alkalis (Na, K)	Agglomeration of boiler parts Fouling of boiler tubes
Chlorine	Fouling of boiler tubes Corrosion of surface HCl contamination Dioxin formation Emissions
Heavy metals	Furnace corrosion Ash deposition
Sulfur	SO_2 emission
Nitrogen	NO_x emission

gaseous incineration where wastes of these crop wastes are burned and combusted in an incinerator or boiler. Table 2 lists some of the problems a common boiler faces due to different constituents of a biomass fuel. Accumulation of fuel deposits, fouling of the surface of the boiler, and hot corrosion are some of the significant problems that are found [13].

3.2 *Gasification*

In Gasification, the biomass is converted by partial oxidation at high temperatures into a gas mixture called syngas or product gas. The product gas formed is then utilized as a fuel in internal combustion engines (IC) engines or in gas turbines. Gasification technology can be used for heat and power production beginning from 1 kW micro-scale applications [14]. For agricultural biomass wastes coconut shells, bagasses and groundnut seeds find good potential for gasification processes as carried out experimentally.

3.2.1 Types of Gasifiers

There are three types of gasifiers that are mostly used for biomass conversion processes:

1. Downdraft Gasifier.
2. Updraft Gasifier.
3. Fluidized Bed Gasifier.
    - (i) Bubbling Fluidized Bed Reactor.
    - (ii) Circulating Fluidized Bed Reactor [15].

In the downdraft gasifier, fuel is fed near the top of the reactor. A schematic of the process is illustrated in Fig. 2 [16].

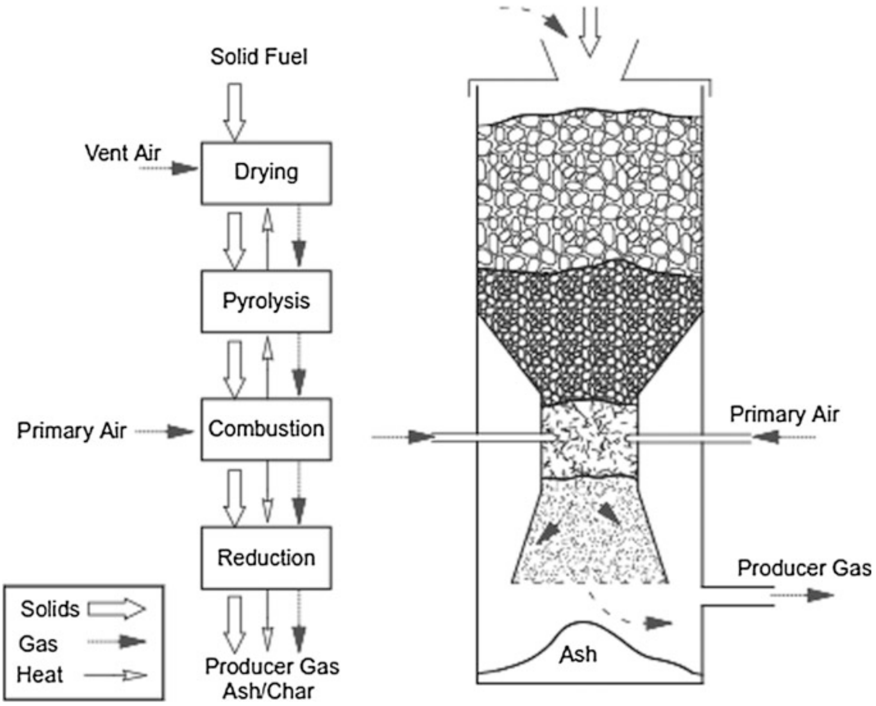

Fig. 2 Downdraft gasifier

In updraft gasification, shown schematically in Fig. 3, air is fed into the bottom of the reactor with the resulting producer gas flowing up through the upper spaces in the solid fuel [16]. The gasification processes used for utilization of waste biomass or crop wastes used in this process are simple updraft gasification only. The gas flow rate is measured with the help of a flow meter attached with the outlet of gas tube where the producer gas exits [17]. The quantity of producer gas produced with respect to amount of primary air entered determines the efficiency of gasification that has produced.

The updraft gasification process is similar to that of the downdraft mode in that the major reaction stages are present: drying, pyrolysis, combustion, and reduction [16].

Overall, the updraft gasifier is more suitable for gasification of crop wastes such as bagasse, coconut shells and rice husks. The producer gas obtained from this gasification processes are suitable for engine applications. The producer gases finds good use in direct heating applications since the presence of heavy tars contains high calorific value. Updraft gasifiers are best suited for direct heating applications, syngas or producer gas produced is suitable for gas or steam turbines running hence these are more conveniently used for waste crop utilization [19].

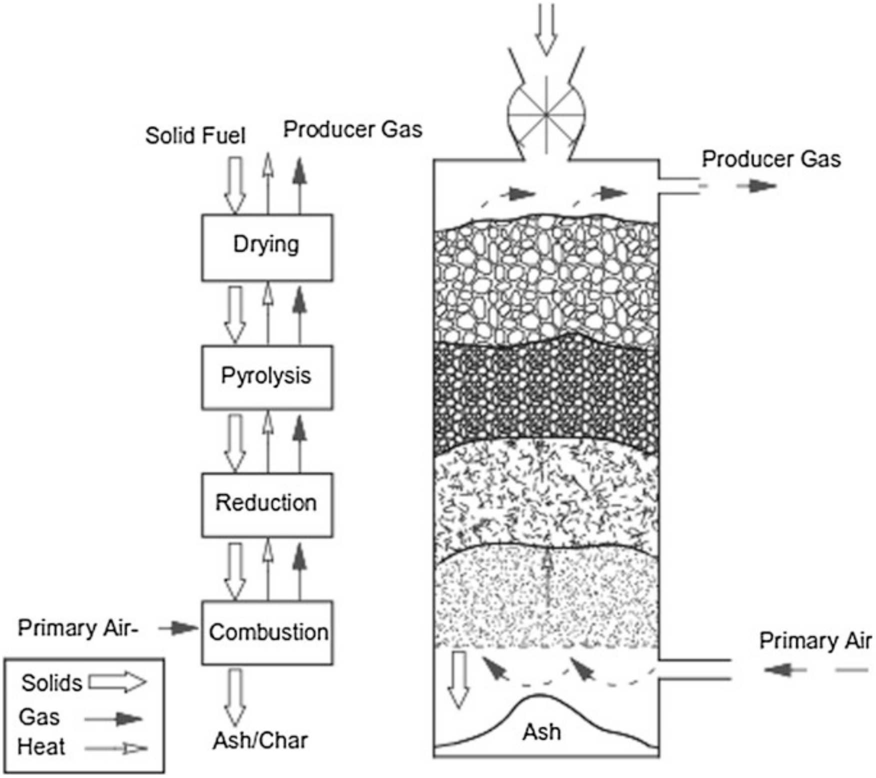

Fig. 3 Updraft gasifier [18]

3.3 Pyrolysis

Pyrolysis is a process of thermal decomposition occurring in the absence of oxygen. It is technically the first step occurring in combustion and gasification, but in these processes it is followed by total or partial oxidation of the primary products. High temperatures and longer residence times increase biomass conversion to gas, and moderate temperatures and short vapor residence time are key factors that contribute for good amount of liquid production [20]. There are three types of products that are produced typically, but the variety of products can be varied by adjusting the process parameters [21]. Table 3 gives us the product distribution obtained from different modes of pyrolysis at different temperatures [22].

The most important component of any pyrolysis process is the reactor. The most important types of pyrolysis reactors that are being used are:

1. Bubbling Fluid Bed
2. Circulating Fluid Bed
3. Ablative pyrolysis

Table 3 Product distribution from different modes of pyrolysis

Type	Process parameters	Liquid (%)	Solid (%)	Gas (%)
Fast	500 °C residence time ~1 s	75%	12% char	13
Intermediate	500 °C residence time ~10–30 s	50%	25% char	25
Slow torrefaction	290 °C residence time ~30 min	0% if vapors are burned	80% solid	20
Slow carbonization	400 °C residence time ~2–3 days	30%	35% char	35
Gasification	750–900 °C	5%	10% char	85

Data courtesy Bridgewater A.V. "Review of pyrolysis"

4. Rotating Cone
5. Entrained Flow
6. Vacuum pyrolysis.

Out of these reactors the fluidized bed reactors are more commonly used for pyrolysis in laboratory as well as in commercial scale. They are well suited to react to a variety of biomass resources starting from agricultural wastes, crop residues, plastic wastes, wood, sawdust, etc. [23] (Figs. 4 and 5).

The versatile and flexible nature of fluidized bed along with high efficiency of liquid fuel obtained gives us the option to utilize this process to maximum use in biomass conversion technologies. Bubbling fluid beds–usually preferred to as opposed to circulating fluid beds this is because they have the advantage of a well made technology that is simple in construction and operation, good temperature control and very efficient heat transfer to biomass particles arising from the high solids density [24].

Fig. 4 Fixed bed pyrolyser reactor on a laboratory scale setup

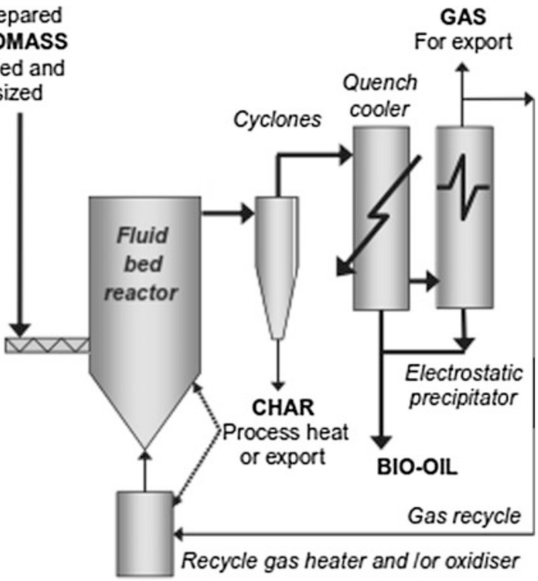

Fig. 5 Bubbling fluidized bed reactor

However for ease in operation and simpler control fixed bed pyrolyser has been used in this analysis in the laboratory scale. The image below shows the lab scale pyrolysis reactor used for analysis and also the schematic figure of bubbling and circulating fluidized bed reactors.

Circulating fluid bed (CFB) have many of the features of bubbling beds present, except that the residence time of the char is almost the same as for vapors and gas, and the char is formed due to the higher gas velocities [25]. The char content in the bio-oil if more then char removal is necessary and this char is recovered with the sand. There are techniques in which the bio-char obtained is utilized for other purposes such as for fertilizers or in making carbon nanotubes but that detail discussion is beyond the scope of the text. A typical layout of a CFB is shown in Fig. 6. The advantage of CFBs is that they are potentially suitable for larger outputs even though the hydrodynamics are more complex, as this technology is widely used at in the petroleum and petrochemical industry [26]. However for laboratory scale the fixed bed pyrolyses are best suited.

The characteristic features of a fast-pyrolysis process for producing liquids are:

1. Very high heating and heat-transfer rates of the reaction at the surface of the reactor, requiring a finely grounded biomass feed of less than 3 mm.
2. Pyrolysis reaction temperature should be controlled at around 500 °C and although the medium of liquid gets formed at around temperature of 400–450 °C.
3. The Hot vapor resides at the reactor are of less than 2 s.
4. We have to rapidly cool the pyrolysis vapors to give the bio-oil product [27].

The main product, bio-oil, is obtained up to 75 wt% yield on a dry weight, produced along with byproduct char and gas, which can be used within the reaction

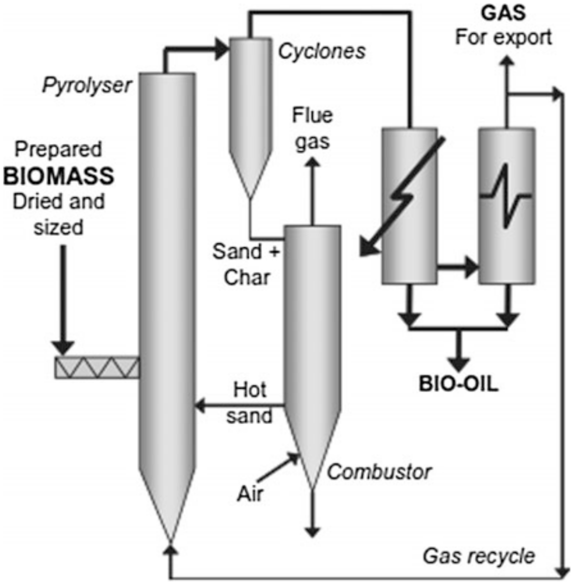

Fig. 6 CFB pyrolyser

system to provide the process heat requirements so there are no waste streams other than flue gas and ash [28].

The bio-oil obtained from pyrolysis liquid depends up on temperature, residence time of products, char content and biomass ash content, also depending on its catalytic effect [29].

A typical pyrolysis process affects the feed to typically less than 10% water content in the product liquid oil. The feed is grinded to around 2–3 mm particle size in this lab scale fluid-bed reactors. Here we have analyzed in fixed bed reactors so feed size can be 6–10 mm size to give sufficiently small particles to ensure rapid pyrolysis reaction. Separation of solids (char), quenching and collection of the liquid product also known as bio-oil [30]. While most of the work has been carried out on other agricultural sources but because of its consistency and comparability between tests in the experiments, agricultural wastes such as bagasse, rice husks, groundnut seed, corn cobs and cotton stalks offers a promising alternative for various liquid fuel uses in the future [31].

4 Results and Discussions

When we look at biomass combustion for all of the crop residues we see that bagasse and rice husk have the best performance characteristic followed by groundnut seed, coconut shell, corn cobs, and cotton stalk. The best efficiency a biomass combustor gives when the quantity of excess air is around 50–60% and efficiency maximum can be achieved up to 70 and 80%. In some cases the excess

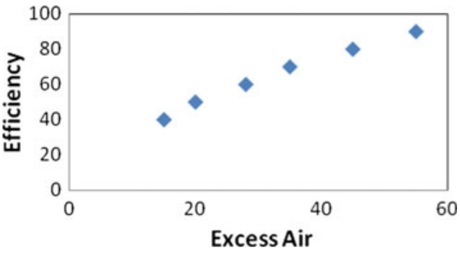

Fig. 7 Graph showing combustion efficiency relation with excess air percentage

air percentage when increased above 50–60% in case of bagasse the efficiency of combustor increase up to 90% (Fig. 7).

In Gasification process we study the efficiency of the gasifier of these crop wastes by measuring the amount of producer gas obtained, the heating value and the gross calorific value of this gas. The Gasification performance was seen best in coconut shells, corn cobs and sugarcane (bagasse).

There were slagging occurrences when rice husk were used as well as in cotton stalks. The gasifier efficiency depends on the amount of actual air supplied, fuel size particle range and moisture content. The particle size range of around 3–10 mm is required for efficient gasification processes, is a must for fluidized bed gasifier, for fixed beds at least 50–100 mm range is required for efficient gasification. The fluidized bed gasifiers require very fine particle size for effective gasification. The Bubbling fluidized bed and Circulating fluidized bed gasifiers shows good operating performance when it comes to handling crop residues, waste biomass feedstock. The producer gas yield obtained is of the range 70–75% with a high heating value sufficient to run a gas turbine or lighting, electrification, running CHP (combined heat and power) plant. Producer gases from air-blown gasification processes have low calorific value and high levels of unwanted components, such as particulate and tar, which should be eliminated prior to utilization in heating, chemical synthesis and engine applications. Additionally, the producer gases need to be dried to some extent if transported for short distances in a pipeline. The degree of gas treatment needed will depend strongly on its desired end use (Fig. 8).

The pyrolysis of biomass feedstock resulted to be one of the most promising thermochemical methods for fuel production as the liquid oil obtained from

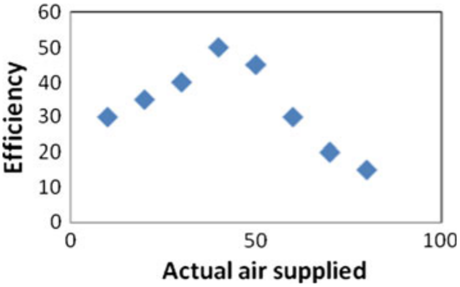

Fig. 8 Graph showing gasification efficiency with actual air supplied

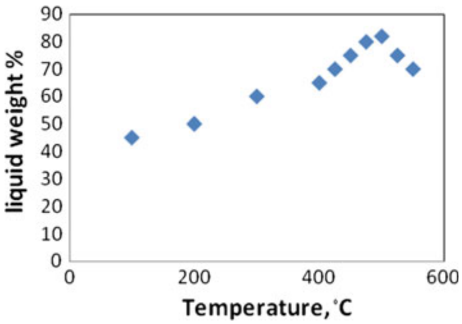

Fig. 9 Graph showing the percent yield of liquid obtained from pyrolysis against temperature

pyrolysis promises to be a great replacement of diesel oil and can be used in IC engines, generator fuel, running turbine to produce electricity. The pyrolysis of the above crop residues when carried out gives the most capable performance in the case of bagasse, followed by groundnut seed, coconut shell, corn cobs, rice husk and cotton stalks (Fig. 9).

The liquid fuel or Bio-oil obtained is of high yield. Fast pyrolysis liquid has a higher heating value but it is not suitable for pyrolysis of agricultural wastes. The batch process of pyrolysis or stage wise process of Pyrolysis is best suited for these kinds of processes from agricultural raw materials. Pyrolysis oil is basically a dark brown, free-flowing liquid. Depending on the type of source feedstock and the mode of pyrolysis, the color of the bio-oil varies from black to dark red-brown to dark green, depending upon its chemical composition. The quality of bio-oil produced at good yield happens to be in bagasse and in groundnut oils.

The bio-oil can be detected by a distinctive odor, also due to slight smoky smell due to the presence of aldehydes and acids, which can irritate the eyes on prolonged exposure. The liquid bio-oil contains several hundred different chemicals in widely varying proportions, from formaldehyde and acetic acid to complex high molecular weight phenols, anhydrosugars and other oligosaccharides.

Some of the characteristics given below:

1. This type of pyrolysis Liquid fuels find good use as a substitute fuel as conventional fuels in many stationary applications such as boilers, engines, turbines and in vehicles.
2. The fuel has good heating value of the range 17–20 MJ/kg which is quite promising compared to that of fuel oil/diesel oil.
3. The fuel has good calorific value and promising sustainability for future use as a substitute liquid fuel than many other hydrocarbon fuels originating from petroleum sources.
4. Although these fuels are cleaner, energy efficient but these are not as stable as fossil fuels.
5. These fuels if find use as a possibility as an alternative fuel source then quality check is must.

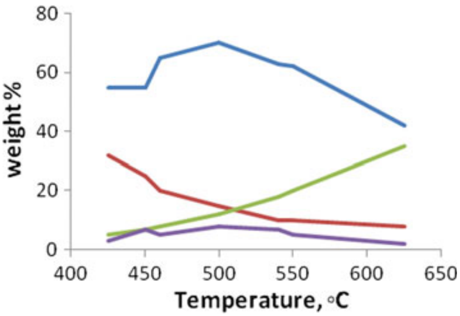

Fig. 10 Showing weight % of different products obtained from pyrolysis: *blue* yield of bio-oil, *red* char content, *green* gas content, *violet* water content (Color figure online)

The following graph demonstrates the composition of various products obtained from pyrolysis of agricultural wastes and its percentages of product composition shown of: gases, liquids, water content and char (Fig. 10).

The main advantages of pyrolysis liquid fuels are:

1. It is a carbon neutral fuel and the carbon balance is clearly positive in biomass fuel.
2. These fuels finds good use in small-scale power generation units as well as in use as a liquid storage fuel.
3. It has good storing and transportable properties as a liquid fuel.
4. Has high energy density, low viscosity compared to biomass gasification fuel.
5. The pyrolysis liquid fuel has good potential to use in power plants as well as in diesel fuel.

Bio-oil can be used as a substitute for fossil fuels for generation of heat, power and chemicals. For smaller applications the used in boilers and furnaces in power plants, whereas turbines and diesel engines can be used for longer periods of time. Depending upon the type of source material used for the biomass and pyrolysis conditions, 10–35% bio-char gets produced normally. At a low temperature (350–400 °C) zone, bio-char quantity gets high due to low devolatilisation rates and low carbon conversion. In a slightly higher temperature (450–550 °C) zone, the production of bio-char was reduced dramatically. The maximum yield of bio-oil gets produced in this region and bio-char produced is found to be about 8–10%. In a high temperature (over 550 °C) zone, bio-char yield was very low. Hence, depending upon composition and physical properties, bio-char can be utilized in various industrial processes such as: (i) as a solid fuel in boilers, (ii) for producing activated carbon, (iii) also finds application for making carbon nanotubes [32].

5 Conclusion and Recommendations

The three thermochemical processes of biomass waste conversion discussed above has the potential to eradicate the problem of carbon emissions in the atmosphere, prevent global warming, stopping the use of fossil fuels and replacing it with a clean energy technology. Among the biomass waste crops that has been used we see that bagasse has the highest usability followed by coconut shells, groundnut seeds, corn cobs, cotton stalks and rice husk. We therefore can describe the following thermochemical processes and their usability limit which it can be utilized. Starting with combustion, the design of proper combustors, controlling the amount of excess air, moisture content are one of the main factors that must be controlled in the combustion processes. However combustion is quite an ineffective way to generate electricity compared to gasification and even unfavorable for producing liquid or gaseous fuels. Nevertheless the biomass combustion process is still useful for generating heating CHP systems and for running steam turbines.

In Biomass gasification process, the producer gas obtained has the potential for running commercial heat engines, IC engines and gas turbines. The gas produced in gasification process can be used in two ways: (i) by using the product gas for combustion to produce a hot flue gas from which steam and then electricity is generated under the principle of Rankine cycle, (ii) Another utilization is direct production of electricity by using cleaned syngas in a gas engine.

The main focus is towards producing cleaned syngas and most of the research in this field deals with the study of CHP technology which can be used in gas engines or combined with heat exchangers in engine exhaust streams of vehicles. The main focus of improvement in the gasification processes of agricultural biomass wastes are maintaining an uniform fuel particle size, reducing the fuel moisture content, particulate removal, tar and oil removal. In pyrolysis process of biomass wastes, the fuel obtained is a liquid fuel, referred to as bio-oil, representing similar in composition to diesel oil. The liquid bio-oil produced by the pyrolysis of agricultural wastes has the properties of a storable and transportable fuel, as well as having the capability of producing valuable chemicals.

It this reason why pyrolysis is considered as the best advantageous process and its production should be chosen as the best alternative to other biomass conversion processes. The pyrolysis technologies for the production of liquid fuel from biomass wastes have been successfully demonstrated on a small scale, and several large pilot plants are in demonstration stage or in operation as well as at an advanced stage of construction. However they are still expensive compared to fossil fuel based energy resources, and thus face economical and other non-technical problems for gaining popularity in the energy market.

The most important challenges that need to be focused and taken care of are:

1. Increase of construction of these pyrolysis plants.
2. Reducing the cost of the pyrolysis processes.
3. Improving the product quality by setting certain standards for producers and users.
4. Environmental health and safety rules and regulations to be set for handling, transport and storage.
5. Implement processes and certain standards that helps users to implement these processes instead of throwing these raw materials as wastes.

6. Spreading out information to create awareness and helping people to encourage using these processes more in future.

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Experimental Investigation on Use of Bitter Apricot Kernel Biodiesel Blends in Single Cylinder Diesel Engine

Virender Singh Gurau, Akash Deep and Sarbjot Singh Sandhu

Abstract The rapid extinction of fossil fuels and global warming issue made the researchers to found some alternative renewable and clean burning fuel. Biodiesel is one of the worldwide renowned substitute for mineral diesel as it is renewable and has low emission profile. In this present work Bitter Apricot kernel oil from Indian origin was used for biodiesel production. The fuel properties of produced biodiesel were investigated as per ASTM D6751. It has been found that measured properties of biodiesel are as per ASTM standards. The biodiesel blends B10, B20, B30 and B50 are investigated for performance and emission analysis and compared them with baseline diesel fuel data. The engine testing results reveled that by using biodiesel blends CO, HC emissions and smoke opacity are decreased while NO_x emission increases as compared to diesel fuel.

1 Introduction

Energy plays an important role in the economic growth of the country. The importance of renewable energy sources come into existence because of the rapid depletion of fossil fuels. Vegetable oils are renewable energy source and significant environmental benefit can be derived from the combustion of vegetable oil based biodiesel rather than petroleum based diesel fuels. The most commonly used feedstock for biodiesel production are soybean, rapeseed, sunflower, safflower, etc. [1]. These oils are essentially edible in nature. Out of total cost of biodiesel, the feedstock contribute about 88% of cost if it is produced from edible oil [2]. Few attempts have been made for producing biodiesel with non-edible oils like karanja, jatropha, neem and palm in India [3]. However, there remain a number of other tree based oilseeds with an estimated annual production potential of more than 20 Mt

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[3]. These oils have great potential to make biodiesel for supplementing other conventional sources.

Therefore, following mentioned objectives are formulated for the present research work.

- Production of biodiesel from Bitter Apricot Kernel oil.
- Characterization of produced biodiesel as per ASTM D6751.
- Performance and emission analysis on the diesel engine test rig to and compare with baseline data of mineral diesel.

2 Materials and Methods

In this research work Bitter Apricot kernel oil (FFA <2%) is used for Biodiesel production. As the oil has low Free Fatty Acid (FFA), so it is suitable for biodiesel production through direct transesterification reaction.

2.1 Transesterification of Bitter Apricot Kernel Oil

Transesterification has been done to produce biodiesel. Transesterification is also known as alcoholysis. A mixture of bitter apricot kernel oil and methanol mixed with potassium hydroxide (used as catalyst) are heated and maintained at 60 °C, while the solution is continuously stirred with the help of magnetic stirrer. Catalyst concentration, 1% (% wt./wt. of oil) and molar ratio of, 6:1 (alcohol:oil) is used. Time taken in transesterification reaction is s to 60 min. When the reaction is over, product is poured into separating funnel. Two distinct layers are formed; the lower layer is of glycerin and the upper layer of ester. The glycerol formed is removed by density separation. The upper layer (ester) is separated out, washed with mild water and then heated to 110 °C to remove any moisture present in the biodiesel. Transesterification process increases the volatility and decreases the viscosity of the oil, making it similar to the diesel fuel in these characteristics.

2.2 Bitter Apricot Kernel Oil Biodiesel Properties

Measured physico-chemical properties of bitter apricot kernel oil biodiesel are shown in Table 1.

Table 1 Measured properties of bitter apricot kernel oil biodiesel

Property	ASTM method	Value
Acid number (mg KOH/g)	D 664	0.10
Density @ 15 °C (g/cm^3)	D 1298	0.88
Kinematic viscosity @ 40 °C (cSt)	D 445	4.32
Calorific value (MJ/kg)		39.5
Flash point (°C)	D 93	115
Ester content (%)	EN 14103	95

Table 2 Specifications of the diesel engine

Make	Kirloskar
Model	TV 1
Rated brake power (kW)	5.2 kW @ 1500 rpm
Rated speed (rpm)	1500
Number of cylinder	One
Bore × Stroke (mm)	87.5 × 110
Displacement volume (cc)	661
Compression ratio	17.5:1
Cooling system	Water cooled
Fuel injection	23° before TDC

2.3 Diesel Engine Test Rig

A kirloskar made single cylinder direct injection diesel engine test rig was used for engine testing. The specifications of Diesel engine are shown in Table 2.

3 Results and Discussion

The first section shows the results of various tests conducted for physico-chemical characterization of biodiesel and diesel fuel. The second section discusses the results of performance and emission analysis on diesel engine.

3.1 Evaluation of Physico-chemical Properties

All the fuels, namely neat diesel and diesel-bitter apricot kernel oil biodiesel blends were analyzed for several physical, chemical properties. Density and viscosity of biodiesel-diesel blends were found to be higher than those of diesel fuel. Blending of biodiesel derived from bitter apricot kernel oil in diesel reduces calorific value of the blend due to lower heating value of biodiesel. Table 3 shows the Physico-Chemical properties of fuels used in engine.

Table 3 Physico-chemical properties of fuel used

Sample	Density (g/cm^3)	K.V. (cSt)	Cal. Val. (MJ/kg)	Flash point (°C)
Diesel	0.85	2.95	42	65.5
B10	0.855	3.087	41.75	70.5
B20	0.857	3.224	41.5	75.5
B30	0.86	3.361	41.25	80.5
B50	0.865	3.635	40.75	90.5

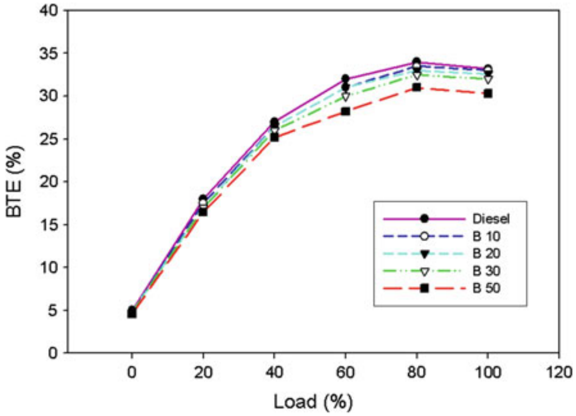


Fig. 1 Variation of brake thermal efficiency with engine load

3.2 *Performance Characteristics*

The performance characteristics of the test engine on neat diesel and biodiesel-diesel blends are summarized below.

3.2.1 Brake Thermal Efficiency

The variation of brake thermal efficiency with different test fuels is shown in Fig. 1. For all fuels brake thermal efficiency increase with increase in engine load reaching a maximum somewhere at 80% load and then decreases. The peak brake thermal efficiency for diesel, B10, B20, B30 and B50 fuels are 34.1, 33.6, 33, 32.4 and 31% respectively. The result shows that brake thermal efficiency with biodiesel blend was little lower than neat diesel fuel [4–6].

3.2.2 Brake Specific Energy Consumption

For comparing the fuels with different calorific value and density, brake specific energy consumption (BSEC) is an ideal parameter. The variation of BSEC with

Fig. 2 Variation of brake specific energy consumption with engine load

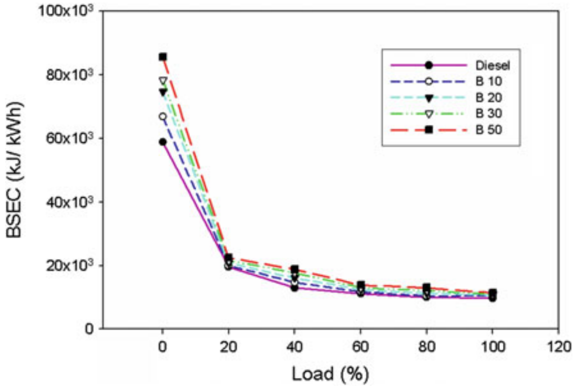
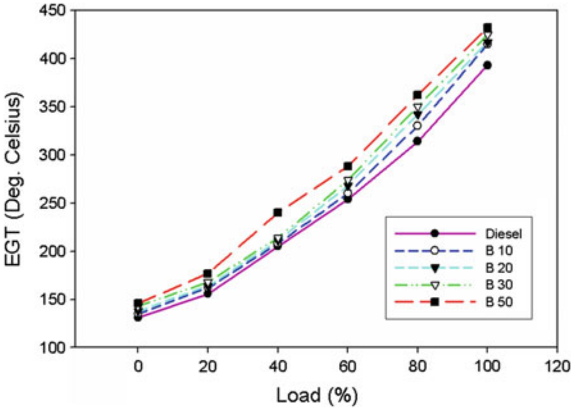


Fig. 3 Variation of exhaust gas temperature with engine load

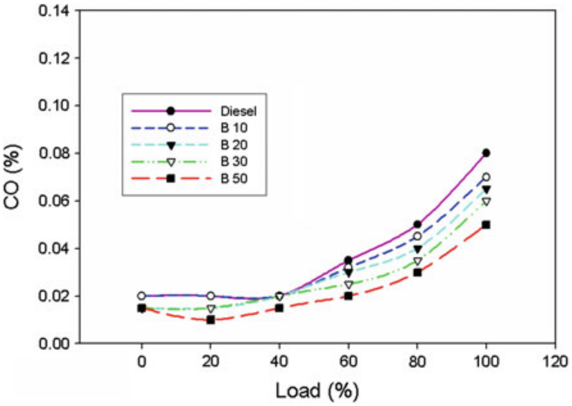


engine load for different test fuels is shown in Fig. 2. The result shows that for all the fuels the BSEC decreases with increase in load. For biodiesel and its blend the BSEC is slightly higher than diesel fuel. This is due to lower calorific value with increase in biodiesel percentage in the blends [7].

3.2.3 Exhaust Temperature

Figure 3 shows the variation of exhaust gas temperature with engine load for all the tested fuels. The results show that the exhaust gas temperature increases with the increase in load for all the test fuels. Exhaust gas temperature is an indicative of the quality of combustion in the combustion chamber. For all loading condition diesel was found to have the lowest temperature. The temperature increases with the concentration of biodiesel in the blends [4, 5].

Fig. 4 Variation of CO emission with engine load



3.3 *Emission Characteristics*

The emissions characteristics of the test engine on neat diesel and biodiesel-diesel blends are summarized in this section.

3.3.1 CO Emissions

Figure 4 shows the CO emissions for the diesel fuel and biodiesel blends. CO formed mainly due to incomplete combustion of fuel. The graph shows that CO increases with load because as the load increases fuel air mixture becomes richer. For biodiesel blends CO emission was less than mineral diesel, the reason may be biodiesel contain about 10% inbuilt oxygen that results in comparatively complete combustion of the fuel [5, 8]. Compared to mineral diesel fuel 20% biodiesel blend reduced CO emissions by 18.75% at full load.

3.3.2 CO_2 Emissions

Figure 5 compares the CO_2 emissions of various test fuels with engine load. The CO_2 emission increases with increase in load as the air-fuel mixture become richer at higher loads. The biodiesel blends emits more amount of CO_2 as compared to neat diesel fuel. More CO_2 emission for biodiesel blends indicates better combustion of biodiesel blends as compared to diesel fuel [4–6].

3.3.3 NO_x Emissions

The variation of NO_x emission for different fuels is indicated in Fig. 6. The result shows that NO_x emission for biodiesel blends are higher than diesel fuel at the same

Fig. 5 Variation of CO_2 emission with engine load

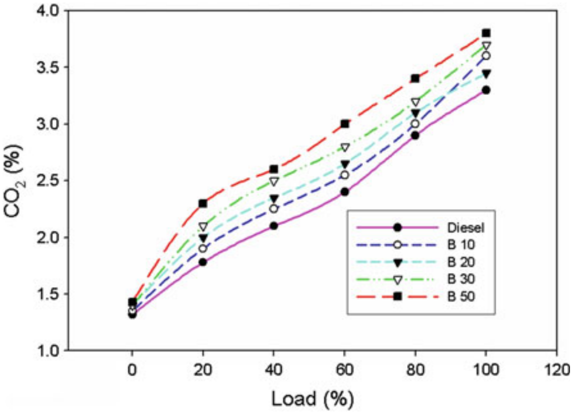
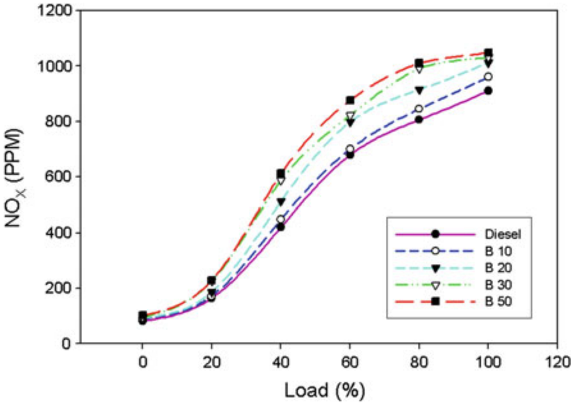


Fig. 6 Variation of NO_x emission with engine load



loading condition. This may be due to the presence of more oxygen content in biodiesel blends. This excess oxygen content in biodiesel blends was responsible for higher exhaust temperature and also NO_x emission [4–6, 9]. Around 11% increase in NO_x emission was observed with 20% biodiesel blend at full load.

3.3.4 HC Emissions

Figure 7 shows the variation of HC emissions for different test fuels with load. The result shows that hydrocarbon emissions tend to increase for all fuels with increasing load. This is due to injection of more fuel with increase in load which make air-fuel ratio richer and make combustion comparatively poor. The results shows that with increasing amount of biodiesel in blends, HC emissions tend to decrease and are lower compared to diesel fuel. This is due to inbuilt oxygen content in biodiesel [8, 10, 11].

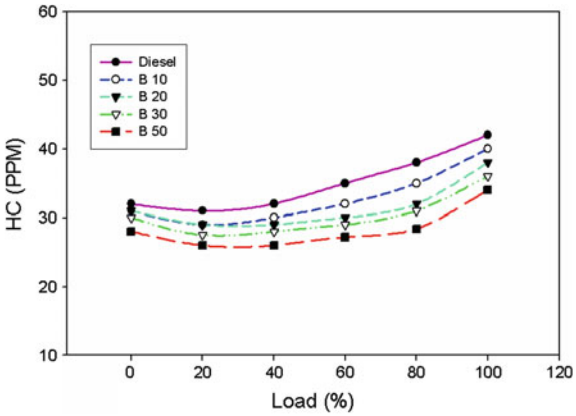


Fig. 7 Variation of HC emission with engine load

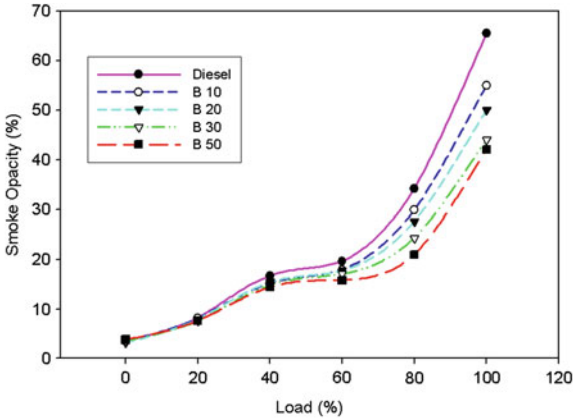


Fig. 8 Variation of smoke opacity with engine load

3.3.5 Smoke Opacity

The variation of smoke opacity with engine load for diesel fuel and biodiesel blends is shown in Fig. 8. It can be seen that smoke opacity increases with increase in load for all test fuels. The results shows that biodiesel blends have less smoke opacity as compared to diesel fuel for all loading conditions because of the comparatively good combustion [12].

4 Conclusions

The bitter apricot kernel oil was taken as a feedstock in the present research work mainly to evaluate the potential suitability of bitter apricot kernel oil for conversion into biodiesel and subsequent engine application. From the series of exhaustive experiments, the following conclusions can be derived.

- The brake thermal efficiency with biodiesel blend was little lower than that of diesel fuel.
- The BSEC decreases with increase in load. For B5, B10, B20, B30 and B50 the BSEC is slightly higher than neat diesel.
- The exhaust gas temperature increases with the increase in load for all the test fuels. At all loading condition diesel fuel was found to have the lowest exhaust temperature.
- CO emission is found to increase with increase in load for all test fuels. Biodiesel blend shows lower CO emission than diesel fuel. Biodiesel blend B20 reduced CO emissions by 18.75% at full load.
- The biodiesel blends emits more CO_2 emission as compared to neat diesel operation.
- The NO_x emission for biodiesel blends are higher than diesel fuel. Approximately 11% increase in NO_x emission was observed with 20% biodiesel blend at full load.
- HC emissions for biodiesel based fuels are lower than diesel fuel. It was found that with increase in concentration of biodiesel in blends, a downward trend in HC emission is observed.
- Smoke opacity for biodiesel blends is found lower than diesel fuel for all loading conditions.

It can be concluded from the research work that B20 blend can be successfully used in Diesel engine without sacrificing much performance and improve emissions.

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CFD Simulation of a Common Rail Diesel Engine with Biobutanol-Diesel Blends for Various Injection Timings

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Abstract Turmoil in petroleum market and stringent environment guidelines, accelerated the research in the field of alternative fuels for Internal Combustion engines. Biofuel is gaining venerable importance as it is renewable and substitute to the fossil fuels. This study investigates the potential of butanol fueling in a diesel engine. In this computational fluid dynamics (CFD) simulation, the effect of injection timing and butanol-blends on the exhaust emission and combustion characteristics of common rail direct injection (CRDI) engine is studied. The simulation is carried out for wide range of injection timings from 0° to 30° BTDC, and butanol-diesel blends from, 10, 20, and 30% at very high injection pressure ($\sim$90 MPa). Three dimensional computational code is implemented to solve conservation equations based on finite volume method. SIMPLE (semi-implicit method for pressure-linked equations) algorithm is used to obtain velocity and pressure at each computational cell. The flow within the combustion chamber is simulated using the k-ξ-f turbulence model. Extended coherent flame model-3 zone (ECFM3Z) is employed to carry out combustion analysis. In-cylinder fuel injection is studied using blob injection which assumes orifice diameter as fuel droplet diameter. As the percentage of the butanol blend increases, NO, CO increases and soot formation decrease as compare to neat diesel. Optimum injection timing obtained for maximum indicated thermal efficiency for 10–30% blend is 27° BTDC, whereas, for neat diesel it is 24° BTDC. Obtained results are validated with available literature data and found good agreement.

Abbreviations

BTDC	Before top dead centre
CO	Carbon monoxide
D_t	Diffusion coefficient
$\tilde{E}_{Fu}^{F\rightarrow M}$	Unmixed fuel

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$\tilde{E}_{O_2}^{A\rightarrow M}$	Unmixed oxygen
ECFM3Z	Extended coherent flame model three zone
EVO	Exhaust valve opening
IMAP	Intake manifold air pressure
IMAT	Intake manifold air temperature
IVC	Inlet valve closing
M_{Fu}	Molar mass of fuel
M^M	Mean molar mass of the gases
NO	Nitrogen oxide
R	Universal gas constant
S_c and S_{ct}	Laminar and turbulent Schmidt numbers
S_e	Energy source term
S_i	Momentum source term
S_m	Mass source term
$\bar{S}_{NO}$	Mean nitric oxide source term
$\tilde{u}$	Density-weighted average velocity
$\bar{\dot{\omega}}_x$	Average combustion source term

Greek Letters

ζ	Transformed coordinate system
$\bar{\rho}^u\vert_u$	Density of the unburned gases
ε	Dissipation rate
ϕ	Equivalence ratio
μ	Dynamic viscosity

1 Introduction

Fossil fuel crisis and stringent imposed emission regulations due to environmental degradation, renewable alternative fuels are driving attention for internal combustion engines. Biofuel is biomass based renewable energy source, produced from natural materials. These can be produced from edible as well as agricultural waste such as corn, sugar cane, molasses, wheat straw, corn stover and other cellulose etc. More oxygen concentration content of alcohol, results in cleaner combustion, which increases the thermal efficiency and reduces the emissions. In addition small water content leads to decrease in combustion temperature hence reduction in NOx [1–3].

The commonly used biofuels are ethanol, methanol and butanol. Hence biofuels are receiving impetus as renewable substitute to fossil fuels. Bio-butanol is competent among the biofuels because of more energy content by volume, better blending stability with diesel, lower vapour pressure, high miscibility, high cetane number, lower heat of vaporization, less corrosive and less auto ignition temperature compared to ethanol and methanol. Hence less ignition problem compared to ethanol and methanol [4–6]. Study is also reported that crude glycerol, by product of biodiesel production during transesterification process cane converted value added bio fuel containing mainly butanol [1].

Rakopoulos et al. [7], experimentally investigated, performance and emission characteristics of diesel engine operated with bio-butanol-diesel blends. Six cylinder, turbo charged water cooled engine was evaluated for two blends and three loads on mini-bus. Studies revealed that, bio-butanol fuel is promising alternate fuel for diesel engines [7].

Yao et al. [8], conducted experimental study on effect of n-butanol as additive in heavy duty diesel engine. The engine is operated with multiple injection and at constant load with exhaust gas recirculation (EGR). They observed significant improvement in CO and soot emission with marginal affecting brake specific fuel consumption [8].

Influence of fuel properties on engine performance and emissions are investigated by Lujaji et al. [9]. Results of two different blend samples are compared with pure diesel. Exhaust emissions such as carbon monoxide and smoke are found to be less in the case of butanol blended fuel compare to the diesel operation.

Dogan et al. [10], observed that nitrogen oxide, smoke opacity and carbon monoxide emissions reduces whereas increase in unburned hydro carbon emission for engine operated with higher n-butanol diesel blends.

Gerardo et al., conducted experiment on, CRDI, water cooled, and high speed diesel engine operated with n-butanol diesel blends under low temperature combustion. It has been revealed that, for 40% biobutanol blends, increase in in-cylinder pressure, faster burning rate and longer ignition delay [11, 12].

Study conducted by Rajesh Kumar et al., observed that reduction of NOx and smoke emissions for engine operated with low EGR, retarded injection timing and higher alcohol diesel blends (iso-butanol and n-petanol) [13].

Atmanli et al. [14] conducted experimental study to evaluate effect of n-butanol addition in vegetable oils (Canola-hazelnut-cottonseed oil (CHC) and neat sunflower–corn–soybean oil (SCS)) blends. The unmodified engine is operated with variable speed and full load condition (100% throttle open). They observed that cold flow properties of vegetable oil can be significantly improved. Brake torque, brake thermal efficiency, brake power and exhaust gas temperatures are decreased for blend operations.

The effect of pre injection timing and pilot injection mass with lower EGR is studied by Haozhong Huang et al. They observed that for the fuels pre injection results in decrease of peak heat release rate and contrarily increases in main injection. Addition of n-butanol in diesel leads to rise in maximum pressure rise rate and brake specific fuel consumption [15].

An experimental investigation to evaluate effect of biobutanol diesel (8, 16 and 24% by Volume) blends were conducted by Rakopoulos et al., The experimentation conducted on 4stroke, high speed Ricardo hydra engine working at constant load and variable speed. Results observed that reduction in NOx and CO and increase unburned hydrocarbon with more biobutanol diesel blends [16].

Diesel engine is operated with Bio diesel with oxygenated fuels such as n-butanol and diethyl ether (DEE) as additives. Experimentation is carried out on four stroke, variable speed, constant load, turbocharged indirect injection engine. 10% blend of n-butanol and DEE improved performance and emission results [17]. Pour point of palm oil methyl ester is improved by adding 1-butanol in diesel blends [18].

2 Problem Identification and Basic Principle

Detailed CFD studies on combustion and emission characteristics of direct injection engines using biobutanol diesel blends are very scant in open literature. In this study, we explore the details of variations in the engine performance, tailpipe emissions and combustion characteristics for various biobutanol diesel blends and different injection timings. The CFD simulation is carried out for a four stroke common rail direct injection (CRDI) engine to better comprehend the in-cylinder combustion. In-cylinder pressure, temperature, and engine-out emissions of soot, NO and CO were measured. Further in-cylinder pressure traces were considered to determine the heat release rates in terms of ignition delay.

3 Methodology

Engine details and fuel properties:

CRDI engine used by Mobasheri et al. [19] and Han et al. [20] is considered for CFD simulation in the present work. The details of the engine system and injection system are listed in Table 1.

Fuel properties and combustion strategy:

Biobutanol-diesel blend is considered in the present study with 0–30% by weight concentration of biobutanol. The neat diesel and butanol fuel properties are considered Rakopoulos et al. [7]. Simulations are carried out for various biobutanol blends and at 10 different injection timings (3–30° BTDC). The Range of simulation parameters is listed in Table 2.

CFD code and meshing of geometry:

AVL ESE CFD tool is used for Engine Geometric modelling and computational meshing as shown in Fig. 1. The injector with 6 holes is located centrally on the top of piston, hence 60° sector is chosen for the computational simulation.

In order to reduce the computational time only high pressure cycle is considered in the present work. Simulation is started and ended at inlet valve close and exhaust valve open position respectively. Grid independence test has been carried out to

Table 1 Engine specifications [19, 20]

	Values
Engine parameters	
Bore × Stroke	0.13719 m × 0.1651 m
Compression ratio	15.1:1
Connecting rod length	0.26162 m
Displacement	2441 cm^3
IVC	147° BTDC
EVO	134° ATDC
Engine speed	1600 RPM
IMAP	184,000 N/m^2
IMAT	310 K
Injector parameters	
Injector type	Common rail
Injection pressure	90 MPa
Number of nozzle holes	6
Nozzle hole diameter	0.00026 m
Injection duration	21.5° CA
Fuel injected	0.0001622 kg/cycle

Table 2 Range of simulation parameters

Parameters	Range
Blend (% of biobutanol)	0, 10, 20, 30
Start of injection	3°–30° BTDC

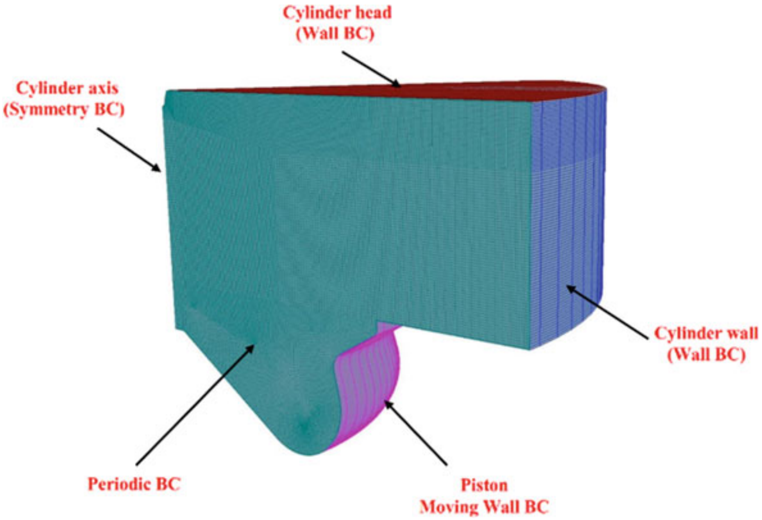


Fig. 1 Three dimensional computational domain at TDC position

obtain optimum grid size as shown in Fig. 2a, b. Simulation is carried out by 64 GB RAM 16 core work station with parallel processing. Results have been checked for peak pressure, peak temperature and computational time for various grid sizes. It has been found that considered parameters are invariant with change in total number of grids at/after 3 × 10^5.

Combustion Model:

ECFM-3Z model is modified version of ECFM, which is based on flame surface density approach. ECFM features take cares of premixed flame, knock and pollution formation. With ECFM features, ECFM-3Z takes care of diffusion flame and mixing process. In this model each computational cell is divided into three mixing zones. The three zones are pure fuel zone, air plus EGR zone and mixed zone [21]. The schematic representation is as shown in Fig. 3.

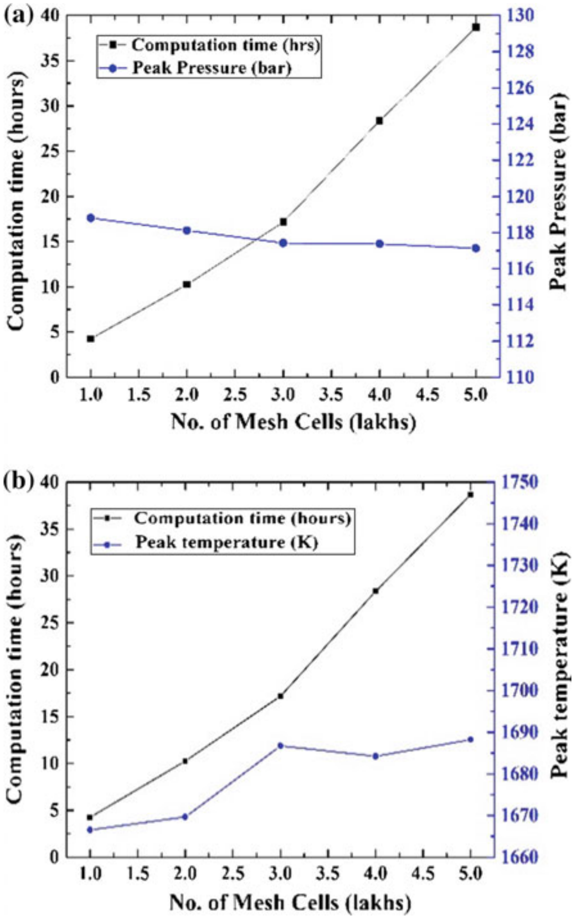


Fig. 2 Grid independence study carried for **a** peak pressure, and **b** peak temperature

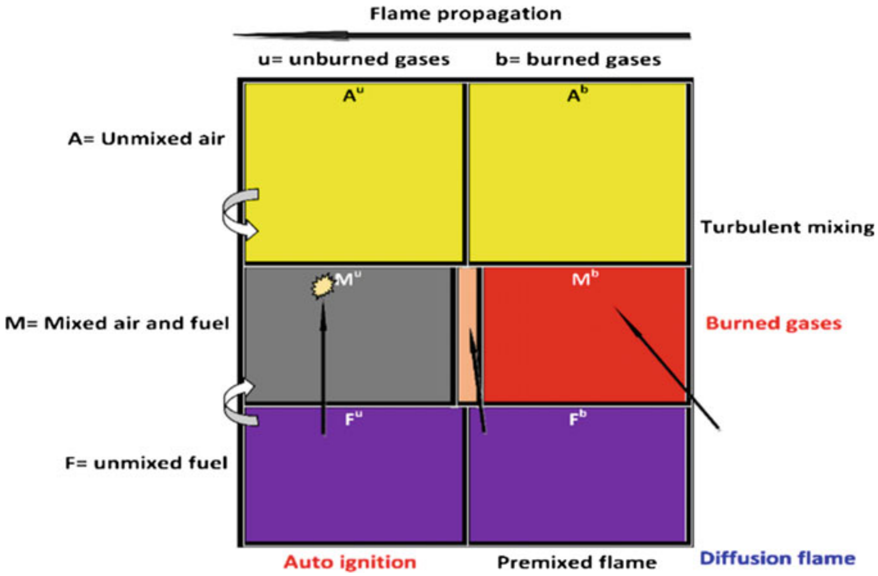


Fig. 3 Three zone combustion modelling

Governing equations
Conservation of mass:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \left(\rho \vec{V}\right) = S_m \tag{1}$$

Conservation of momentum equation:

$$\frac{\partial (\rho \vec{V})}{\partial t} + \nabla \cdot \left(\rho \vec{V} \vec{V}\right) = -\nabla p + \nabla \cdot \left(\bar{\bar{\tau}}\right) + \rho \vec{g} + S_i \tag{2}$$

Where, the stress tensor can be written as:

$$\bar{\bar{\tau}} = \mu \left[\left(\nabla \vec{V} + \nabla \vec{V}^{\mathrm{T}}\right) - \frac{2}{3} \nabla \cdot \vec{V} I \right]$$

The second term in stress tensor is the effect of volume dilation, and I is the unit tensor.

Conservation of energy:

$$\frac{\partial (\rho E)}{\partial t} + \nabla \cdot \left(\vec{V}(\rho E + p)\right) = \nabla \cdot \left(\lambda_{eff} \nabla T + \bar{\bar{\tau}} \cdot \vec{V}\right) + S_e \tag{3}$$

The k-ζ-f model is employed to treat turbulent flows. To improve numerical stability $\bar{v}^2 - f$ model by solving a transport equation for the velocity scale ratio $\zeta = \bar{v}^2/k$ instead of velocity scale $\bar{v}^2$ [21].

Global species Equation:

$$\frac{\partial\left(\bar{\rho}\tilde{Y}_x\right)}{\partial t} + \frac{\partial\left(\bar{\text{u}}_i\bar{\rho}\tilde{Y}_x\right)}{\partial x_i} = \frac{\partial}{\partial x_i}\left(\left(\frac{\mu}{S_c} + \frac{\mu}{S_{ct}}\right)\frac{\partial\tilde{Y}_x}{\partial x_i}\right) + \bar{\dot{\omega}}_x \tag{4}$$

where μ and μ_t are the laminar and turbulent viscosities respectively, and S_c and S_{ct} are the laminar and turbulent Schmidt numbers. $\bar{\dot{\omega}}_x$ is the average combustion source term and $\tilde{Y}_x$ is the averaged mass fraction of species x.

The fuel transport equations are [22]:

$$\frac{\partial\left(\bar{\rho}\tilde{Y}_{Fu}^u\right)}{\partial t} + \frac{\partial\left(\bar{\rho}\tilde{\text{u}}_i\bar{\rho}\tilde{Y}_{Fu}^u\right)}{\partial x_i} = \frac{\partial}{\partial x_i}\left(\left(\frac{\mu}{S_c} + \frac{\mu_t}{S_{ct}}\right)\frac{\partial\tilde{Y}_{Fu}^u}{\partial x_i}\right) + \bar{\rho}\tilde{\dot{S}}_{Fu}^u + \bar{\dot{\omega}}_{Fu}^u - \bar{\dot{\omega}}_{Fu}^{u\rightarrow b} \tag{5}$$

$$\frac{\partial\left(\bar{\rho}\tilde{Y}_{Fu}^b\right)}{\partial t} + \frac{\partial\left(\bar{\rho}\tilde{\text{u}}_i\tilde{Y}_{Fu}^b\right)}{\partial x_i} = \frac{\partial}{\partial x_i}\left(\left(\frac{\mu}{S_c} + \frac{\mu_t}{S_{ct}}\right)\frac{\partial\tilde{Y}_{Fu}^b}{\partial x_i}\right) + \bar{\rho}\tilde{\dot{S}}_{Fu}^b + \bar{\dot{\omega}}_{Fu}^b - \bar{\dot{\omega}}_{Fu}^{u\rightarrow b} \tag{6}$$

Species Tracer equation:

$$\frac{\partial\left(\bar{\rho}\tilde{Y}_{Tx}\right)}{\partial t} + \frac{\partial\left(\bar{\text{u}}_i\bar{\rho}\tilde{Y}_{Tx}\right)}{\partial x_i} = \frac{\partial}{\partial x_i}\left(\left(\frac{\mu}{S_c} + \frac{\mu}{S_{ct}}\right)\frac{\partial\tilde{Y}_{Tx}}{\partial x_i}\right) + \bar{\rho}\tilde{\dot{S}}_x \tag{7}$$

The equations for unmixed species are:

$$\frac{\partial\left(\bar{\rho}\tilde{Y}_{Fu}^F\right)}{\partial t} + \frac{\partial\left(\bar{\rho}\tilde{\text{u}}_i\tilde{Y}_{Fu}^F\right)}{\partial x_i} - \frac{\partial}{\partial x_i}\left(\left(\frac{\mu}{S_c} + \frac{\mu_t}{S_{ct}}\right)\frac{\partial\tilde{Y}_{Fu}^F}{\partial x_i}\right) = \bar{\rho}\tilde{\dot{S}}_{Fu}^F + \bar{\rho}\tilde{\dot{E}}_{Fu}^{F\rightarrow M} \tag{8}$$

$$\frac{\partial\left(\bar{\rho}\tilde{Y}_{O_2}^A\right)}{\partial t} + \frac{\partial\left(\bar{\rho}\tilde{\text{u}}_i\tilde{Y}_{O_2}^A\right)}{\partial x_i} - \frac{\partial}{\partial x_i}\left(\left(\frac{\mu}{S_c} + \frac{\mu_t}{S_{ct}}\right)\frac{\partial\tilde{Y}_{O_2}^A}{\partial x_i}\right) = \bar{\rho}\tilde{\dot{E}}_{O_2}^{A\rightarrow M} \tag{9}$$

The NOx model:

NO_x contains nitrogen oxide as a major components in internal combustion (IC) engine emissions. Formation of NO_x during combustion is due to three main sources [23, 24]: (a) Thermal NO_x (b) Prompt NO_x (c) Fuel NO_x.

The transport equation for Nitrogen monoxide model [25]

$$\frac{\partial\left(\bar{\rho}\tilde{Y}_{NO}\right)}{\partial t}+\frac{\partial\left(\bar{\mathrm{u}}_i\bar{\rho}\tilde{Y}_{\mathrm{NO}}\right)}{\partial x_i}=\frac{\partial}{\partial x_i}\left(\bar{\rho}D_{\mathrm{t}}\frac{\partial\tilde{Y}_{\mathrm{NO}}}{\partial x_i}\right)+\bar{S}_{\mathrm{NO}} \tag{10}$$

The term $\bar{S}_{NO}$ represents NO_x pollutant formation in the equation.

$$\bar{S}_{\mathrm{NO}}=M_{\mathrm{NO}}\left(\frac{dc_{\mathrm{NO\ thermal}}}{dt}+\frac{dc_{\mathrm{NO\ prompt}}}{dt}\right) \tag{11}$$

The terms M_{NO}, $\frac{dc_{\mathrm{NO\ prompt}}}{dt}$ and $\frac{dc_{\mathrm{NO\ thermal}}}{dt}$ in the (11) are molar mass, prompt mechanisms and thermal mechanisms respectively.

The Soot model:

Under high temperature and fuel rich conditions, as typically found in diesel combustion, hydrocarbon fuels exhibit a strong tendency to form carbonaceous particles.

Following stoichiometric reaction gives details of soot formation during combustion.

$$\mathrm{C}_x\mathrm{H}_y+a\mathrm{O}_2\rightarrow 2a\mathrm{CO}+\frac{y}{2}\mathrm{H}_2+(x-2a)C_s \tag{12}$$

In (12), when x is greater than 2a i.e. C/O is greater than unity, solid carbon soot (C_s) is produced during combustion [23].

The equivalence ratio is given by

$$\phi=2\left(1+\frac{y}{4x}\right)\left(\frac{\mathrm{C}}{\mathrm{O}}\right) \tag{13}$$

Models employed and boundary conditions for present study are listed in Tables 3 and 4 respectively.

Table 3 Models employed in FIRE software

Turbulence model	k-ζ-f model
Breakup model	Wave
Turbulent dispersion model	Enable
Wall treatment	Hybrid wall treatment
Wall impingement model	Walljet 1
Heat transfer wall model	Standard wall function
Evaporation model	Dukowicz, multi component
Combustion model	CFM
Ignition model	ECFM-3Z
Soot formation and oxidation	Kinetic model
NO_x mechanism	Extended Zeldovich
Chemistry solver	Fire internal chemistry interpreter (CHEMKIN-II)

Table 4 Calculation domain boundaries

Boundary type	Boundary condition	Values
Piston	Moving mesh	Temperature 550 K
Axis	Periodic inlet/outlet	Periodic
Cylinder head	Wall	Temperature 550 K
Compensation volume	Wall	Thermal/Adiabatic boundary
Liner	Wall	Temperature 425 K

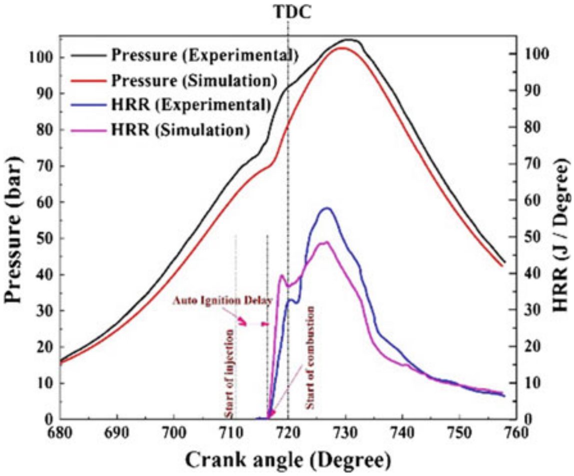


Fig. 4 In-cylinder pressure versus crank angle experimental and simulation

4 Results and Discussions

Validation:

In the present study, the engine simulation software AVL-FIRE was coupled with CHEMKIN II for simulating the engine combustion and emission formation processes with detailed reaction mechanisms. The simulation is validated from the literature [19, 20] for conditions listed in Table 1. Results are obtained for in-cylinder pressure and heat release rate versus crank angle portrayed in Fig. 4. Simulation results show good agreement with published experimental data. The differences in numerical and experimental validation results, are found to be 6.5 and 7.6% for in-cylinder pressure and heat release rate (HRR) respectively. These differences are calculated based on the area under the curve.

Effect of various injection timings and biobutanol-diesel blends on engine performance:

Figure 5 shows the effect of injection timing and biobutanol blends on performance characteristics of common rail engine.

Fig. 5 Effects of various injection timings and different biobutanol–diesel blends **a** indicated thermal efficiency versus blends, **b** $\mathrm{ITE}_{\mathrm{max}}$ versus blends, and **c** $\mathrm{IP}_{\mathrm{max}}$ versus blends

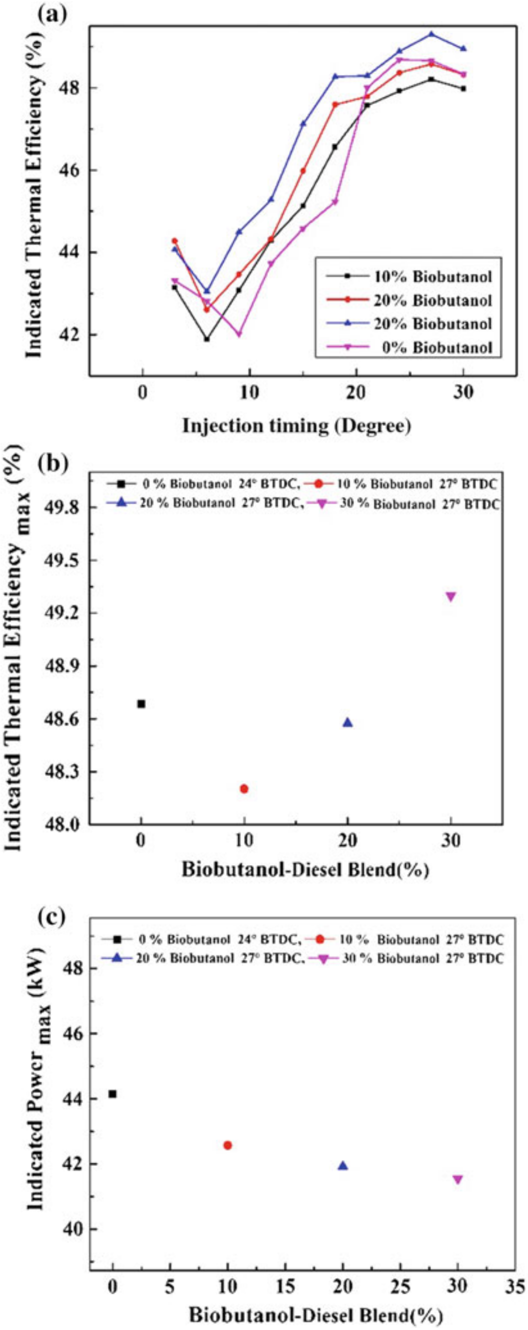


Figure 5a shows variation of indicated thermal efficiencies versus injection timings (3°–30° BTDC) for biobutanol-diesel blends (10, 20 and 30%). It has been found that for all cases indicated thermal efficiency (ITE) increases with advance injection timing. ITE is defined as ratio of in-cylinder power to the energy input. The energy input is deceases with increase in blend ratio, hence ITE is increasing for higher blend ratios.

The simulation is carried for 40 cases in the step of 3°. The maximum ITE for diesel and biobutanol-diesel blends (10, 20 and 30%) is found at 24° and 27° BTDC respectively. Figure 5b shows the $\mathrm{ITE}_{\max}$ versus biobutanol-diesel blends. From the results the max ITE is found to be at 27° BTDC and for 30% biobutanol diesel blend.

Figure 5c indicates the $\mathrm{IP}_{\max}$ versus biobutanol-diesel blends. From the results, it is found that with increase in blend ratio IP is decreasing and 30% biobutanol diesel

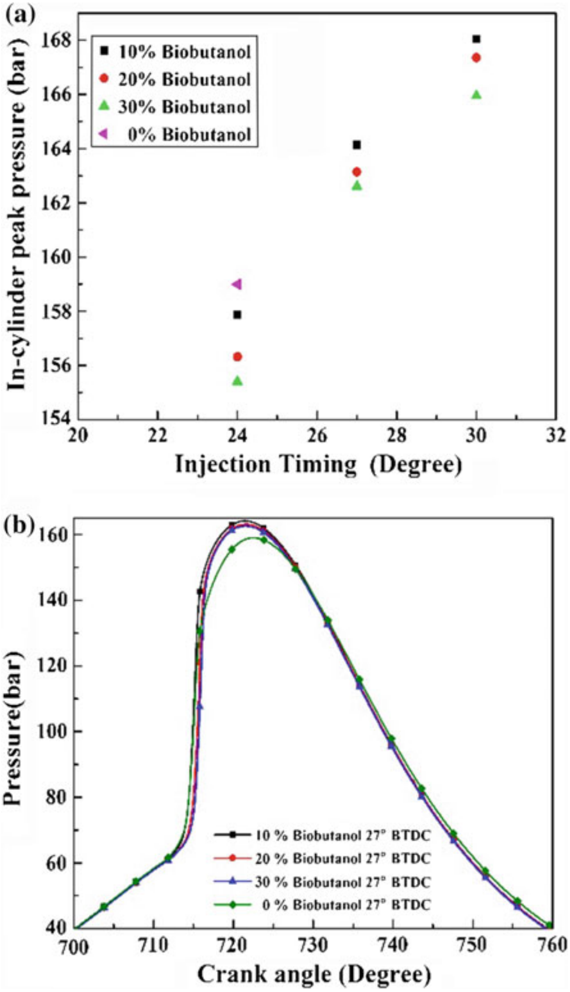


Fig. 6 Effects of various injection timings and different biobutanol–diesel blends on **a** in-cylinder peak pressure versus injection timings, **b** pressure versus crank angle

blend is found to least power. The energy content in biobutanol is less compared to diesel, hence in-cylinder power is less.

Effect of various injection timings and biobutanol-diesel blends on in-cylinder pressure:

Figure 6 depicts the influence of injection timing on in-cylinder pressure. Figure 6a shows the effect of injection timing and biobutanol-diesel blends on in-cylinder peak pressure. It is observed that advancing injection timing yields higher in-cylinder peak pressure for all biobutanol-diesel blends. Even though biobutanol contains lower calorific value, it is interesting to see slightly higher in-cylinder pressure in the case of advance injections, which occurs due to better combustion.

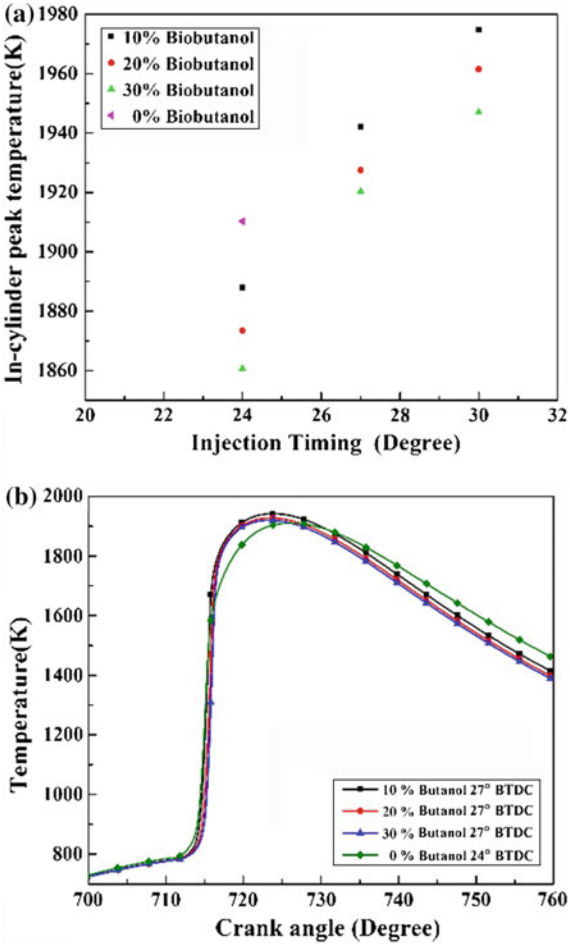


Fig. 7 Effects of various injection timings and different biobutanol–diesel blends **a** in-cylinder peak temperature versus injection timings, **b** temperature versus crank angle

Figure 6b shows the influence of biobutanol diesel blends and optimised injection timing on in-cylinder pressure. It is found that in-cylinder pressure is decreased for diesel and marginal variation for blends.

Effect of various injection timings and biobutanol-diesel blends on in-cylinder temperature:

Figure 7 depicts the influence of injection timing on in-cylinder temperature. Figure 7a shows the effect of injection timing and biobutanol-diesel blends on in-cylinder peak temperature. It is observed that advancing injection timing yields higher in-cylinder peak temperature for all biobutanol-diesel blends. Which occurs due to better combustion.

Figure 7b shows the influence of biobutanol diesel blends and optimised injection timing on in-cylinder temperature. It is found that in-cylinder temperature is decreased for diesel and marginal variation for blends.

Effect of injection timing on auto-ignition delay:

Figure 8 shows the effect of injection timing on ignition delay for different fuel blends. Cetane number plays a crucial role in deciding the start of combustion. Since biobutanol has lower cetane number, it increases the ignition delay as percentage of biobutanol in the fuel increases. Higher latent heat of vaporization of fuel (biobutanol) causes lower in-cylinder temperature and hence escalates the ignition delay. For all the cases of advanced injection timing, ignition delay is more as expected.

Effect of various injection timings and biobutanol-diesel blends on in-cylinder mean CO mass fraction:

Figure 9 shows the effect of injection timing and biobutanol-diesel blends on in-cylinder CO formation. It is observed that advancing injection timing CO mass

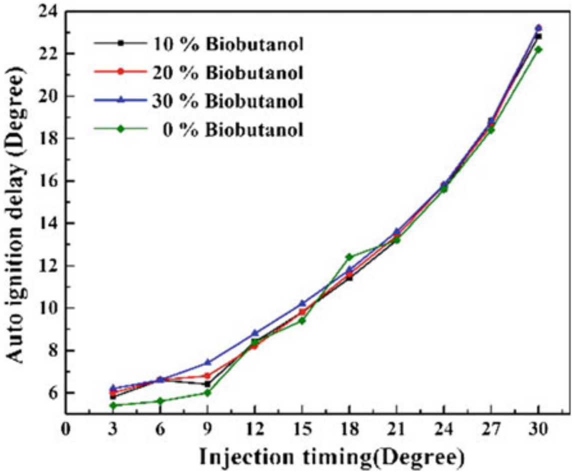


Fig. 8 Auto ignition delay versus Injection timing for different fuel blends

Fig. 9 Effects of various injection timings and different biobutanol–diesel blends on CO mass fraction

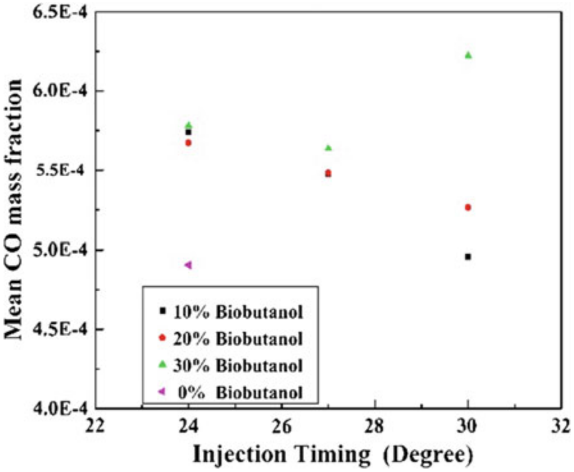
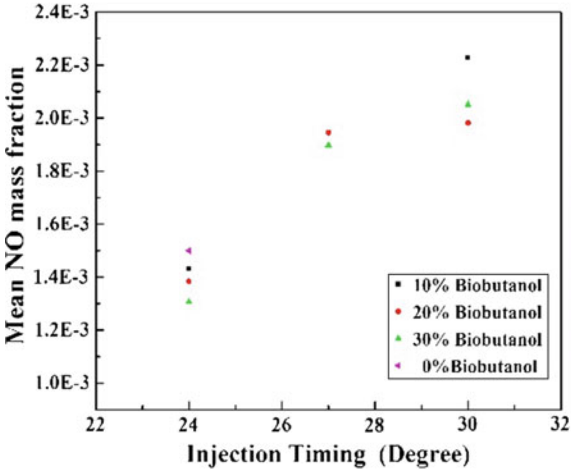


Fig. 10 Effects of various injection timings and different biobutanol–diesel blends on NO mass fraction

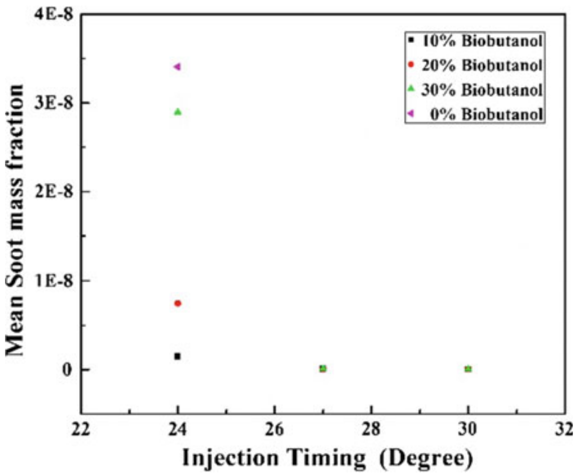


fraction formation is more for biobutanol blends compared to the diesel at optimum injection angles. This may be attributed due to the thick quenching layer caused by high latent heat of butanol, which result in a lower CO oxidation rate. The similar results are observed by Chen et al. [26].

Effect of various injection timings and biobutanol-diesel blends on NO formation:

Figure 10 shows the effect of injection timing and biobutanol-diesel blends on in-cylinder NO mass fraction formation. It is observed that advancing injection timing yields higher in-cylinder NO mass fraction formation for all biobutanol-diesel blends. This may be attributed due to the more premixed combustion where NO is mainly formed.

Fig. 11 Effects of various injection timings and different biobutanol–diesel blends on Soot mass fraction



Effect of various injection timings and biobutanol-diesel blends on in-cylinder mean Soot mass fraction:

Figure 11 shows the effect of injection timing and biobutanol-diesel blends on in-cylinder Soot mass fraction formation.

It is observed that advancing injection timing yields nearly zero soot mass fraction formation for all biobutanol-diesel blends. This may be attributed to the engine running effectively over all leaner since the aspirate mass remains same, combustion being assisted by fuel bounded oxygen [7].

5 Conclusions

CFD analysis of 4-stroke CRDI engine with biobutanol-diesel blends for various injection timings is carried out. Following conclusions are made based on the obtained simulation results.

- For more advanced injection, higher in-cylinder pressure is observed in all the cases of studies.
- Optimum injection timing for biobutanol blends (10–30%) and pure diesel are 27° BTDC and 24° BTDC, respectively. Maximum indicated thermal efficiency is obtained in the case of 30% biobutanol-diesel blend.
- It is found that with increase in blend ratio, IP decreases, and reaches minimum at 30% biobutanol diesel blend.
- It is observed that at optimum injection timing (27° BTDC), almost zero soot formation has been obtained for all biobutanol-diesel blends (10–30%).
- Higher latent heat of vaporization and lower cetane number of biobutanol escalate the ignition delay.

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Recovery of Reducing Sugar from Food Waste: Optimization of Pretreatment Parameters Using Response Surface Methodology

Marttin Paulraj Gundupalli and Debraj Bhattacharyya

Abstract Renewable energy sources, environmental pollution and climate change have been the main focus of research nowadays. Increase in energy demand and pollution and consequent depletion of fossil fuel reserve have forced scientists to look for alternative source of energy. Bioethanol is the most promising replacement fuel for petrol. The advantage of bioethanol is low Green House Gas (GHG) emission and high octane number. Traditionally, bioethanol is generated from sugar-rich crops like corn, sugarcane, beetroot etc., which are considered as first-generation sources. The second-generation sources of bioethanol constitute agricultural residues, municipal and industrial wastes, energy deficit crops etc. This study focuses on bioethanol synthesis from food waste, one of the major constituents of Municipal Solid Waste (MSW). As per estimations, more than 55 million tons of municipal solid waste is generated in India per year; the yearly rise is assessed to be about 5%. About 50% of the MSW is due to organic waste. Carbohydrates, proteins and starch are the main constituents of food waste. Reducing sugars are the building unit of carbohydrates and starch in food. The main objective of this study is to increase the recovery of reducing sugar from food waste using different pretreatment methods and simultaneously optimizing the conditions using Response Surface Methodology (RSM), a statistical tool. Characteristics of food waste such as pH, total solids, volatile solids, total organic carbon, total inorganic carbon, and total sugar were determined using standard procedures. Dilute sulphuric acid (0.5–2.5% v/v), sodium hydroxide (1–3.5% w/v), and hydrogen peroxide (0.5–3.5% v/v) were used as pre-treatment reagents. Strength of the reagents and time of autoclaving (0–60 min) were varied. Temperature and pressure of 121 °C and 1 bar, respectively, were kept constant during the pretreatment. Central Composite Design (CCD) was used to obtain optimum conditions for recovery of reducing sugar from food waste. Reducing sugar concentration in the hydrolysate after each experimental run was determined using 3, 5 Dinitrosalicylic acid method. The highest yield of

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reducing sugar—0.67 g/g of food waste was observed using 1.5% (v/v) dilute sulphuric acid as pre-treatment reagent and 30 min of autoclaving. Sodium hydroxide yielded a maximum reducing sugar of 0.129 g/g of food waste and Hydrogen peroxide produced a maximum yield of 0.37 g/g of food waste.

1 Introduction

Renewable energy source, environmental pollution and climate change have been the main focus of research nowadays. Increase in energy demand and pollution and consequent depletion of fossil fuel reserve have forced scientists to look for alternative source of energy. Alternative fuel can be generated through biological transformation of different carbon sources. Bioethanol is the most promising alternative fuel for petroleum with low Green House Gases (GHG) emission and high octane number. Bioethanol is produced by fermentation of reducing sugar from renewable biomass which has glucose as an important constituent. Various sources like agricultural residue, domestic and industrial wastes, starch-containing biomass, lignocellulosic biomass, food waste, can be suitable feedstocks for production of bioethanol. As per different estimates, more than 55 million tons of Municipal Solid Waste (MSW) is generated in India per year; the yearly rise is assessed to be about 5%. About 50% of the MSW is due to organic waste. The current approaches to treat the organic waste are—anaerobic digestion, composting, and disposal to Landfill [1, 2]. Food waste consists for cellulose, hemicellulose, lignin, proteins, lipids, starch etc. Reducing sugar obtained from hemicellulose and cellulose can be used for synthesis of bioethanol. Pre-treatment is a crucial step for recovery of reducing sugar.

2 Approach

The main objective of this study is to increase the recovery of reducing sugar from food waste using three different pre-treatments methods—Dilute sulphuric acid (0.5–2.5% v/v), sodium hydroxide (1–3.5% w/v), and hydrogen peroxide (0.5–3.5% v/v)—and determine optimum conditions in terms of reagent concentrations and time of autoclaving. Response surface methodology (RSM) was used to obtain the optimum conditions. RSM is useful in designing experiments, creating multi-regression models, evaluating the effects caused by different variables and recognizing the optimum conditions for desired responses, and decreasing the number of experimental runs [3, 4]. Prior to pre-treatment, food waste was characterized for pH, total solids, volatile solids, total organic carbon, total inorganic carbon, and total sugar.

3 Methodology

3.1 Source of Substrate

Food waste was collected from hostel mess of Indian Institute of Technology Hyderabad, Telangana. The sample was dried in oven at 80 °C overnight and the size of the sample was reduced to 2 mm using food processor [5]. The sample was stored until further use.

3.2 Characterization of Food Waste

Food waste was mixed in distilled water in ratio 10:100 (w/v). pH was determined using pH meter (Elico make). Moisture content was determined according to the standard methods [6]. Total reducing sugar concentration in hydrolysate was determined using 3, 5-Dinitrosalycylic acid method (DNS method) [7]. Total organic and inorganic carbon was determined using a Shimadzu Total Carbon Analyser. Characteristics of food waste is shown in Table 1.

3.3 Pretreatment

Concentrated sulphuric acid was diluted using deionized water in different ratios −0.5, 1, 1.5, 2 and 2.5% (v/v). Dry food waste sample was mixed in the dilute sulphuric acid solutions in 10:100 (w/v) ratio. The mixtures were then autoclaved at 121 °C under 1 bar pressure for 0, 15, 30, 45 and 60 min. Similar procedure was followed for pre-treatment using sodium hydroxide and hydrogen peroxide. Dilution series for sodium hydroxide (w/v) and hydrogen peroxide (v/v) were prepared by mixing the reagents in deionized water in the ratio—0.5, 1, 2, 3, and 3.5%. The variables ranges were taken from study conducted by Jamaluddin et al. [8].

Table 1 Characteristics of food waste

S. No	Parameter	Value
1.	pH	4.98 ± 0.2
2.	Moisture, %	72.07 ± 0.054
3.	Total solids, g/g	0.714 ± 0.03
4.	Total organic carbon, g/g	0.673 ± 0.05
5.	Total inorganic carbon, g/g	0.0405 ± 0.02
6.	Total reducing sugar, g/g	0.453 ± 0.05

3.4 Response Surface Methodology (RSM) and Central Composite Design (CCD)

Central Composite Design (CCD) was applied for investigating the combined effect of reagent concentration and time of autoclaving in order to obtain the optimum conditions for maximum recovery of reducing sugar. Different concentration of dilute sulphuric acid (X_1, % v/v), sodium hydroxide (X_1, % w/v) and hydrogen peroxide (X_1, %, v/v), time of autoclaving (X_2, min) were chosen as the independent variables which are illustrated in Table 2. The coded value of α was fixed at the default value of 1.414.

Reducing sugar (g/g) was taken as the response for various pretreatment techniques. A total of 13 runs was fixed based on the matrix shown in Table 3 for different chemical pretreatment. Each run was conducted in duplicate as shown in Table 3. MINITAB version 17.0 was used for experimental design analysis, regression analysis and ANOVA. Surface plots and contour plots were drawn to study the interaction of variables and to obtain the optimum conditions for maximum recovery of reducing sugar.

4 Results and Discussions

Different concentrations of reducing sugar were obtained from experimental runs. The predicted response and experimentally obtained reducing sugar for different pretreatment methods are shown in Table 4. The effect and significance of different pretreatment techniques were studied.

4.1 Effect of Dilute Sulphuric Acid

The reducing sugar concentrations were obtained between 0.5378 and 0.67 g/g as shown in Table 4. The values of the model coefficients were, $\beta_o = -0.129$; $\beta_1 = 0.339$; $\beta_2 = 0.03232$; $\beta_3 = -0.0949$; $\beta_4 = -0.000371$; $\beta_5 = -0.00244$.

Table 2 Coded and un-coded values for central composite design (CCD)

Variable	Coding	Unit	Levels		
			−1	0	+1
H_2SO_4	X_1	% (v/v)	1	1.5	2
NaOH	X_1	% (w/v)	1	2	3
H_2O_2	X_1	% (v/v)	1	2	3
Time	X_2	min	15	30	45

Table 3 Experimental design matrix

H_2SO_4 % (v/v)	NaOH % (w/v)	H_2O_2 % (v/v)	Time (min)
0.5	2.0	2.0	30
2.0	2.0	1.0	45
1.5	2.0	3.0	45
2.0	1.0	2.0	30
1.5	2.0	3.5	30
1.5	2.0	2.0	0
1.5	2.0	2.0	30
2.0	3.5	2.0	30
1.5	2.0	2.0	0
1.0	3.0	0.5	30
0.5	2.0	2.0	30
2.5	3.0	3.0	15
1.5	1.0	2.0	30
2.5	2.0	3.0	15
1.5	2.0	3.0	45
1.5	1.0	2.0	60
1.0	2.0	2.0	30
1.5	2.0	2.0	30
1.5	3.0	2.0	30
1.5	2.0	1.0	15
1.0	0.5	0.5	30
1.5	2.0	1.0	45
1.0	0.5	1.0	15
1.5	1.0	3.5	30
2.0	3.5	2.0	30
1.5	3.0	2.0	60

$$\begin{aligned} Y_1 = {} & -0.129 + 0.339\,X_1 + 0.03232\,X_2 - 0.0949\,X_1^2 \\ & - 0.000371\,X_2^2 - 0.00244\,X_1 * X_2 \end{aligned}$$

The regression coefficient, p-value and t-value for the corresponding equation are shown in Table 5. The model terms X_1, $X_{2,}$ X_2^2 and X_1^2 were significant ($p < 0.05$). Other interaction terms X_1X_2, were not found to be significant ($p > 0.05$).

Table 4 Experimental response and predicted response

Dilute Sulphuric acid		Sodium hydroxide		Hydrogen peroxide	
TR g/g	PR (Y_1)	TR g/g	PR (Y_2)	TR g/g	PR (Y_3)
0.6158	0.6158	0.1282	0.1235	0.2368	0.2345
0.6301	0.6529	0.0833	0.0803	0.2437	0.2048
0.6795	0.6922	0.0988	0.0967	0.2839	0.3069
0.6376	0.6529	0.0847	0.0917	0.2359	0.2345
0.6187	0.5490	0.0984	0.0967	0.3720	0.3584
0.6712	0.6922	0.0833	0.0803	0.1366	0.1448
0.6749	0.6922	0.0984	0.0967	0.2350	0.2345
0.6356	0.4984	0.0440	0.0377	0.2336	0.2345
0.6790	0.6922	0.0988	0.0967	0.1304	0.1448
0.6575	0.7081	0.0445	0.0505	0.0947	0.1289
0.6114	0.6158	0.0984	0.0967	0.2327	0.2345
0.5378	0.5788	0.0785	0.0830	0.2158	0.2070
0.6753	0.6922	0.0842	0.0917	0.2363	0.2345
0.5429	0.5788	0.0989	0.0967	0.2172	0.2070
0.0751	0.1667	0.0984	0.0967	0.2839	0.3069
0.0618	0.1667	0.0933	0.1024	0.2939	0.3109
0.6479	0.7081	0.1281	0.1235	0.2341	0.2345
0.6799	0.6922	0.0988	0.0967	0.2354	0.2345
0.5945	0.5490	0.0436	0.0505	0.2336	0.2345
0.6708	0.6922	0.0983	0.0967	0.1651	0.1385
0.5730	0.4803	0.0906	0.0832	0.0947	0.1289
0.6776	0.6922	0.0988	0.0967	0.2345	0.2048
0.5885	0.4803	0.0906	0.0832	0.1610	0.1385
0.6790	0.6922	0.0933	0.1024	0.3729	0.3584
0.6347	0.4984	0.0440	0.0377	0.2318	0.2345
0.6721	0.6922	0.0709	0.0830	0.2998	0.3109

TR Experimentally obtained total reducing sugar, g/g of dry food waste; *PR* Predicted reducing sugar, g/g of dry food waste

Table 5 Sulphuric acid method: Test of Significance

Model terms	Coefficient	Standard error	t-value	p-value
X_1	0.339	0.160	−0.70	0.047
X_2	0.03232	0.00571	2.12	0.000
X_1X_2	−0.00244	0.00328	−0.74	0.465
X_1^2	−0.0949	0.0411	−2.31	0.032
X_2^2	0.000371	0.000046	−8.14	0.000

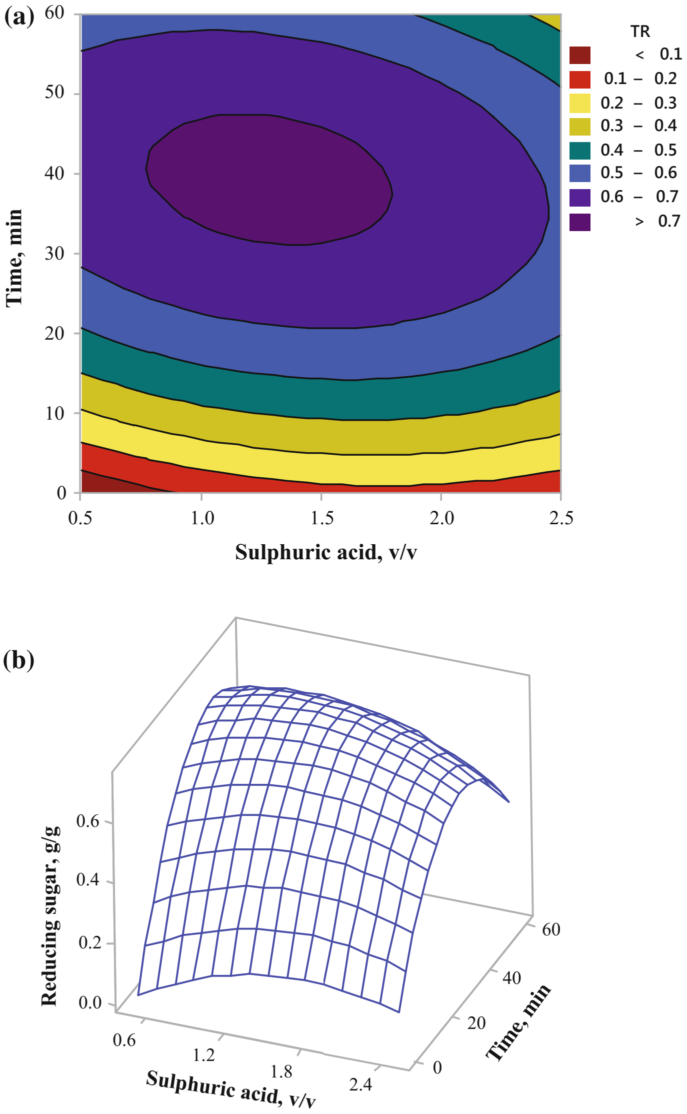

Fig. 1 **a** Contour plot; **b** response surface plot showing the effect of sulphuric acid concentration and autoclaving time on reducing sugar concentration

The result shows that the model was significant (p <0.05) for maximum recovery of reducing sugar with R-square value of 95.3% for quadratic model. Figure 1 shows the response plot and contour plots for the respective CCD design.

The correlation between two variables can be understood and optimum levels can be recognized through observation of the response surface plot. It is understood from the figures that time and concentration of sulphuric acid have significant effect on the concentration of reducing sugar. Responses with low yield, can be due to several factors like product inhibition, a decrease in reactivity of cellulose substrates and concentration of chemicals [9, 10].

From the regression equation, the optimum value were calculated. The optimum value for X_1 and X_2 in the decoded units were found to be 1.5 (%, v/v) and 30 min of autoclaving at 121 °C, and under 1 bar pressure. The predicted and experimental values for reducing sugar from the corresponding CCD design were 0.692 and 0.674 g/g, respectively. Based on these optimum condition these optimum condition experiment was conducted to obtain reducing sugar of 0.068 g/g of dry food waste. It can be concluded that concentrations of sulphuric acid and autoclaving period do have a significant effect on the recovery of reducing sugar.

4.2 *Effect of Sodium Hydroxide*

The reducing sugar concentration from sodium hydroxide pretreatment were obtained between 0.044 and 0.129 g/g as shown in Table 4. In order to evaluate the coefficients in multi regression model, a regression analysis was performed in order to fit the response function and determine the reducing sugar concentration. The following equation represents the regression model for sodium hydroxide using actual values

$$\begin{aligned} Y_1 = {} & 0.0676 + 0.06026\,X_1 - 0.000340\,X_2 - 0.01613\,X_1^2 \\ & + 0.000006\,X_2^2 - 0.000364\,X_1 * X_2 \end{aligned}$$

The regression coefficient, p-value and t-value for the corresponding equation is shown in Table 6. It was observed the concentration of sodium hydroxide, the interaction and the quadratic term of X_1, X_1X_2 and X_1^2 were significant ($p < 0.05$) but other terms X_2, X_1X_2, X_1^2 had no significant effect.

Table 6 Sodium hydroxide method: Test of Significance

Model terms	Coefficient	Standard error	t-value	p-value
X_1	0.0602	0.007	7.57	0.000
X_2	−0.000340	0.0004	−0.85	0.405
X_1X_2	−0.000364	0.000150	−2.42	0.025
X_1^2	−0.0161	0.00160	−10.1	0.000
X_2^2	0.000006	0.000004	1.39	0.179

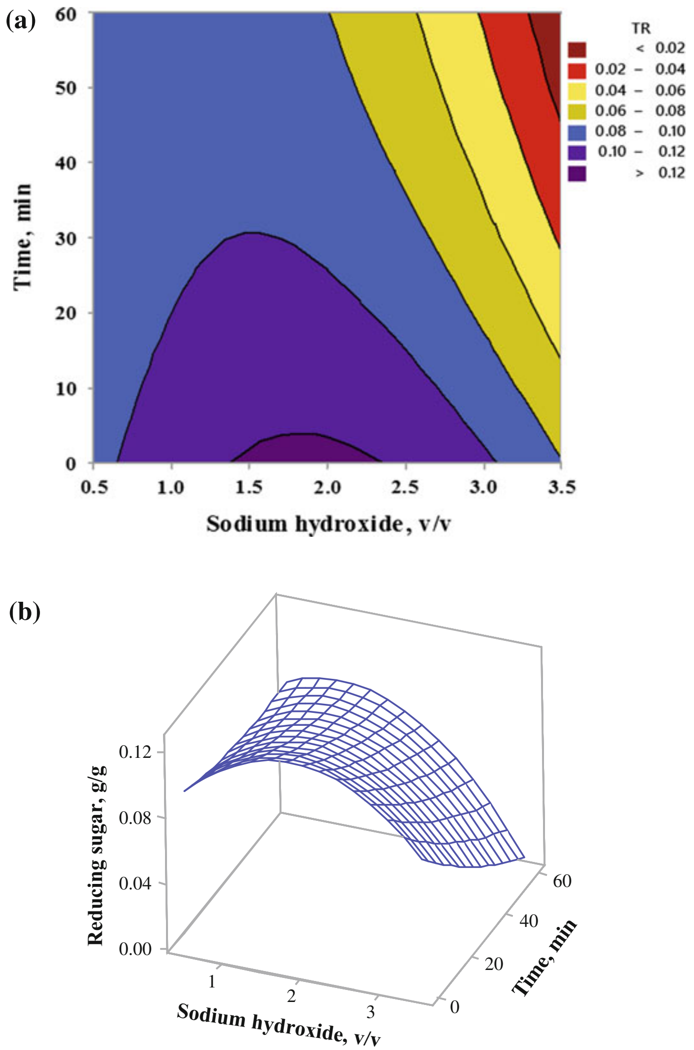

Fig. 2 **a** Contour plot; **b** response surface plot showing the effect of sodium hydroxide concentration and autoclaving time on reducing sugar concentration

The result shows that the model is significant ($p < 0.05$) for reducing sugar concentration with R-square value of 93.57% for quadratic model. Figure 2 shows the response plot and contour plots for the respective CCD design.

The correlation between two variables can be understood and optimum levels can be recognized through the usage of the response surface plot. It is understood from the figures that time and concentration of sodium hydroxide have significant effect on recovery of reducing sugar.

It was observed that the maximum reducing sugar was recovered at 2 % (w/v) sodium hydroxide concentration. Autoclaving was not required. The predicted and experimental value for reducing sugar from the corresponding CCD design were 0.111 and 0.129 g/g, respectively.

4.3 *Effect of Hydrogen Peroxide*

The reducing sugar concentration for hydrogen peroxide method were obtained between 0.094 and 0.37 g/g as shown in Table 4. The following equation represents the regression model for hydroxide peroxide pretreatment method.

$$\begin{aligned} Y_1 = {} & 0.0191 + 0.0999\,X_1 + 0.0029\,X_2 - 0.01850\,X_1^2 \\ & - 0.000007\,X_2^2 + 0.000559\,X_1 * X_2 \end{aligned}$$

The model was evaluated for regression coefficients, p-value and t-value and shown in Table 7. It was observed that for hydrogen peroxide pretreatment method, the main effect term (X_1) and quadratic term $X_1{}^2$were significant ($p < 0.05$) and other terms were not significant ($p > 0.05$).

The contour curves directly display whether the interfaces exist between the factors. If contour lines are parallel, no interaction exists between these variables, or else the interaction exist [11]. The model clearly depicts that interaction between the main terms exists. The result shows that the model is significant as most of the model term p values are less than 0.05. R-square value of 93.12% was observed for regression model.

Figure 3 shows the response plot and contour plots for the respective CCD design. The correlation between two variables can be understood and optimum levels can be recognized through observation of the response surface plot. It is understood from the figures that time and concentration of hydrogen peroxide have significant effect on recovery of reducing sugar.

Table 7 Hydroxide peroxide method: Test of Significance

Model terms	Coefficient	Standard error	t- value	p-value
X_1	0.0999	0.0210	4.76	0.000
X_2	0.0029	0.00103	2.04	0.055
X_1X_2	0.000559	0.000376	1.48	0.153
X_1^2	−0.01850	0.00581	−3.18	0.005
X_2^2	−0.000007	0.000013	−0.58	0.570

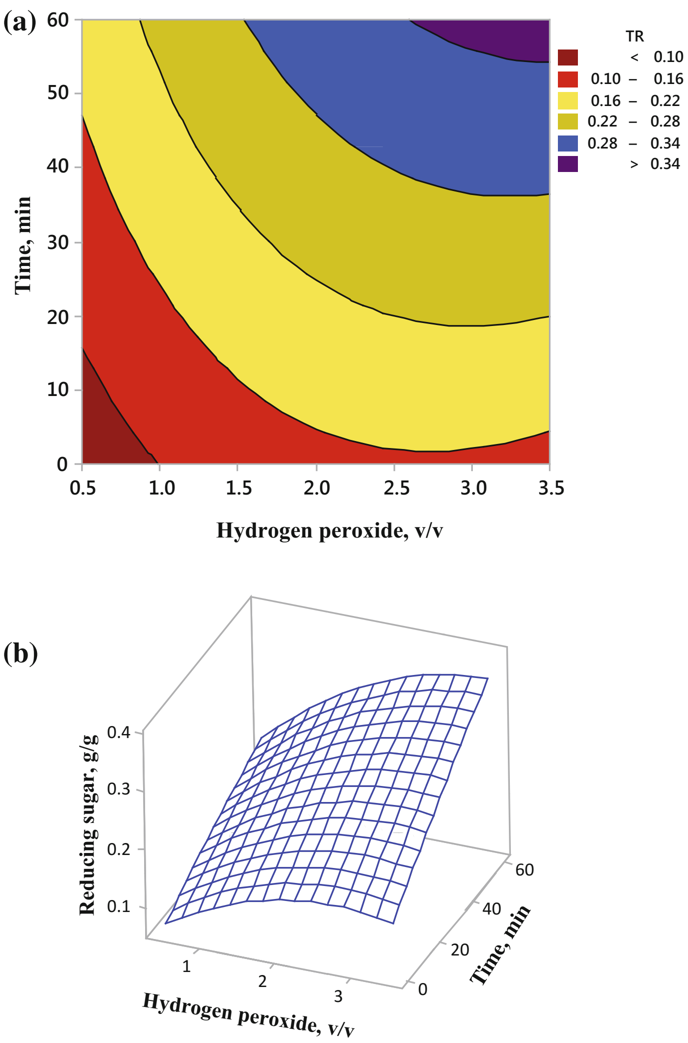

Fig. 3 **a** Contour plot; **b** response surface plot showing the effect of hydroxide peroxide concentration and autoclaving time on reducing sugar concentration

From the regression equation, the optimum value were calculated. The optimum value for X_1 and X_2 in the decoded units were found to be 3 (%, v/v) and 60 min of autoclaving period at 121 °C, and under 1 bar pressure. The predicted and experimental value for reducing sugar from the corresponding CCD design was 0.32 and 0.37 g/g respectively.

5 Conclusions

This study investigated the recovery of reducing sugar from food waste using three different pre-treatment methods. Maximum reducing sugar of 0.068 g/g of dry food waste was obtained by autoclaving for 30 min using 1.5% (v/v) sulphuric acid. Lower yields were observed when dry food waste was pre-treated with sodium hydroxide and hydrogen peroxide. Central Composite Design was used to optimize the pre-treatment conditions. Optimum conditions for maximum recovery of reducing sugar: sulphuric acid −1.5% (v/v); autoclaving temperature −121 °C; autoclaving time −30 min; pressure −1 bar. Future work may include techno-economic feasibility study at pilot-scale and subsequent commercialization of the process.

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Optimizing Bio-energy Crop Farm Profitability with Spatial Distribution of Bio-fuel Refinery Sites

Kevin Duemmel and Anand Plappally

Abstract With increase in prices of food grains and non-renewable fuel, the scientific community has turned to nature for answers. Biomass and bio-fuel production system must be optimized to enhance bio-fuel production. This can be done with a bio-energy crop production system concentrating on farm profitability and resource energy management. The system defined here stands on climatic and geo-spatial characteristics of potential energy crops, production and availability of infrastructure, socioeconomic parameters, public (subsidies) as well as private fuel consumption, qualitative and quantitative analysis of bio-fuel crops, cultural guards and intrusions. This article presents a linear programming model considering the above parameters as inputs. The model seeks to accurately determine the profitability of each bio-fuel crop pair which can be rotated in a specific geography. Simulations to relate mean distance to bio-refinery and net biomass crop profit are performed for four region specific bio-fuel crop pairs in the United States. The model helps in understanding the connections that agricultural management is having with various parameters connected with production starting from cost of seeds to value of the final biomass in hand. This helps in the derivation of a stochastic model providing an insight on statistical impacts of multiple parameters on improving the feasibility of the proposed bio-fuel production system. This analysis implies closer bio-refinery spacing than current grain elevator spacing under most anticipated circumstances signifying that transportation infrastructure plays a significant, perhaps dominant, role in creating successful regional biofuel production programs and policies.

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Abbreviations

LP	Linear programming
MMR	Multi-parameter multiplicative regression

1 Introduction

The promise of renewable bio-energy is both exciting and daunting. First, let it be said that simply meeting the current energy demand in some "green" (i.e., "sustainable") manner is not, in the long run, ecologically sustainable. Why? Our pattern of consumption is always increasing [1]. Therefore any effort to meet present energy demands in a sustainable manner is almost certain to be insufficient at some future date. The typical leadership response to such knowledge is to assume that "technology will develop to meet the increasing energy demands of our developing technology." The obvious cyclical nature of this conundrum should be foremost in the minds of any "developers" (usually academia) and promoters (usually government leadership) of sustainable energy technology and policy. Otherwise, we risk a continued spiral into an over-consumptive application of even our "greenest" technologies. Ultimately, ecological sustainability, and not simple mathematical sustainability, must be the goal.

2 Problem Assessment

Despite the seemingly anti-technology language above, it is proposed to use technology to meet energy demand in the most ecologically-minded manner possible. However, recognizing that all such efforts must occur within the framework of modern civil government, we feel that certain critical aspects of implementation are often overlooked. For example, the current research focus in bio-fuels is on process development, and to a lesser extent, feedstock development. Sparse research is being conducted toward guiding the regional implementation of bio-fuel production once it becomes practical, especially in western countries.

Some countries, such as India, which has a mix of socioeconomic groups and regions with widely varying patterns of energy usage, have recognized that the mathematical efficiency of large-scale biofuel production at widely-spaced plants does not necessarily translate into efficiency and usage at the local level [2]. It is supposed that such conditions also exist in the most developed countries, too, where the tacit assumption is that existing infrastructure is more than sufficient to economically distribute bio-energy to all who need it. Unfortunately, assumptions often prove false much later in the development or implementation phases, when they are difficult to correct. Therefore, this paper presents a simple mathematical model aimed at providing guidance for the locating of bio-fuel refineries. The usefulness of this kind of model for planning purposes is obvious, and its output might someday be used by planners in the regional selection and/or promotion of a particular bio-refinery technology over another.

The proposed bio energy decentralization will also accomplish a major goal of farm profitability with energy management. It has been stressed by researchers that an option to increase the biomass per unit land area is to grow different crop varieties which are adapted to local climate in the region at a time [3]. This emphasis points to practice of crop rotation. Swapping of crops by a farmer provides us insight on the importance of social choices and private decision which plays an important role in farm profitability and management practices [3]. This will provide to us a boon at this time of political chaos on nexus food energy security water table depletion and climatic change [4]. The term energy management is not restricted to just ethanol or the bio fuel produced but other related resources too such as irrigation water, manual labor, machinery utilized to carry activities such as tillage, threshing, cutting which needs to be justified [5, 6].

Energy producing diversity and volatility of oil producing crops, development of rural socio-economy, green house gas reduction, availability of location specific bio fuel crops for optimized fuel production are the major positive externalities that help us stick to motivating bio fuel refinery management practice [7]. Even though current literatures report that there is an efficiency of over 50% in production of ethanol from glucose, costs such as transport, climatic conditions, demand for transportation fuels and public opinion concerning low productivity concerns affect the final profitability from the biofuel production system [8].

Many crops are found to be suitable for bio fuel production and are compatible with climatic conditions. Table 1 in the appendix lists some of the most promising bio-energy crops and their geographical and climate suitability. The national program in India supported Jatropha because of the following advantages, low cost of seeds, high oil content, small gestation period, growth on any soil type without dependence on rainfall, seeds can be grown in non-rainy season, plant size [9].

In the last decade, research helped to prove that corn had a proven advantage over available bio fuel producing crops [3]. Also that grain produce controlled the fuel production other than amount of land on which other crops such as Switch grass and Miscanthus depended [3]. For the year 2006, major crops converted for ethanol were maize or sugarcane [3]. The uncertainity in production, transportation, blending, use and their related policies of management of biofuel production and their inter-correlations will hit fuel markets in developing nations across the globe [10]. This chapter illustrates the prominent inter-correlations between various stages from agricultural biofuel crop production to biofuel farm profitability and identifies the major predictors influencing agricultural (biofuel) crop farm profitability.

3 Modelling Framework

Linear programming (LP) is a proven technique to aid in agro-economic decision-making [11, 12], which is exactly the context in which we apply it. Most such LP models grow in complexity (i.e., more variables) and accuracy (refined coefficients) over time, as they are applied.

Here, the framework consists of two sub-models: the LP and Multi-parameter Multiplicative Regression (MMR) models [13]. The LP model provides the input variables to the MMR model, so they are completely independent. The LP algorithm shown in Fig. 7 of the appendix is designed to work on crop pairs, a biomass crop and an agronomic (typically grain or other food) crop. This is intended to reflect a typical producer-level decision between two options. In reality, there are likely to be more than two choices, but for the purposes of model development this is considered sufficient. These are considered only for four regions of the United States in this initial modeling effort, but the model is designed to be applicable world-wide.

The LP model is implemented in Fig. 8 in the appendix and seeks to accurately determine the profitability of each crop pair. Land costs (rent or loan payments) are not considered as part of the input and must be considered both geographically and individually when interpreting the results, but since these costs will, in general, be similar for all farmers in a given locale, it is best to disregard them in a simple model. The inputs and outputs grouped in clusters, with estimated mean values entered for all input variables (light shading). The top cluster is the agronomic characteristics of the agronomic and biomass crops for a given geographic area (also shown). The next two clusters, side-by-side, represent the production input costs of the two crops. Below that on the left are the estimated failure rates for the two crops, which are factored into the net profit cluster of cells shown in the center. Transportation costs are on the right and also feed into the net profit, of course. To the far right are some indices derived from these inputs and outputs that prove helpful both as inputs to the MMR model and for illustrative purposes.

The primary variable is the “Mean Distance to Biorefinery.” An assumption is that the bio-refinery and crop delivery point are the same. All other inputs are reflections of *existing* economic and infrastructure state, but the bio-refinery site locations (and hence their mean distance from producers) is a *proposed* state. The model is intended to show that net profit of biomass production is related most strongly to these relative distances, and thus the appropriate mean spacing of proposed bio-refinery sites is determined by the illustration in Fig. 7.

In this article, an approach to perform linear programming simulations of the mean distance to bio-refinery input value to get a series of positive net profits for biomass crops. From those values we generate the MMR that further quantifies the relationship between distance to bio-refinery and net biomass crop profit. Figure 8 shows the spreadsheet for the Maize versus Switch grass scenario, with the Mean Distance to Bio-refinery manually adjusted to give the “break even” point between the two crop choices (i.e., the net profit, $235/acre, is identical for each crop). From this breakeven point, any decrease in distance to bio-refinery increases biomass crop profit relative to the traditional agronomic crop.

By putting in several values for the mean distance to bio-refinery, the present LP formulation provides a very basic simulation manipulating only one input variable. Seven such values were chosen for each of the four crop pairs considered yielding 28 data points to serve as inputs the MMR model. The use of ratios as primary inputs to the MMR was desired at the model's conception. This was done as a quantitative representation of the human decision-making process used by farmers, whereby they consider the relative magnitudes of various fundamental inputs in deciding which crops to grow [6]. In the end, the four spreadsheet parameters chosen as MMR model inputs included two ratios and two absolute inputs. These were (1) "T-bio," the transportation cost ($/acre) of the biomass crop, (2) "Dist," the mean distance (km) to the proposed bio-refinery sites, (3) "DisRatio," the ratio of distance to bio-refinery site to agronomic crop delivery point (e.g., grain elevator), and (4) "F/bio," the fertilizer cost to crop value ratio for the biomass crop.

The crops were selected in accordance with their potential growth occurring at the geographical location of the US namely Mid West, South, South East and West. The crops selected also have qualitative and quantitative inclination towards bio fuel production and are one of the latest with high potential for fuel production. Scenarios for crop rotation and profitability with growing of these crops have been taken into consideration.

Productivity of a crop is dependent on various parameters and each operation from seeding or stem planting, tilling, irrigations, fertilizing, growing time and harvesting are in itself stochastic in nature to take place in a sequential way one after the other [6]. Similarly productivity is also dependent on the post harvest practices of time and type of storage and also the means and distance of transportation. These procedures are dependent on multiple variables and which seem to be interdependent. Therefore it would be appropriate to model the net profit of bio fuel production from the crop rotation system as a function of traversing distance, maintenance of the system, efficacy or potential of oil production, manual and water energies expended, keeping in mind the effects of social cause and personal decision of the farmer will overshadow these calculations. The wide implication incur variability in data with time which will produce chaos or randomness in the data generated with high correlations.

This will encourage removal of correlation between the variables before proceeding calculating the feasibility or R^2 value for the bio fuel refining system [13]. This will enhance the influence of parameters of the system feasibility.

The crop pairs chosen are representatives for initial model development only and cannot be considered the top choices, except as determined by our initial literature searches and intuition. They were chosen for each of four regions of the United States (see Table 8 in Appendix): Midwest (Maize vs. Switch grass), South (maize vs. Jatropha), California (Peach vs. Eucalyptus), and Florida (Coconut vs. Citrus). The basic idea for the model input is to pick biomass and traditional agronomic crops in pairs for comparison, and subsequently arrive not only at an understanding of the required bio-refinery infrastructure required for profitability, but also an equation that describes the potential quantities of that profit based on LP simulation.

Maize and switch grass are considered representative of a biomass versus grain crop decision faced by a Midwestern U.S. farmer by using yield and input estimates from the state of Ohio [14]. Fertilizer and chemical inputs as well as commodity grain prices are highly volatile (almost entirely upward) in the present market, therefore older price and input cost data were of little use. Thus, discussions with local producers were used to estimate these parameters [15].

Jatropha is a tropical evergreen plant with a shrub or small tree growth habit [16]. Its use as a biomass crop is chiefly for its seed oil as a feedstock for biodiesel. It is a candidate for extreme southern U.S. production. Although Maize is not a common agronomic crop in these areas, the comparison is considered adequate for model development purposes. Coconut is another potential biomass crop for Florida [17]. Its chief use as a biomass crop is for its oil, and it is compared in this capacity to the traditional Florida citrus crop [14]. In California, a major agricultural state, we considered Eucalyptus as an oilseed biomass crop [18] versus a traditional California tree fruit crop, peaches.

4 Methodology

Figure 1 shows that the expenditure to transport maize and switch grass is directly proportional to the increase on distance to the bio-refinery with a slope close to unity. It is observed that transportation cost of citrus and coconuts remained identical even if the distance to transport these crops to the bio-refinery increased.

If the major energy crops were to be fitted with a curve, a nonlinear nature of biomass production will reflect from the results plotted in Fig. 2 for different crops. The citrus and coconut crop proposed for the semi-arid south US emerges as a major profitable bio-energy crop—rotation food crop pair as illustrated in Fig. 3.

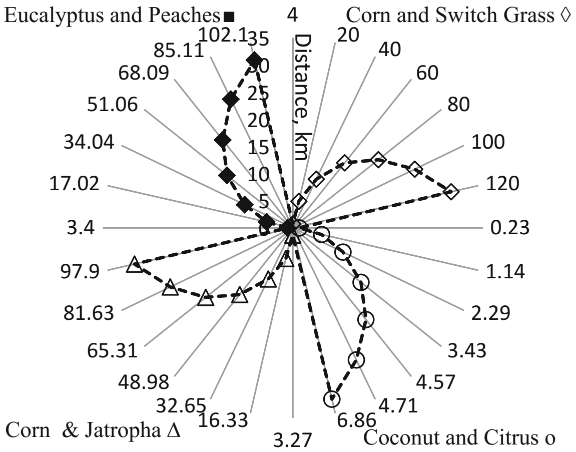


Fig. 1 Expected expenditure (in US dollars) to transport crops as a function of distance to the bio-refinery (in km)

Fig. 2 Net energy crop profit versus transportation cost for a 30 km radial distance from the crop field to the bio-refinery

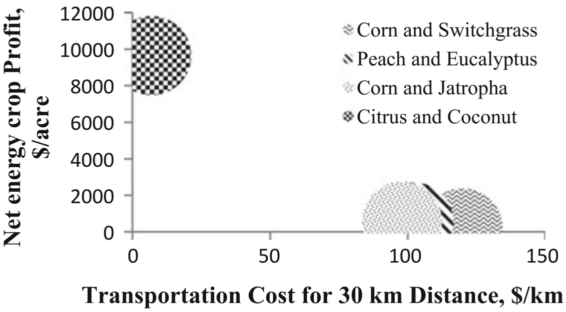
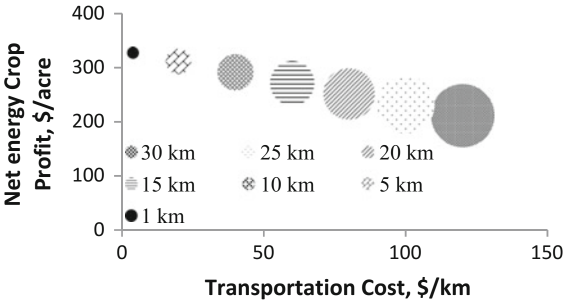


Fig. 3 Corn and Switch grass crop profit as a function of transportation cost



It is also observed that corn planted with Jatropha was much more profitable compared to corn and switch grass in the Midwest. The current commodity grain crop price increases in the United States are to some degree a reflection of subsidized grain ethanol production for fuel using maize feed-stocks [19]. From Fig. 2 the non-linearity in the profit with respect to the different crops grown at a specific known distance from the crop field to the refinery is clearly enumerated. Therefore this nonlinearity can be expressed using a lognormal or multiplicative expression as:

$$P_i / P_{i-1} = M_i^{q_i} \tag{1}$$

where the P_i is the net energy crop profit, the M_i are each of the different parameters influencing profit, and q_i is the model constant for i = 1, 2…k [13]. Equation (1) expounds the relationship between the net profit P_i at step i and its value at step $i-1$. The right hand side of (1) represents the effect of all the profit influencing variable at step i. Since there are k different parameters in the generalized multi-parameter statistical model, (11) represents only one of the steps for $i = 1, 2, \ldots, k$. Using (1), net profit P_i can be rewritten as a function of expected bio-material transport cost M_1 and a reduced non-dimensional parameter of distance M_2. M_2 is defined as the ratio of the mean distance from the bio-energy crop farm to the bio refinery and mean radial distance from the food grain farm to the grain elevator or market. Mean radial distance from a farm to the grain market or grain elevator is assumed to be constant at 55 km throughout the study. Therefore M_2 is a reduced non-dimensional variable defining distance. Hence (11) can be re-written as,

$$P_i = r\prod_{i=1}^{2} M_i^{q_i} \tag{2}$$

where r is model constant and $i = 1, 2$. Let $p = p_i = \ln P_i$, (2) can be linearized as shown

$$p = p_i = \ln r + \sum_{i=1}^{k} q_i \ln M_i \tag{3}$$

The parameters M_i in (2) and (3) have different dimensional units and are represented using different units. Therefore (2) is reformulated to provide dimensional similarity. This is performed as [13],

$$P/P_o = \prod_{i=1}^{k} (M_i/M_{io})^{q_i} \tag{4}$$

where: P_{io} is the maximum constant value to the predictor variable M_i for $i = 1, 2$ and has the same physical units as M_i. The left and right hand side of (4) is dimensionless. The model constant r can be represented by Soboyejo and Nestor [13]

$$r = P_0\left\{\prod_{i=1}^{k} M_{io}^{q_i}\right\}^{-1} \tag{5}$$

Here the value of r will be distinct for each energy crop-food crop pair that has been studied in this article. The value of r denotes all the characteristic influences of a specific regional energy crop-food crop pair [20, 21]. Therefore the new net energy crop profit P_i for any energy crop-food crop pair irrespective of any specific region in the United States can be expressed as

$$P_i = r'\prod_{i=1}^{3} M_i^{q_i} \tag{6}$$

where: M_1 is expected bio-material transport cost, M_2 is ratio of the mean distance from a specific bio-energy crop farm to the bio refinery and mean radial distance from a specific food grain farm to its grain elevator or market and M_3 is derived as the natural logarithm function of r calculated for specifically for each specific energy crop-rotation food crop pair [22]. Further explanation of the framework followed in (6) is found elsewhere and interested readers are requested to refer Soboyejo et al. [21] and Plappally et al. [20]. But the parameters M_1, M_2 and M_3 are correlated to each other as shown in Table 1.

Table 1 Correlation coefficient $\rho_{M_{i,j}}$ between transportation cost, ratio of distances and a specific variable constant to the concerned energy crop pair proposed for a specific location in the US which are also predictor variables of (6)

Predictor variables	M_1	M_2
M_2	$\rho_{M_{1,2}} = 0.679$	$\rho_{M_{2,2}}$
M_3	$\rho_{M_{1,3}} = -0.577$	$\rho_{M_{2,3}} = -0.00001$

Regression can only be performed using independent variables. Therefore the correlated variables are converted to non-correlated independent variables using multivariate mathematical framework. Equation (6) can be consequently expressed as:

$$P_i = \ddot{r} \prod_{i=1}^{3} V_i^{\ddot{q}_i} \tag{7}$$

where: $\ddot{r}$ is the new model constant for the regression equation predicting P_i and $\ddot{q}_i$ is the new coefficients for the independent variables, V_i. These coefficients provide the actual independent influences of each of the correlated M_i variables. The framework to derive (7) is illustrated in Plappally et al. [20, 22].

5 Results and Discussions

From Fig. 2, an independent influence on the profit which can be reaped from a specific energy crop pair is visible.

Figures 3, 4, 5 and 6 plots the net profit in cultivation of proposed energy crops for the Midwest USA, Western USA, Semi-Arid South and South East USA respectively. These results point at a high return from energy crops with short distance transportation to the bio-refinery or grain elevator irrespective of the

Fig. 4 Peach and Eucalyptus crop profit as a function of transportation cost

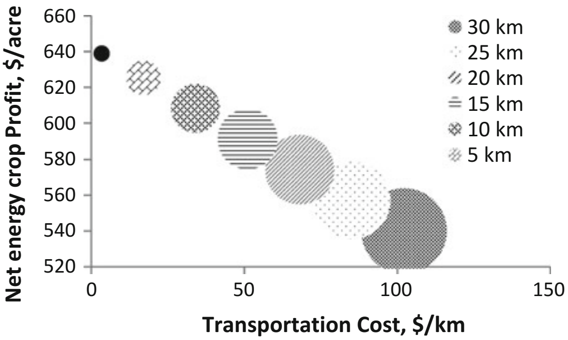


Fig. 5 Corn and Jatropha crop profit as a function of transportation cost

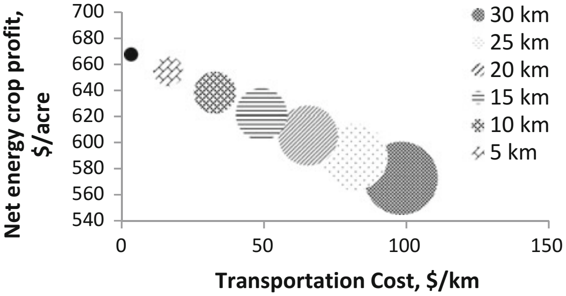
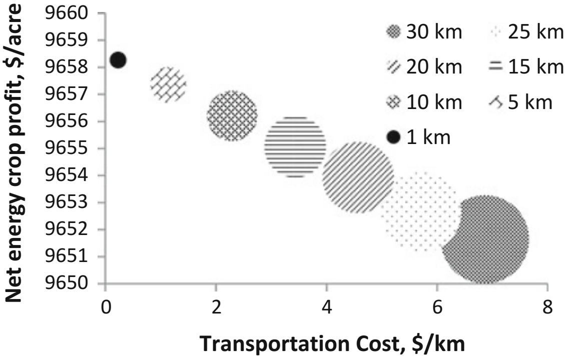


Fig. 6 Citrus and Coconut crop profit as a function of transportation cost



geographical location. It is also observed that transportation cost of corn-swtich grass crop is relatively the most expensive energy crop-rotation crop pair as a function of distance. Transportation cost ranges are the least for citrus-coconut energy crop pair.

Table 2 represents the regression model based on (2). Equation (7) is used to express the model for corn and switch grass energy crop profit as,

$$P = e^{5.59} V_1^{-0.0994} V_2^{-4.71} \tag{8}$$

where: V_1 and V_2 represent the independent form of M_1 and M_2. The coefficient of the V_1 suggests a greater influence of transportation cost on the overall profit for the corn-switch grass energy crop profit.

Table 3 represents a regression model based on (2). Equation (7) is used to express the model for peach and eucalyptus energy crop profit as,

$$P = e^{6.38} V_1^{-0.0389} V_2^{-1.71} \tag{9}$$

The coefficient of the V_1 in (9) suggests a greater influence of transportation cost on the overall profit for the peach-eucalyptus energy crop profit.

Table 4 represents a regression model based on (2). Equation (7) is used to express the model for corn and jatropha energy crop profit as,

$$P = e^{6.43} V_1^{-0.0355} V_2^{-1.57} \tag{10}$$

The coefficient of the V_1 in (10) suggests a greater influence of transportation cost on the overall profit for the corn-jatropha energy crop profit.

Table 5 represents a regression model based on (2). Equation (7) is used to express the model for citrus and coconut energy crop profit as,

$$P = e^{9.18} V_1^{-0.0001} V_2^{0.007} \tag{11}$$

The coefficient of the V_2 in (11) suggests a greater influence of the ratio of the mean distance from the bio-energy crop farm to the bio refinery and mean radial distance from the food grain farm to the grain elevator or market on the overall profit for the citrus coconut energy crop profit. Realizing the fact that individual energy crop-rotation crop pairs are location specific, therefore following the framework developed in (6), the new model for profit irrespective of any specific location is given in Table 6 below [20].

Table 6 represents a regression model based on (6). The interdependence between M_1, M_2 and M_3 enumerated in Table 1 is removed using the framework proposed by Plappally et al. [22]. The model in Table 6 can be reformulated and expressed in terms of independent variables as shown below,

$$P = e^{6.89} V_1^{-0.701} V_2^{0.896} V_3^{1.29} \tag{12}$$

The coefficient of the V_3 in (12) suggests a major dependence on the location of the farm area (in turn, the energy crop-rotation crop pair) on the overall profit for bio-energy crop production in a specific region. Apart from location, distance of transport is another major variable positively influencing the profit made from bio-energy crop farming (Table 7).

To test the validity of the assumed multiplicative modeling approach a Kolmogorov-Smirnov test was performed for (12). Table 7 compares the calculated the $D_n^{\propto}$ with the critical $D_n^{\propto}$ values of Kolmogorov Smirnov Test [23]. Since the $D_n^{\propto}$ value is less than the critical $D_n^{\propto}$ at p = 0.01, the proposed multiplicative

Table 2 Summary of change in model constants, coefficient of determination R^2 and error value S, with injection of predictor variables M_1 and M_2 while modeling Corn and Switch grass profit using (3)

Predictor variables/model coefficients	r	q_1	q_2	R^2	S
M_1	6.03	−0.118	–	77.7	0.082
M_2	−9.15	2.74	−2.94	96.6	0.035

Table 3 Summary of change in model constants, coefficient of determination R^2 and error value S, with injection of predictor variables M_1 and M_2 while modeling Peach and Eucalyptus profit using (3)

Predictor variables/model coefficients	r	q_1	q_2	R^2	S
M_1	6.54	−0.0461	–	80.4	0.029
M_2	1.07	0.991	−1.07	97.3	0.012

Table 4 Summary of change in model constants, coefficient of determination R^2 and error value S, with injection of predictor variables M_1 and M_2 while modeling Corn and Jatropha profit using (3)

Predictor variables/model coefficients	r	q_1	q_2	R^2	S
M_1	6.58	−0.0421	–	80.5	0.026
M_2	1.58	0.913	−0.918	97.4	0.010

Table 5 Summary of change in model constants, coefficient of determination R^2 and error value S, with injection of predictor variables M_1 and M_2 while modeling Citrus and Coconut profit using (3)

Predictor variables/model coefficients	r	q_1	q_2	R^2	S
M_1	9.18	−0.00019	–	81.8	0.00011
M_2	9.16	0.0043	−0.0046	98.1	0.00004

Table 6 Summary of change in model constants, coefficient of determination R^2 and error value S, with injection of predictor variables M_1, M_2 and M_3 while modeling Citrus and Coconut profit using (6)

Predictor variables/model coefficients	r′	q_1	q_2	q_3	R^2	S
M_1	8.72	−0.629	–	–	56.1	0.935
M_2	12.0	−1.12	1.10	–	96.4	0.274
M_3	10.7	−0.855	0.824	0.0608	99.7	0.075

Table 7 The calculated the $D_n^{\propto}$ with the critical $D_n^{\propto}$ values of Kolmogorov Smirnov Test for the model in (12)

p-value	$D_n^{\propto}$ for (12)	Number of data points	Critical $D_n^{\propto}$
0.01	0.0154	28	0.308

distribution for the net profit for the energy crop-rotation crop pair production is accepted.

6 Conclusions

An efficient framework using linear programming and multivariate MMR to obtain bio-fuel crop farm profitability is proposed. Bio-refinery spacing is found to be closer than current agronomic crop delivery point spacing (e.g., grain elevators) under most anticipated circumstances. These circumstances are characterized by a per acre price advantage in traditional agronomic crops relative to biomass crops unless heavily subsidized. The implication of the results obtained in this article is very significant for infrastructure planning. If biomass for bio-fuel is to become a viable economic reality for agricultural producers, then the network of delivery points represents a profound private and public investment. Local delivery for refining seems to be the inescapable conclusion.

There are, however, some caveats here. For instance, if bio-methanol is used rather than bio-ethanol, then pipeline transportation using existing infrastructure becomes a possibility. Similarly, bio-methane might use existing natural gas pipeline infrastructure. These possibilities were beyond the scope of this modeling effort. Still, as a tool for illustrating model development, strategy and pitfalls, it has proved fruitful.

Acknowledgements We are very grateful to Prof. Ann Christy for teaching us the subject of Bio-fuels and all our colleagues at the Department of Food Agricultural and Biological Engineering, The Ohio State University who provided constructive comments while we were putting this work together. We also thank the Indian Institute of Technology Jodhpur for providing the financial support. We also greatly acknowledge the advice from Prof. Alfred Soboyejo and Prof. Larry C. Brown. We also thank Amrita Kaurwar and Sandeep Gupta for reviewing this work.

Appendix

(see Table 1; Figs. 7 and 8).

Table 1 Biofuel crops and their geographical and climate suitability

Energy crops	Country	Climate and geography	References
Sugarcane	Brazil, India, USA, UK	Tropical	[3]
Soyabean	Brazil, USA	Sub tropical	[24]
Micanthus	Canada, UK, USA	Spring and summer species	[25]
Switch grass	USA	Summer	[25]
Sweet Sorghum	Australia, India and Venezuela	Semi-arid in tropics	[26]
Coconut	India, New Zealand, Philippines, Sri Lanka, Vietnam, Thailand, Hawaii, USA	Tropical sandy shorelines	[17]
Jatropha	Cameroon, Caribbean, China, Florida, USA, India, Kenya, Philippines,	Arid to semi arid	[16, 27–29]
Eucalyptus	Australia, Brazil, India, Taiwan, USA	No climate or soil barrier	[30]
Palm	Cameroon, Saudi Arabia	Tropical	[30]
Pongamia	India	Semi arid-sub humid	[31]
Croton Megalocarpus	Kenya	Semi-arid in tropics	[7]
Oleander	Kenya	Semi-arid in tropics	[7]
Rapeseed (Canola)	Argentina, Canada, Denmark, France, Italy,	Winter and springs	[30]
Bamboo	Nigeria, india	Semi humid-marshes	[30]
Peaches	USA	Subtropical climate	[30]
Algae	Japan, USA	Lagoon and sea shores	[30]
Cassava	China, India	Humid conditions	[28, 29]
Artichokes	Argentina	Springs	[30]

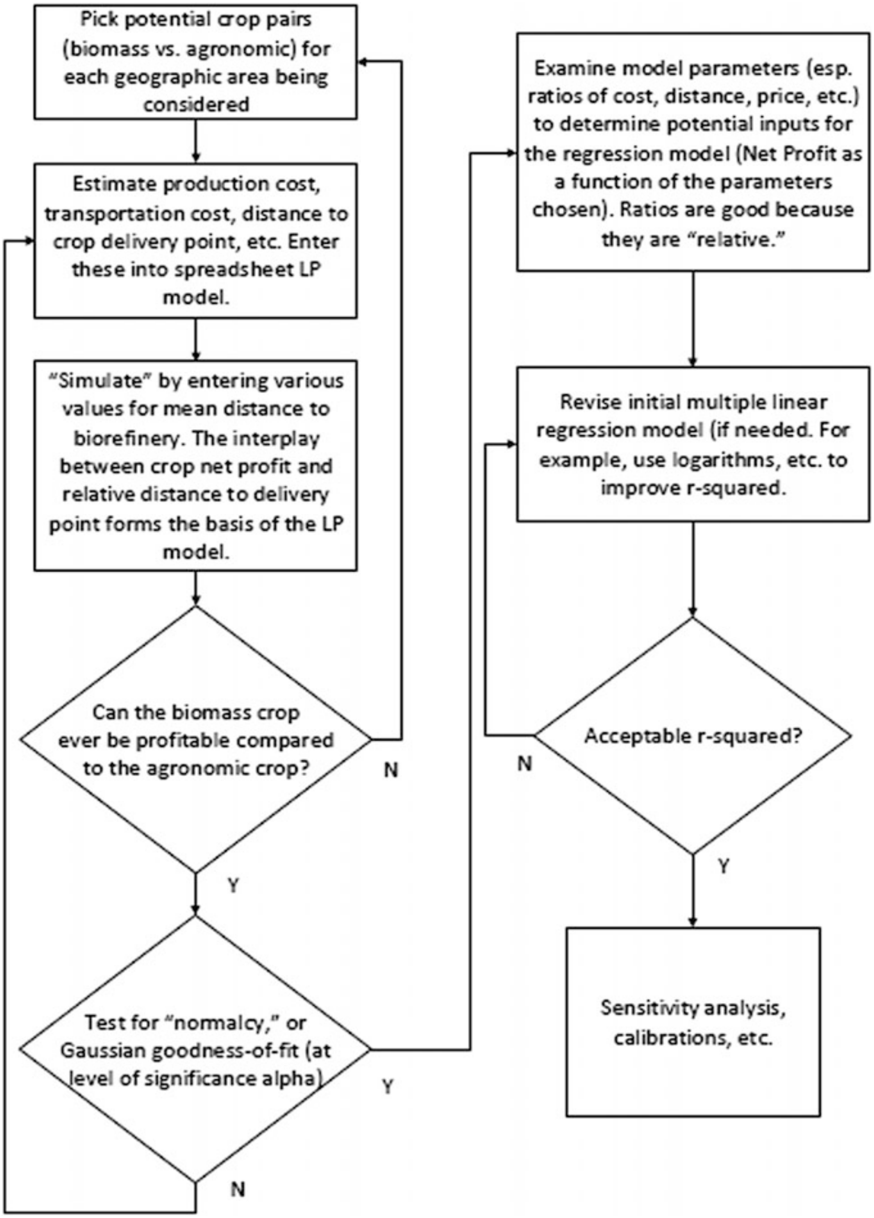
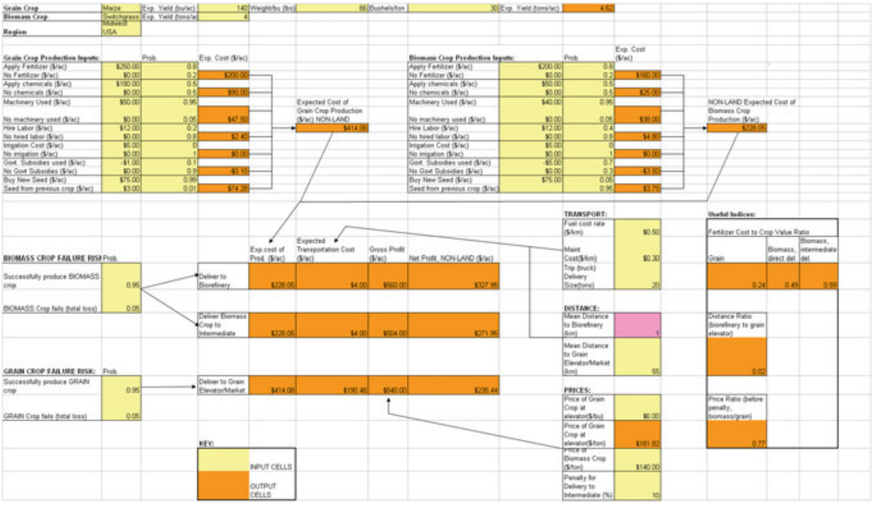


Fig. 7 The LP and MMR modeling framework



Grain Crop	Maize	Exp. Yield (bu/ac)	140	Weight/bu (lbs)	66	Bushels/ton	30	Exp. Yield (tons/ac) 4.62
Biomass Crop	Switchgrass	Exp. Yield (tons/ac)	4					
Region	Midwest USA							

Grain Crop Production Inputs:		Prob	Exp. Cost ($/ac)
Apply Fertilizer ($/ac)	$250.00	0.8	
No Fertilizer ($/ac)	$0.00	0.2	$200.00
Apply chemicals ($/ac)	$180.00	0.5	
No chemicals ($/ac)	$0.00	0.5	$90.00
Machinery Used ($/ac)	$50.00	0.95	
No machinery used ($/ac)	$0.00	0.05	$47.50
Hire Labor ($/ac)	$12.00	0.2	
No hired labor ($/ac)	$0.00	0.8	$2.40
Irrigation Cost ($/ac)	$6.00	0	
No irrigation ($/ac)	$0.00	1	$0.00
Govt. Subsidies used ($/ac)	-$1.00	0.1	
No Govt Subsidies ($/ac)	$0.00	0.9	-$0.10
Buy New Seed ($/ac)	$75.00	0.99	
Seed from previous crop ($/ac)	$3.00	0.01	$74.28

Expected Cost of Grain Crop Production ($/ac) NON-LAND $414.08

Biomass Crop Production Inputs:		Prob	Exp. Cost ($/ac)
Apply Fertilizer ($/ac)	$200.00	0.8	
No Fertilizer ($/ac)	$0.00	0.2	$160.00
Apply chemicals ($/ac)	$50.00	0.5	
No chemicals ($/ac)	$0.00	0.5	$25.00
Machinery Used ($/ac)	$40.00	0.95	
No machinery used ($/ac)	$0.00	0.05	$38.00
Hire Labor ($/ac)	$12.00	0.4	
No hired labor ($/ac)	$0.00	0.6	$4.80
Irrigation Cost ($/ac)	$6.00	0	
No irrigation ($/ac)	$0.00	1	$0.00
Govt. Subsidies used ($/ac)	-$5.00	0.7	
No Govt Subsidies ($/ac)	$0.00	0.3	-$3.50
Buy New Seed ($/ac)	$75.00	0.05	
Seed from previous crop ($/ac)		0.95	$3.75

NON-LAND Expected Cost of Biomass Crop Production ($/ac) $228.05

BIOMASS CROP FAILURE RISK	Prob
Successfully produce BIOMASS crop	0.95
BIOMASS Crop fails (total loss)	0.05

	Exp.cost of Prod. ($/ac)	Expected Transportation Cost ($/ac)	Gross Profit ($/ac)	Net Profit, NON-LAND ($/ac)
Deliver to Biorefinery	$228.05	$4.00	$560.00	$327.95
Deliver Biomass Crop to Intermediate	$228.05	$4.00	$504.00	$271.95
Deliver to Grain Elevator/Market	$414.08	$190.48	$840.00	$235.44

GRAIN CROP FAILURE RISK:	Prob
Successfully produce GRAIN crop	0.95
GRAIN Crop fails (total loss)	0.05

KEY:

🟨	INPUT CELLS
🟧	OUTPUT CELLS

TRANSPORT:	
Fuel cost rate ($/km)	$0.50
Maint Cost($/km)	$0.30
Trip (truck) Delivery Size(tons)	20
DISTANCE:	
Mean Distance to Biorefinery (km)	1
Mean Distance to Grain Elevator/Market (km)	55
PRICES:	
Price of Grain Crop at elevator($/bu)	$6.00
Price of Grain Crop at elevator($/ton)	$181.82
Price of Biomass Crop ($/ton)	$140.00
Penalty for Delivery to Intermediate (%)	10

Useful Indices:

Fertilizer Cost to Crop Value Ratio		
Grain	Biomass, direct del.	Biomass, intermediate del.
0.24	0.49	0.59

Distance Ratio (biorefinery to grain elevator)
0.02

Price Ratio (before penalty, biomass/grain)
0.77

Fig. 8 The spreadsheet implementation of the LP formulation [Microsoft Excel 2010 version, The Ohio State University]

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Experimental Study on Jatropha Oil Pool Fire in Full Scale Compartment

Avinash Chaudhary, Akhilesh Gupta, Surendra Kumar and Ravi Kumar

Abstract A compartment of size 4 m × 4 m × 4 m has been constructed to carry out the experiments. A door of size 2 m height and 1 m width is created on the front facing wall, for ventilation purpose. Fuel is burned in the centre of the compartment in cylindrical pan of diameter 0.6 m. Total depth of fuel pan is 0.12 m, initial fuel thickness is 0.05 m in the pan. Various parameters like mass loss rate, hot gas layer temperature, corner temperature in the compartment, heat flux and doorway temperature are measured. Experiments results showed that maximum heat release rate achieved is 302.5 kW (based on the mass loss method) and the average mass loss rate per unit area was found to be 30.54 $gs^{-1}\ m^{-2}$.

Abbreviations

$\dot{Q}$	Heat release rate (kW)
$\dot{m}''$	Mass loss rate per unit area ($kg\ s^{-1}\ m^{-2}$)
A	Fuel surface area (m^2)
ΔH_c	Heat of combustion (kJ/kg)
χ	Combustion efficiency (–)

1 Introduction

Limited availability of conventional fuels and increase in energy prices forces us to focus on renewable energy alternatives. Biodiesel is one of the several alternatives fuels, use of which will have a positive impact on improved economy and cleaner environment. Jatropha oil is used in the production of biodiesel, so from the point of

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safe designing of Biodiesel manufacturing plants and storage of these fuels, it is necessary to understand the burning characteristics of these fuels.

Pool fires are basically categorized by the establishment of diffusion flame on the fuel surface where buoyancy forces plays the major role in transport mechanism. Pool fires can be laminar or turbulent depending on the size of fire. Studies on petroleum fuels have been performed in the past by many researchers [1–4]. Flame near the base of pool fire is fluctuating and laminar flame. As it moves upward, it becomes turbulent and intermittent [2]. Turbulent structure of medium scale methanol pool fire showed that flow develops in manner similar to buoyant shear flow but moves to classical shear flow only in regions of strongly entraining and in thermal plume zone [5].

Exposure to nearby surfaces from small scale alcohol pool fire is less than that due to hydrocarbon fuels. Experiments on two ethanol pool fire, one with 97% ethanol and 3% gasoline and other with 85% ethanol and 15% gasoline shows that increasing the ethanol content decreases the thermal impact on nearby surroundings [6]. The results on vertical turbulent sonic and subsonic exit velocity propane jet fires shows that gas fed fires are almost transparent with good combustion efficiency and most heat released by convection mode [7]. Mass burning flux in pool fires is greatly affected by the heat feedback fractions it gets from the three mechanism (conduction, convection and radiation) and convection feedback increases with cross air flow speed [8].

There is no data available on the burning of Jatropha oil pool fire, so the present work is carried out with the objective to understand the burning characteristics of Jatropha oil in compartment fire. During the experiment, various parameters like mass loss rate, corner temperature in the compartment, upper layer temperature and heat flux at various locations are recorded.

2 Experimental Facility

A test facility as shown in Fig. 1 has been developed in Mechanical and Industrial Engineering Department, IIT Roorkee to perform full scale compartment fire experiments. The compartment is of dimensions 4 m × 4 m × 4 m. A door of size 2 m height and 1 m width is created at the front facing wall for ventilation purpose. Cylindrical pan of outer diameter 0.6 m, thickness 0.003 m with depth 0.12 m is used to burn the fuel. Experimental details are shown in Table 1. The fuel used in the study was crude Jatropha oil. The pan was filled with the fuel up to a height of 0.05 m, leaving a gap of 0.07 m between the fuel surface and the edge of container. The fuel pan is placed at the centre of the floor the compartment. The centre of fuel pan is connected with a oil heating assembly. The oil heating assembly is made of GI pipe with 2 kW heater attached to it. The setup of fuel pan was placed on a load cell of resolution 5 g and mass loss rate is calculated by recording the change in fuel consumption. Temperature measurements are performed at corner of the

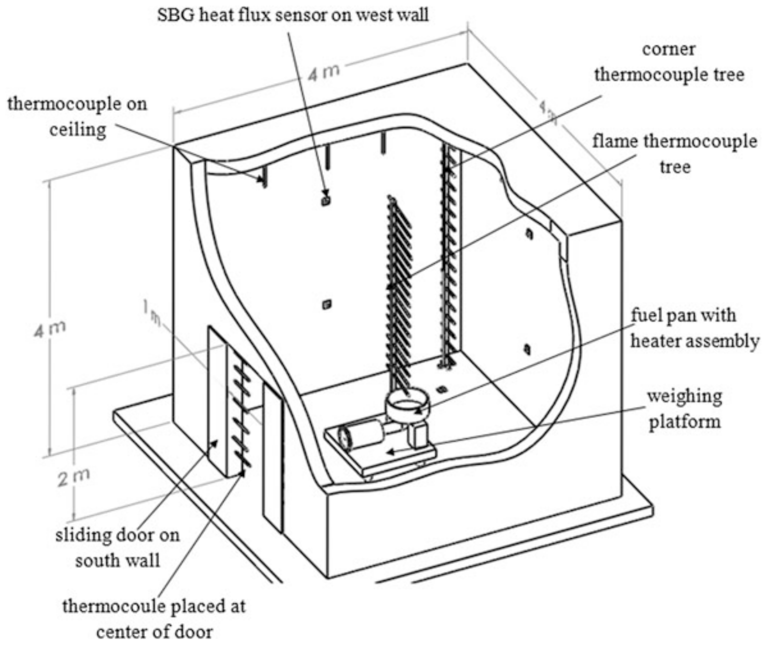


Fig. 1 Schematic of experimental setup

Table 1 Experimental details

Pool diameter (m)	Initial quantity of fuel (kg)	Ventilation	Maximum heat release rate (kW)
0.6	12.725	Open	302.5

compartment, doorway and on the ceiling. The layout of the thermocouples at different locations are shown in Figs. 2 and 3. The output of thermocouple are obtained by data acquisition system run by Labview software.

3 Instruments Layout Inside the Compartment

3.1 Hot Gas Layer Temperature

Hot gas layer temperature is measured with the help of 16 K type Cr–Al thermocouples, placed 0.5 m below the ceiling. Figure 2 shows the locations of these thermocouples.

Fig. 2 Thermocouple locations at a depth of 0.5 m below the ceiling

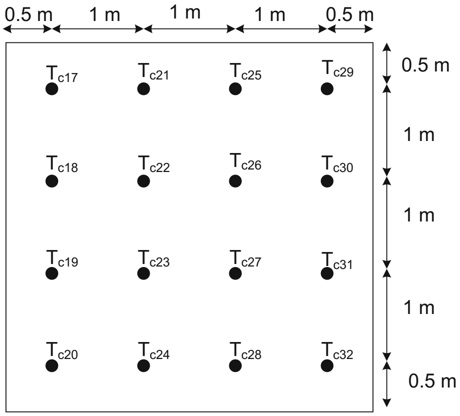
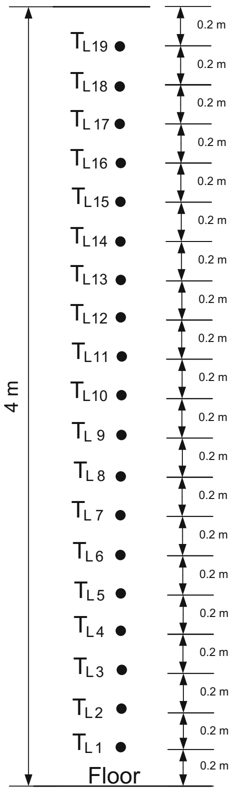


Fig. 3 Thermocouple tree placed at corner of the compartment



3.2 Corner Temperature

Corner temperature in the compartment is measured with the help of a thermocouple tree placed at a distance of 5 cm from adjacent walls as shown in Fig. 1. A total of 19 thermocouples are placed in the tree, layout shown in Fig. 3, at a distance of 20 cm between them to monitor the temperature variations along with the height.

3.3 Heat Flux

A total of 19 SBG01 water cooled heat flux sensors of rating 0–50 kW/m^2 are placed at different locations in the compartment. The layout of heat flux sensors is shown in Fig. 4.

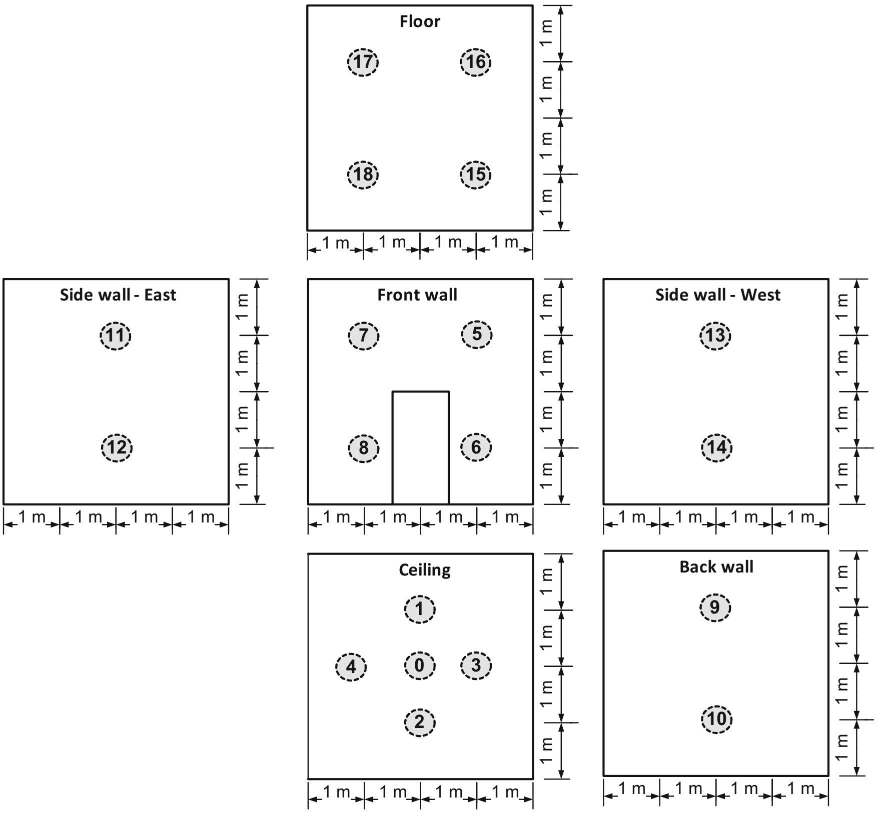
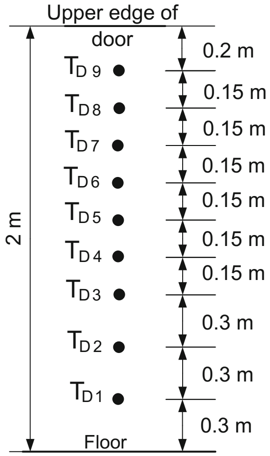


Fig. 4 Heat flux sensors layout at different surfaces

Fig. 5 Layout of thermocouples at centerline of door



3.4 Doorway Temperature

A total of 9 thermocouples are placed in the centre of door to measure the temperature of exhaust gases and incoming air. Layout of thermocouples is shown in Fig. 5.

4 Procedure

The fuel pan along with heater assembly was insulted with ceramic wool and heater was switched on. It took about six hours to obtain the flash point of oil. When flash point temperature is obtained then it was ignited with LPG pilot flame. Data was taken at an interval of 20 s from the data acquisition system.

5 Results and Discussions

5.1 Mass Loss Rate

Figure 6 shows the mass loss rate obtained by weighing scale. It shows that after the ignition of fuel, mass loss rate per unit area increases sharply to 30 gs^{-1} m^{-2} at 700 s, then it becomes almost steady till 1600 s, after that it decreases.

Fig. 6 Variations of mass loss rate with time

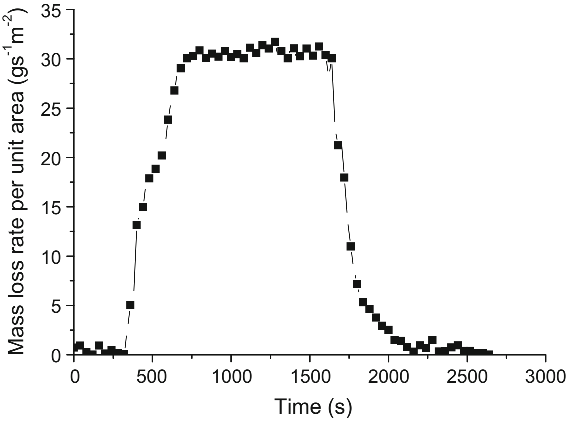
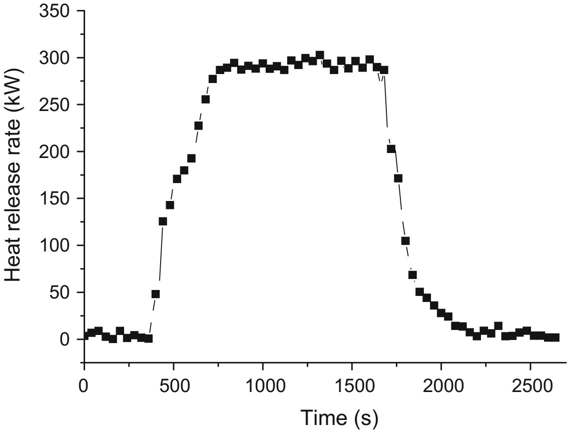


Fig. 7 Heat release rate obtained using mass loss method



5.2 *Heat Release Rate*

$$\dot{Q} = \dot{m}''A\ \Delta H_c \chi \tag{1}$$

Figure 7 shows the heat release rate, obtained by mass loss method using (1). The value of combustion efficiency, χ is assumed to be 0.87 and heat of combustion is 38,800 kJ/kg, obtained using bomb calorimeter. Maximum value of heat release rate obtained is 302.5 kW at 1320 s.

5.3 Hot Gas Layer Temperature

Hot gas payer temperature at a depth of 0.5 m below the ceiling is shown in Fig. 8. The temperature is measured at 4 different locations (T_{c17}–T_{c20}). It shows that there is not much difference between the temperature at these locations, highest recorded temperature is 239.3 °C at 1480 s at location of T_{c19}.

5.4 Corner Temperature

Figure 9 shows the variations of corner temperature with height. This graph shows the formation of two zone layer in the compartment, where upper zone consists of hot gases while lower zone consists of relatively cold air. Also, during the steady

Fig. 8 Variations of hot gas layer temperature with time at different locations

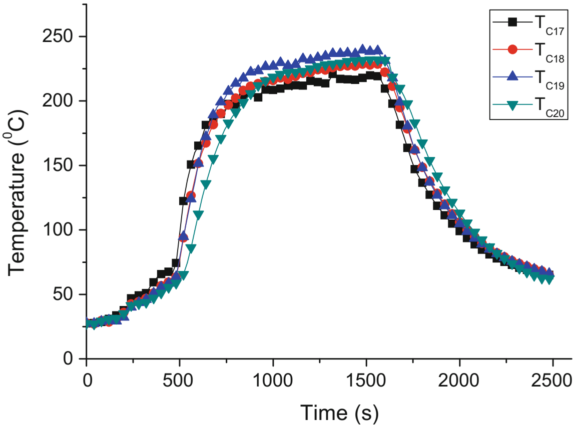
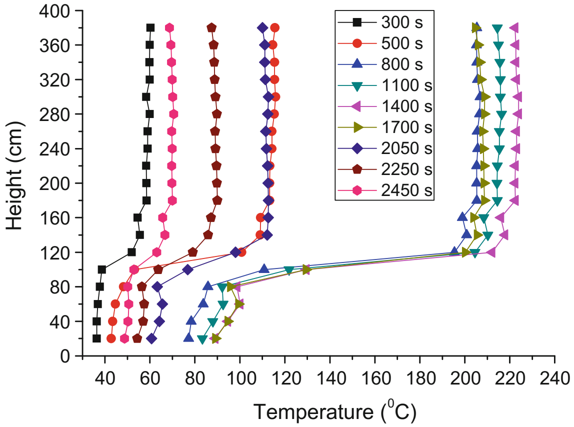


Fig. 9 Corner temperature distributions along height



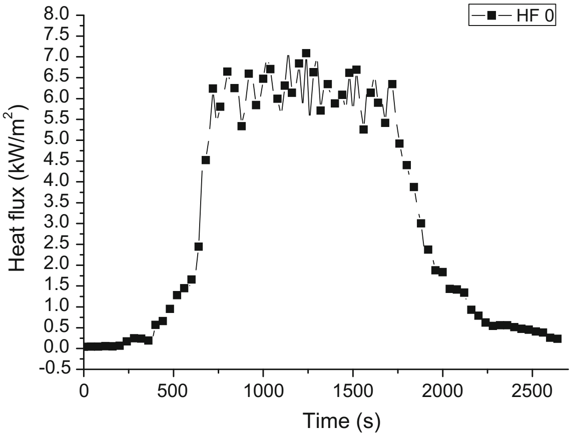


Fig. 10 Heat flux (HF 0) at centreline of ceiling

profile period, there is not much variation in temperature above the height of 120 cm.

5.5 Heat Flux

Figure 10 shows the centreline heat flux at the ceiling. The SBG01 heat flux sensors measures the total heat flux. Pool fire in this case is buoyancy dominated. The hot gases rises upward, strikes to the ceiling and spreads horizontally along the ceiling after losing its momentum. So the highest heat flux is recorded at the ceiling. The average heat flux during the steady profile is 6.24 kW/m^2.

The heat flux sensors are placed in such a way that the whole domain gets covered. As shown earlier in Fig. 9, about the two zone formation, so the Fig. 11 represents the heat flux in upper zone (HF 7) as well as in lower zone (HF 8) of the compartment. Pool fire is axisymmetrical, i.e. thermal environment on one side will be the same as on the other side. This is also validated from the fact that heat flux at locations HF 7 and HF 8 are same as HF 5 and HF 6 in author's previous work [9].

5.6 Doorway Temperature

Figure 12 shows the doorway temperature distribution along with height. At the door, both types of flows exist i.e. outward flows of exhaust gases from the upper portion of door and inward flow of fresh air from the lower portion of door. As seen in Fig. 12, the temperature recorded at the upper portion is as high as 219 °C.

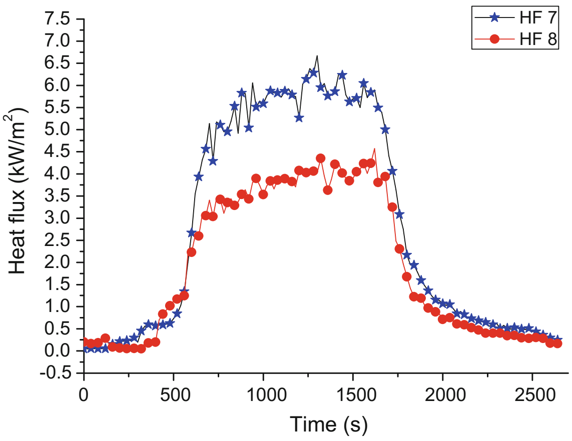


Fig. 11 Heat flux (HF 7) and HF (8) at the upper and lower portion of compartment

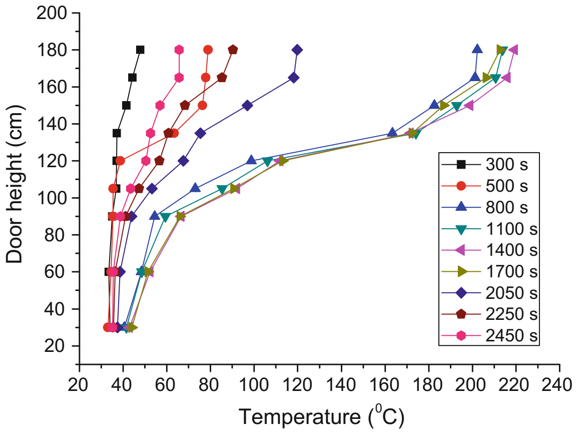


Fig. 12 Variations of doorway temperature with height

6 Experimental Error Analysis

The basic quantities observed during experiment are temperature, mass loss rate and heat flux. Thermocouples are bare bead K type with an error margin of ±1.5 K. The fuel consumption is recorded by weighing scale with uncertainty of ±5 g. Heat flux is measured by SBG01 water cooled heat flux sensors, factory calibrated. Overall uncertainty is estimated to be within ±6%, based on a standard uncertainty multiplied by a coverage factor of 2 and providing a confidence level of 95%.

7 Conclusions

Experiment is conducted on 0.6 m pool fire of Jatropha oil in full scale compartment of size 4 m × 4 m × 4 m. The main conclusions are summarized as follows:

1. Highest mass loss rate and heat release are 31.7 $\mathrm{gs^{-1}\ m^{-2}}$ and 302.5 kW respectively.
2. Compartment can be divided into two zone, where upper zone is mainly of hot gases while lower zone contains cold air.
3. Highest heat flux is recorded at the ceiling due to the direct impingement of hot gases on the ceiling.

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Rheology of Karanja (Pongamia) Oil Based Biolubricant

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Abstract Rheology is the science of flow and deformation of liquids and semi-solid materials under the effect of an applied force. Rheological characterization of lubricating oils is important to predict their flow behaviour in each stage starting from preparation to processing up to application. Vegetable oils with high oleic acid content are considered the best candidate to substitute conventional mineral oil based lubricating oils and synthetic esters. The present article discusses the synthesis of biolubricant from non-edible Karanja oil in a two-stage transesterification process followed by reaction with branched neopentyl polyol to form polyol esters as the desired biolube product. The viscosity of synthesized biolubricant is measured at increasing temperatures using Rheometer model MCR302 by Anton Paar, Austria. The same apparatus was used for measuring shear stress, speed and torque. The study undertaken here intends to reveal relationship between viscosity and temperature, shear stress and shear rate; viscosity and shear rate and torque with shear rate of Karanja oil biolubricant. Variations in coefficient of viscosity with temperature, shear stress (τ) and shear rate (Υ) are plotted accordingly. The synthesized biolubricant depicts Newtonian behaviour in hydrostatic regime.

1 Introduction

The role of lubrication is an important part in the field of tribology. Lubrication is the use of material to improve the smoothness of movement of one surface over another and to maintain the viscoelastic behaviour [1]. Lubricants are commonly

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used for lubrication purposes to reduce the friction and wear of surfaces in contact [2] and effective heat transfer due to good thermal conductivity. Most lubricants are liquids (such as mineral oils, synthetic oil, silicon fluids, water, etc.). Selection of proper lubricants is crucial for providing machine tools a longer life. To select an appropriate lubricant, it is necessary to know the properties of lubricant, lubrication system of applied machinery, conditions of machinery, cost of lubricant, etc. [3]. Common properties of lubricating oils are: viscosity, viscosity index, density, compressibility, surface tension, cloud point, pour point or low temperature property, flash point, friction coefficient, high boiling point, low freezing point, thermal stability, corrosion prevention, high resistance to oxidation, etc. which needs to be optimized.

2 Experimental

2.1 Synthesis of Biolube Base Oil from Non-edible Karanja Oil

Pure Karanja oil for research purpose was procured from a reliable source in the local market in the city of Kanpur. The properties of Karanja oil were analyzed in Laxmi Oil and Vanaspati Private Limited, Rania, Kanpur (Table 1). The oil was first filtered to remove any solid material and then preheated at 110 °C for 30 min to remove moisture, as the moisture is responsible for saponification in the reaction. Since the oil is having FFA higher than 1%, acid-catalyzed transesterification was done prior to base-catalyzed reaction. An appropriate quantity of oil was reacted with methanol taking oil-to-methanol molar ratio of 1:6 in presence of acid catalyst. The reaction was carried out at 65 °C temperature for a period of 5 h with continuous stirring of reaction materials at 150 rotations per minute (rpm). The product of acid-catalyzed transesterification reaction was taken further for base-catalyzed transesterification in presence of base catalyst under similar reaction conditions. Karanja Oil Methyl Ester (KOME) formed as reaction product of base-catalyzed transesterification serves as basic raw material for synthesis of Karanja oil based biolube oil. KOME is reacted with branched neopentyl polyol in presence of acid catalyst at 150 °C for 3 h under vacuum to form polyol esters as final reaction product (Fig. 1).

2.2 Measurement of Viscosity with Shear Rate

Viscosity of synthesized biolubricant with rise in temperature was measured using Anton Paar Rheometer MCR 302 (Fig. 2). Same rheometer was used for measuring shear stress, speed and torque. Variations of coefficient of viscosity with temperature, shear stress (τ) and shear rate (Υ) were plotted. Variation in coefficient of

Table 1 Analysis of Karanja oil

S. no.	Parameter	Value
1	Density	0.9088 gm/ml at 27 °C
2	Free fatty acid (FFA)	4.27% by weight
3	Colour (1/4 in)	20 Y + 3.1 R [Y = 1, R = 5]
4	Moisture index	0.17% by weight
5	Refractive index	1.4770 at 40 °C
6	Saponification value	189.8
7	Iodine value	87.2
8	Unsaponifiable matter	2.1% by weight
9	Peroxide value	2.5 milli-equivalents per 1000 g sample

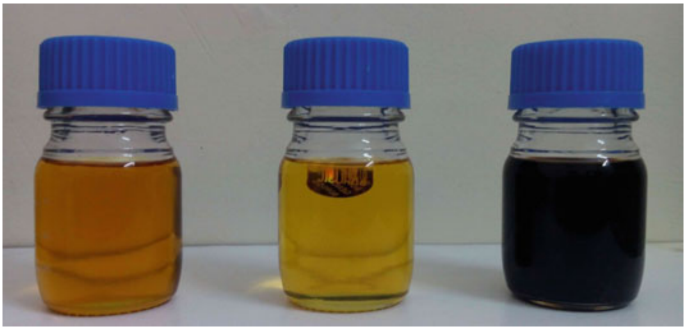


Fig. 1 Karanja oil (*left*), Karanja oil methyl ester (*centre*) and Karanja oil based biolubricant (*right*)

viscosity with shear rate was also studied. In this study, we have considered rheological parameters like viscosity, shear stress, torque and speed of lubricating oil and studied their variation with temperature and shear rate for carrying out comparative study. 100 measure points were selected with duration of 2 s and shear rate was varied from 1 to 100/s. All the measurements were done at room temperature with variation in speed while the duration of measurement was fixed at 2 s.

3 Results and Discussion

3.1 Variation of Viscosity with Temperature

Figure 3 shows the exponential variation of coefficient of viscosity with temperature for the sample. The graph depicts that viscosity is very high at low temperatures and decreases with increase in temperature. At initial values of temperature,

Fig. 2 Anton Paar rheometer model MCR 302

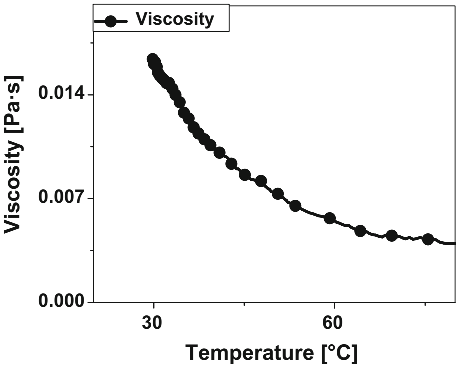


Fig. 3 Variation of viscosity with temperature

viscosity changes abruptly and after a certain temperature either the change in viscosity is negligible or very little. A lubricant for use in engines should possess viscosity high enough to provide lubrication for the engine parts and low enough to get easy flow at operational temperature. The fuel filter and injection system in engines can be plugged by high viscosity [4].

3.2 Variation of Relaxation Modulus with Time

The relaxation time is strongly dependent on temperature and other factors that affect the mobility of the material and is roughly inverse to the rate of molecular motion (Fig. 4).

Fig. 4 Variation of relaxation modulus with time

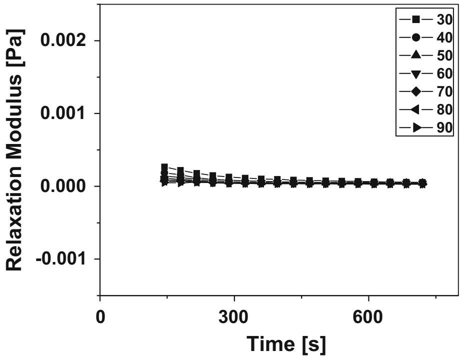
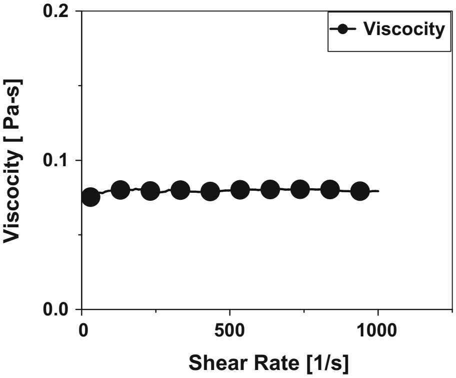


Fig. 5 Variation of viscosity with shear rate at room temperature



3.3 Variation of Viscosity with Shear Rate

The measurement was carried out at room temperature. Viscosity versus shear rate graph shows no variation indicating that the fluid is Newtonian (Fig. 5).

3.4 Ultrasonic Velocity Measurements

Sound is a molecular disturbance caused by vibration. The velocity of sound is measured in terms of distance travelled per unit time, which is the multiplication of wavelength and frequency. It depends on the nature of the medium through which it is travelling and also how molecules are close together. So velocity of sound is directly related to its bulk modulus and density. The Wood equation, $U = 1/(\beta\rho)^{1/2}$ expresses the sound velocity in terms of adiabatic compressibility β and density ρ. If sound velocity U can be measured with high accuracy, then adiabatic bulk modulus K ($=1/\beta$) can also be calculated accurately. The measurements of

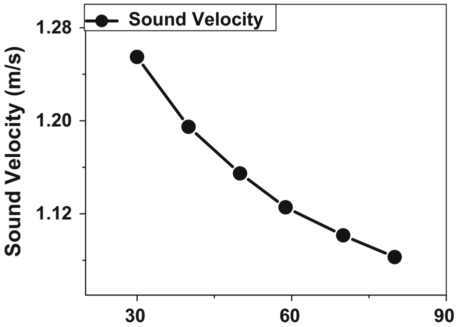


Fig. 6 Variation of ultrasonic velocity with temperature

ultrasonic velocity in Karanja oil bio lubricant have been made at 2 MHz of frequency with the help of variable path interferometric technique. Water is circulated around the sample using a specific thermostat. The measurement value of ultrasonic velocity is accurate to ±0.1% with an error of measurement of ±0.5 °C in the temperature. The plot of ultrasonic velocity as a function of temperature is shown above (Fig. 6). It is found that the ultrasonic velocity in the biolubricant is an exponential function of temperature. Sound velocity is higher at low temperatures. As the temperature increases, the ultrasonic velocity decreases, which shows the weakening of intermolecular forces due to thermal agitation.

4 Conclusion

The viscosity variation with temperature shows a linear behaviour indicating the Newtonian behaviour of synthesized biolubricant in the defined range of temperature. The sound velocity variation with temperature explains the weakening of intermolecular forces due to thermal agitation.

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Removal of Phenylacetic Acid from Aqueous Streams

Sapana S. Madan and Kailas L. Wasewar

Abstract Phenylacetic acid is a carboxylic acid found in the active auxin. Phenylacetic acid is extensively used in the biotechnological and pharmaceutical industry for the production of β-lactam, antibiotics, penicillin G etc. Phenylacetic acid has wide range of biological activity, antibacterial, analgesic, and virucidal properties. Because of versatile biological and medicinal activities of the phenylacetic acid, it is necessary to recover it from the aqueous streams. Separation of phenylacetic acid from aqueous streams is an essential fraction of their manufacturing process which directly affects the economy of the process. Number of separation methods such as ion-exchange, adsorption, reverse osmosis, electro-dialysis, distillation, precipitation, ultrafiltration, extraction etc. Most of these methods have their certain drawback. Among all these methods, adsorption method is preferable including biological, physical, and chemical, natural systems due its low cost, high treatment stability, easy operation and compact facility. Further the exhaustive comparisons of these methods have been discussed.

1 Introduction

Phenylacetic acid is a carboxylic acid found in the active auxin [1]. It is a white solid with a disagreeable odor. Phenylacetic acid is extensively used in the biotechnological and pharmaceutical industry for the production of β-lactam, antibiotics, penicillin G etc. [2]. Phenylacetic acid is commonly used in pesticides, pharmaceutical, perfume, cosmetics industries, etc. Phenylacetic acid has a wide range of biological activity, antibacterial, analgesic, and virucidal properties [3]. Phenylacetic acid is a by-product of the enzymatic hydrolysis of penicillin G by penicillin acylase (PA) [4]. Phenylacetic acid is also used to treat type II hyperammonemia to help reduce the amount of ammonia in a patient's blood stream by

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forming phenylacetyl-CoA, which then reacts with nitrogen-rich glutamine to form phenylacetyl glutamine [5, 6]. Phenylacetic acid is the produce by the catabolic activities of microorganisms from different synthetic and natural aromatic compounds, such as aromatic amino acid and lignin [7]. Human isolates (Bacteroides gingivalis and Bacteroides asaccharolyticus) tested produced phenylacetic acid. The production of phenylacetic acid by the variety of strains of Bacteroides melaninogenicus tested animal source [8]. Phenylacetic acid can be produced by the fermentation of soya beans using Bacilus Licheniformis [9, 10]. Phenylacetic acid can be used as a therapeutic agent for the treatment of cancer [11]. Because of the phenylacetic acid has lots of versatile biological, medicinal activities, and industrial application, they released into the environment thus leading to pollution. Therefore, it is necessary for recovery of phenyl acetic acid acids as well as separation of acid mixtures from aqueous streams. Further the exhaustive comparisons of these methods have been discussed.

2 Conventional Methods

Phenylacetic acid strongly reduces the activity of penicillin acylase (PA). It is usually removed by addition of aqueous ammonia to form soluble ammonium salt. The recovery of phenylacetic acid from this aqueous solution of ammonium salt of phenylacetic acid is done through breaking the salt among acid. This method is not sustainable because it consumes acid, alkali and produces a waste containing ammonium sulfate [4, 12]. The usual method for the production of phenylacetic acid is hydrolysis of benzyl cyanide with each alkali or acid [13]. By the use of carbonation of benzylmagnesium chloride and the catalytic reduction of mandelic acid also prepare phenylacetic acid.

3 Techniques for the Separation Process

A number of separation process such as coagulation, stripping, precipitation, distillation, membranes, ion-exchange, electro-dialysis, pervaporation, reverse osmosis, ultrafiltration, reactive extraction, and adsorption have been studied for the recovery and removal of carboxylic acids [14–18]. All these methods have their own advantages and disadvantages.

3.1 Reactive Extraction

Reactive extraction is an alternative to conventional process. Reactive extraction is the separation process with the reactions of extractants and the materials extracted.

The extractant in the organic phase combines with the material in the aqueous phase and the reaction complexes formed are then solubilized in the organic phase [19]. Gaidhani et al. studied the equilibria and kinetics of extraction of phenyl acetic acid by Alamine 336 in various diluents (kerosene and MIBK) [12]. They found that the kerosene as a diluent yields a higher equilibrium constant for complex formation between the acid and Alamine 336. Athankar et al. studied the separation of α-toluic acid using triglycerides of fatty acids such as castor oil, soybean oil, and sunflower oil by reactive extraction [20]. Athankar et al. reported the reactive extraction of phenylacetic acid using tri-n-butyl phosphate in benzene, hexanol, and rice bran oil at 298 K. It signifies the removal was observed 95% extraction [21]. The separation of phenyl acetic acid with phosphoric acid tributyl ester in CCl_4, decanol, kerosene, toluene, and xylene were observed the extraction efficiency more than 95% with all these diluents [22]. The reactive extraction data were shown in terms of overall distribution coefficients loading ratio, degree of extraction, and equilibrium complexation constants.

3.2 Adsorption

Adsorption is a process which occurs the liquid or gas molecules accumulates on the surface of a solid (adsorbent) forming a molecular film. In recent year, adsorption technique has more popular in natural systems, including physical, biological, and chemical for the recovery and removal of valuable acids, heavy metal, dyes from aqueous streams etc. Adsorption is influenced by many factors such as phenylacetic acid/adsorbent interaction, temperature, contact time, adsorbent's surface area, and pH. It is one of the effective and separation purification technique used in industry for the wastewater treatments. Selection of the adsorbent will be based on properties such as low cost, high surface area, reuse, and industrial scale use. Low cost adsorbent is an important factor for the recovery of acid. Carboxylic acids are the most attractive compounds which can be made from biomass [23]. Tung and King studied that the carboxylic acids can be separated from water by solid sorbents [24]. Solid sorbents have an excellent selection for carboxylic acids. Kawabata et al. reported the carboxylic acid separated by using a polymer adsorbent of pyridine skeletal structure and a cross-linked structure [25]. Inci et al. reported the adsorption of malic acid [26], citric acid [27], and glycolic acid [28] on charcoal activated. Madan et al. reported the removal of phenylacetic acid (α-toluic acid) from aqueous solution using calcium peroxide nanoparticles as an adsorbent [29]. Nanoparticles have larger surface areas than bulk particles which make them particularly attractive as sorbents. Nanosize adsorbents with strong affinity toward phenylacetic acid can be considered as a helpful tool in enhancing the adsorption capacity in water treatment. The effect of various parameters studied such as CaO_2 nanoparticles dosage, contact time, initial concentration, agitation speed, and temperature have been studied. The removal efficiency of 97.7% for α-toluic acid was obtained using 0.05 g/L of CaO_2 nanoparticles and 13.47 g/L of α-toluic acid.

4 Conclusion

Phenylacetic acid has an effective for the separation and recovery from aqueous streams. Several techniques have been studied for the removal and recovery of carboxylic acids. Some techniques are not cost effective. Adsorption is a promising technique including biological, physical, and chemical natural systems due its low cost, high treatment stability, easy operation and compact facility for the separation of phenylacetic acids from aqueous streams.

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Investigation of the Kinematic Viscosity of Cottonseed, Palm, Soybean and Jatropha Biodiesel with Diesel Fuel

S. Madiwale and V. Bhojwani

Abstract Biodiesel is a biodegradable and non-toxic alternative fuel produced from various feedstocks of vegetable oil and animal fats and used as an alternative fuel in the transportation sector such as automotive, marine and small aircraft. The higher viscosity of biodiesel causes serious problems when it is used in the conventional engine without modification. Considering this problem the study has been carried out towards two objectives. The first objective is to identify the different feedstock of biodiesel and to study the variation of kinematic viscosity as a function of temperature and blend ratio with diesel fuel. The second objective is to correlate and develop the mathematical model of variation of kinematic viscosity as a function of temperature and blend ratio with diesel fuel by using non–linear regression analysis. Test fuels used were a conventional diesel, neat biodiesel of Cottonseed, Palm, Soybean and Jatropha oil, and their blends with blending ratio of 20, 40, 60 and 80% with diesel fuel. The blends were prepared on the volume basis and viscosities were measured as per IS: 1448 [P: 25]-1976 test methods. Equation given by Arrhenius and studied by Grunberg and Nissan was used to predict the viscosities of the biodiesel blends. For all blends of Cottonseed, Palm, Soybean and Jatropha oil biodiesel, it is reported that, there is an excellent agreement between the measured and predicted values of the viscosities and have an absolute maximum error up to 0.001. The viscosities of the test fuels were found to decrease linearly with increasing temperature and decreasing blend ratio.

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1 Introduction

In the last century, over all the world scientists and researchers are attracted towards the non conventional energy resources because of the environmental concerns and depleting the stock of oil reserves [1]. There are many non conventional energy resources and biodiesel is one of the most favorable source of renewable energy. Any vegetable oils or animal fats can be converted into biodiesel with the transesterified process and can be used as alternative fuel in the conventional compression ignition engines [2]. Biodiesel is naturally degradable, non-toxic and non conventional energy fuel [3]. It can be used as pure biodiesel or blends of biodiesel with conventional diesel fuel in the diesel engine. Compared to diesel fuels biodiesel has many considerable advantages. It has high cetane number and not having any presence of aromatics. Sulfur contains are negligible and also contain 10–15% oxygen by weight. Biodiesel propelled engines produces CO, HC and particulate matter, but amount of these emissions were very less as compared with engines those were propelled with conventional diesel fuels [1]. Lubricity of engine can be increase when biodiesel used as a fuel. The flash point of conventional diesel fuel is lower than the biodiesel. There are few drawbacks of biodiesel when it used in an engine such as its unfavorable cold flow properties which limit use of biodiesel in all temperature conditions. At high temperature biodiesel used to oxidize with air. The energy content in the fuel is defined by its calorific value. Biodiesel possesses lower calorific value than the diesel fuel [4].

Viscosity of biodiesel is higher than the conventional diesel fuel. Because of higher viscosity of biodiesel or blends of biodiesel there is poor atomization of the injected fuel in the compressed air which increased the fuel droplet size through injector nozzle which leads deposition of the fuel near the nozzle tip [5].

2 Problem Identification and Basic Principle

Viscosity is a measure of the internal fluid friction or resistance of oil to flow, which tends to oppose any dynamic change in the fluid motion. As the temperature of oil is increased its viscosity decreases and it is therefore able to flow more readily. The lower the viscosity of the oil, the easier it is to pump and atomize and achieve finer droplets. Fuel evaporation and its atomization in the combustion chamber are greatly influenced by the kinematic viscosity of biodiesel or blends of biodiesel with conventional diesel fuel. Scientists and researchers done a lot of research on the physical properties of biodiesel and on blends of biodiesel with conventional diesel fuel. But the kinematic viscosity is not been sufficiently investigated in the high temperature zone. Considering this problem the study has been carried out towards two objectives. The first objective is to identify the different feedstock of biodiesel and to study the variation of kinematic viscosity as a function of temperature and blend ratio with diesel fuel. The second objective is to correlate and develop the mathematical model of variation of kinematic viscosity as a function of temperature and blend ratio with diesel fuel by using non–linear regression analysis.

3 Methodology

Test fuels used were a conventional diesel, neat biodiesel of Cottonseed, Palm, Soybean and Jatropha oil, and their blends with blending ratio of 20, 40, 60 and 80% with diesel fuel. The blends were prepared on the volume basis and viscosities were measured as per IS: 1448 [P: 25]-1976 test methods. Equation given by Arrhenius and studied by Grunberg and Nissan was used to predict the viscosities of the biodiesel blends [6].

Redwood viscometer is based on the principle of laminar flow under a falling head. The objective was to determine the kinematic viscosity of blends of biodiesel of Jatropha, Palm, Soybean and Cottonseed oil (B20, B40, B60, B80, and B100) with the standard diesel fuel. Viscosity is the property of a fluid to oppose relative motion between its layers. Kinematic viscosity of a liquid was determined with the help of the redwood viscometer as give below.

$$v = A(t) - B/(t) \tag{1}$$

where A = 0.0026 and B = 1.175

$$v = [0.0026(t) - [1.175/(t)]] * 100$$

A and B are the calibration constants of the instruments.

v kinematic viscosity in cSt
t Time in seconds required to collect a volume of 50 c.c of liquid in a measuring flask

It consists of a vertical cylinder of specific size having orifice of designed diameter in its base. The diameter of the orifice was so small that the flow through it was laminar. The cylinder was filled up to a specific level with a liquid of which the viscosity was to be determined and time of emptying this cylinder for a specific volume was noted. A jacket of water, was heated by means of electric heater, surrounds the cylinder. With the help of this arrangement the variation of viscosity with temperature was studied. It works on the principle that as temperature increases, viscosity of a liquid decreases and thus same amount of liquid can be collected in much lesser time at higher temperature.

Following procedure was adopted at the time of experiments

1. Leveled the viscometer with the help of leveling screws.
2. Filled the water jacket with water.

3. Closed the orifice by means of ball valve and poured the diesel and blends of biodiesel of Jatropha, Palm, Cottonseed and Soybean, of which viscosity was to be determined into cylinder, up to an index mark.
4. Started heating of water and stirred continuously, in order to avoid any localization of heat around the cylinder.
5. Record the temperature of test fuel sample.
6. Ball valve then lifted and recorded the time required to collect 50 c.c. of test fuel sample in the measuring flask.
7. Procedure was repeated for the various temperature as 25, 40, 50, 60, 70, 80, 90, 100 °C.

4 Results and Discussions

Viscosities of diesel, blends of Jatropha biodiesel, Palm oil Biodiesel, Cottonseed oil biodiesel and Soybean oil biodiesel with diesel were measured as per IS: 1448 [P: 25]-1976 test methods. Tables 1, 2, 3 and 4 shows the experimental values of kinematic viscosities of blends of Jatropha, Palm, Cottonseed and Soybean biodiesel with diesel at temperatures in the range of 25–100 °C respectively.

Figures 1, 2, 3 and 4 shows the variation of kinematic viscosities of blends of Jatropha, Palm, Cottonseed and Soybean biodiesel with diesel at different temperatures which are ranges between 25 and 100 °C.

The measured values of viscosities of blends of Jatropha oil, Palm oil, Cottonseed oil and Soybean oil biodiesels were increases with increase in blend ratio and decreased with increase in temperature of blends. All the reported values of viscosities were within specified limits at standard reference temperature i.e. 40 °C. Viscosities of JB20, JB40, JB60, JB80 and JB100 were 12, 14, 15.4, 18.4 and 19% higher than the conventional diesel fuel at a standard temperature of 40 °C respectively. Similarly similar trend were also observed in the all the blends of Palm, Cottonseed and Soybean oil biodiesel at 40 °C.

In order to identify the effect of temperature on the kinematic viscosities of the blends of biodiesel with diesel fuel at various temperature and blend ratio, the experimental values were fitted by means of regression analysis. Most commonly recommended equation of Andrade type from the literature is used to predict the viscosities of Jatropha oil, Palm oil, Cottonseed Oil and Soybean oil biodiesel with diesel fuel. Tables 5, 6, 7 and 8 shows the constant values of A, B, and C and the regression coefficient R^2 for Jatropha oil, Palm oil, Cottonseed oil and Soybean oil biodiesel at 40 °C respectively.

Figures 5, 6, 7 and 8 shows the variation in the measured and predicted values of kinematic viscosity of various blends of Jatropha oil, Palm oil, Cottonseed oil, and Soybean oil biodiesel at 40 °C with biodiesel fraction respectively.

Table 1 Experimental values of kinematic viscosity for blends of Jatropha oil biodiesel

Sr. No.	Temp in °C	JB100		JB80		JB60		JB40		JB20		Diesel	
		Time in seconds	Viscosity in (cst)	Time in seconds	Viscosity in (cst)	Time in seconds	Viscosity in (cst)	Time in seconds	Viscosity in (cst)	Time in seconds	Viscosity in (cst)	Time in seconds	Viscosity in (cst)
1	25	39.5	7.29532	38	6.78789	36.1	6.13115	35.24	5.82812	33.68	5.26808	32.32	4.76768
2	40	33.52	5.20983	32.88	4.9752	31	4.26968	30.14	3.93793	28.55	3.30741	27.2	2.75215
3	50	30.6	4.11613	29.94	3.85988	28.05	3.10405	27.2	2.75215	25.7	2.11002	24.35	1.50554
4	60	28.18	3.15718	27.52	2.88558	26	2.24077	24.78	1.70107	23.5	1.11	22.16	0.45925
5	70	28	3.08357	26.8	2.58367	25.4	1.97802	24.5	1.57408	22.98	0.86166	21.9	0.3287
6	80	26.52	2.46458	25.87	2.18426	24.12	1.39972	23.41	1.06738	22	0.37909	21.4	0.07335
7	90	24.59	1.61503	23.92	1.30699	23.43	1.07686	22.35	0.55373	21.83	0.2933	21.36	0.05266
8	100	23.7	1.20419	23.4	1.06263	22.56	0.65727	22	0.37909	21.55	0.15056	21.27	0.00599

JB100-100% Jatropha oil biodiesel, JB80-80% Jatropha oil biodiesel, JB60-60% Jatropha oil biodiesel JB40-40% Jatropha oil biodiesel, JB20-20% Jatropha oil biodiesel)

Table 2 Experimental values of kinematic viscosity for blends of Palm Oil Biodiesel

Sr. No.	Temp in °C	PB100		PB80		PB60		PB40		PB20		Diesel	
		Time in seconds	Viscosity in (cst)	Time in seconds	Viscosity in (cst)	Time in seconds	Viscosity in (cst)	Time in seconds	Viscosity in (cst)	Time in seconds	Viscosity in (cst)	Time in seconds	Viscosity in (cst)
1	25	39.47	7.285255	37.96	6.774236	36.08	6.124148	35.18	5.806834	33.6	5.246257	32.32	4.7676802
2	40	32.92	4.989941	32.68	4.901329	30.85	4.212248	30.05	3.90285	28.5	3.266947	27.2	2.7521471
3	50	30.48	4.069813	29.78	3.797199	28.04	3.099958	26.98	2.659722	25.7	2.101255	24.35	1.505538
4	60	28.16	3.149015	27.48	2.868963	25.98	2.23209	24.72	1.673964	23.4	1.076862	22.16	0.4592534
5	70	27.95	3.063064	26.74	2.558234	25.37	1.964746	24.4	1.528426	22.9	0.832673	21.9	0.3287032
6	80	26.5	2.456038	25.68	2.101255	24.05	1.367345	23.4	1.062632	22	0.379091	21.4	0.0733458
7	90	24.45	1.551274	23.9	1.297682	23.38	1.053137	22.34	0.548776	21.8	0.283163	21.36	0.0526637
8	100	23.64	1.176011	23.36	1.043634	22.55	0.652357	22	0.379091	21.5	0.135163	21.27	0.0059875

PB100-100% Palm oil biodiesel, PB80-80% Palm oil biodiesel, PB60-60% Palm oil biodiesel, PB40-40% Palm oil biodiesel, PB20-20% Palm oil biodiesel

Table 3 Experimental values of kinematic viscosity for blends of Cottonseed oil biodiesel

Sr. No.	Temp in °C	COB100		COB80		COB60		COB40		COB20		Diesel	
		Time in seconds	Viscosity in (cst)	Time in seconds	Viscosity in (cst)	Time in seconds	Viscosity in (cst)	Time in seconds	Viscosity in (cst)	Time in seconds	Viscosity in (cst)	Time in seconds	Viscosity in (cst)
1	25	39.32	7.2349	37.95	6.770821	36.05	6.113638	35.15	5.796183	33.54	5.21712	32.3	4.76768
2	40	32.78	4.9383	32.51	4.838327	30.75	4.173862	29.79	3.801123	28.3	3.206057	27.2	2.752147
3	50	30.2	3.9613	29.57	3.714578	27.9	3.04253	26.95	2.647074	25.53	2.035371	24.4	1.505538
4	60	28.15	3.1449	27.44	2.85233	25.95	2.219062	24.65	1.642266	23.32	1.024607	22.2	0.459253
5	70	27.88	3.0343	26.57	2.485919	25.26	1.915977	24.22	1.445837	22.89	0.818154	21.9	0.328703
6	80	26.45	2.4347	25.49	2.017749	23.97	1.330239	23.38	1.053137	21.98	0.369031	21.4	0.073346
7	90	24.37	1.5147	23.88	1.288364	23.25	0.991237	22.33	0.543821	21.79	0.273018	21.4	0.052664
8	100	23.55	1.1336	23.25	0.991237	22.54	0.647445	21.99	0.374062	21.48	0.114595	21.3	0.005987

COB100-100% Cottonseed oil biodiesel, COB80-80% Cottonseed oil biodiesel, COB60-60% Cottonseed oil biodiesel, COB40-40% Cottonseed oil biodiesel, COB20-20% Cottonseed oil biodiesel

Table 4 Experimental values of kinematic viscosity for blends of Soybean oil biodiesel

Sr. No.	Temp in °C	SOB100		SOB80		SOB60		SOB40		SOB20		Diesel	
		Time in seconds	Viscosity in (cst)	Time in seconds	Viscosity in (cst)	Time in seconds	Viscosity in (cst)	Time in seconds	Viscosity in (cst)	Time in seconds	Viscosity in (cst)	Time in seconds	Viscosity in (cst)
1	25	39.12	7.16762	37.92	6.76057	36	6.096111	34.82	5.6787	33.37	5.15507	32.3	4.76768
2	40	32.53	4.84575	32.12	4.69304	30.54	4.092987	29.36	3.63156	27.9	3.04253	27.2	2.752147
3	50	29.58	3.71852	29.16	3.55211	27.72	2.968383	26.68	2.53275	25.32	1.9426	24.4	1.505538
4	60	28.1	3.12451	27.22	2.76052	25.81	2.158101	24.45	1.55127	23.12	0.92902	22.2	0.459253
5	70	27.45	2.85649	26.14	2.30137	25.13	1.858114	23.92	1.30699	22.81	0.77935	21.9	0.328703
6	80	26.41	2.41753	25	1.8	23.78	1.241673	23.32	1.02461	21.95	0.35392	21.4	0.073346
7	90	24.22	1.44584	23.81	1.2557	23.14	0.938613	22.32	0.53886	21.75	0.2527	21.4	0.052664
8	100	23.42	1.07212	23	0.8713	22.52	0.637616	21.95	0.35392	21.42	0.08367	21.3	0.005987

(SOB100-100% Soybean oil biodiesel, SOB80-80% Soybean oil biodiesel, SOB60-60% Soybean oil biodiesel, SOB40-40% Soybean oil biodiesel, SOB20-20% Soybean oil biodiesel)

Fig. 1 Variation of kinematic viscosity of Jatropha oil biodiesel with diesel at various temperatures

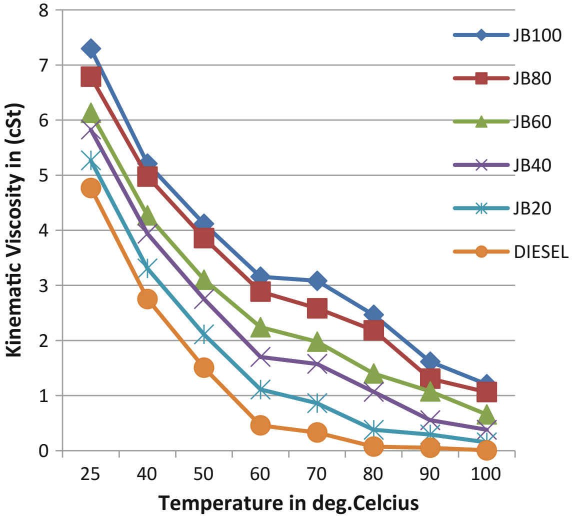
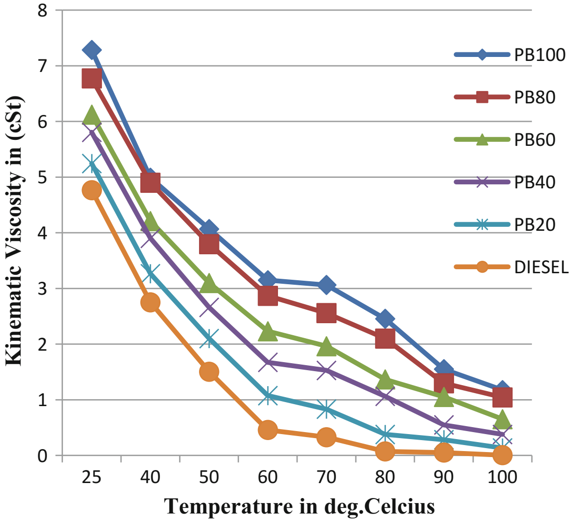


Fig. 2 Variation of kinematic viscosity of Palm oil biodiesel with diesel at various temperatures



From Figures 5, 6, 7 and 8 it is concluded that predicted values are in good agreement with the measured values for Jatropha, Palm, Cottonseed and Soybean oil biodiesel.

Figure 9 shows Comparison of Kinematic viscosity of blends of biodiesel with biodiesel fraction at 40 °C. It is observed that for all the blends of soybean oil biodiesel with diesel all the values used to be lower than other viscosity values of Jatropha, palm and cottonseed oil biodiesel.

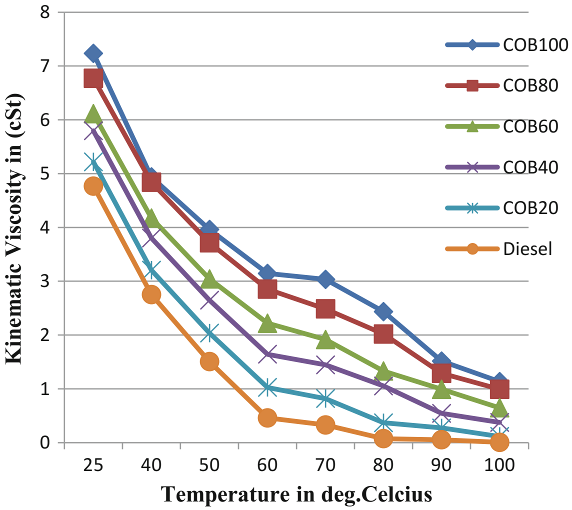


Fig. 3 Variation of kinematic viscosity of Cottonseed oil biodiesel with diesel at various temperatures

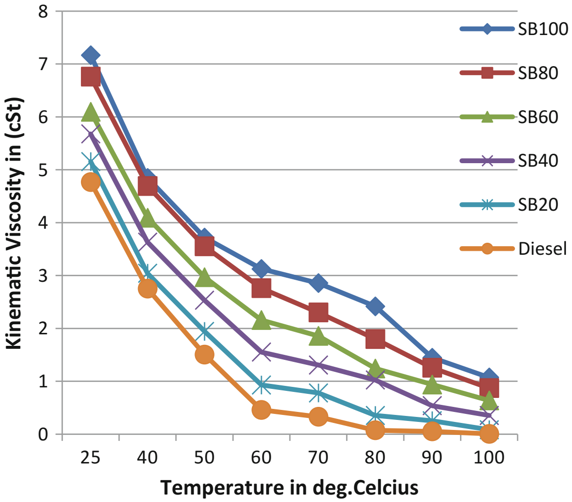


Fig. 4 Variation of kinematic viscosity of Soybean oil biodiesel with diesel at various temperatures

Table 5 Regression parameters for Jatropha oil biodiesel

Fuel type	Regression equation $\ln(v) = A + \frac{B}{T} + \frac{C}{T^2}$				
	A	B	C	Absolute error	R^2
JB 100	−3.89	848.858	2.78×10^5	0.0012	0.954
JB 80	−23.19	0.13×10^5	-17.8×10^5	0.0021	0.984
JB 60	−25.75	0.14×10^5	-18.9×10^5	0.0059	0.991
JB 40	−40.06	0.23×10^5	-31.6×10^5	0.0062	0.987
JB 20	−47.98	0.267×10^5	-35.44×10^5	0.0512	0.993

Table 6 Regression parameters for Palm oil biodiesel

Fuel type	Regression equation $\ln(v) = A + \frac{B}{T} + \frac{C}{T^2}$				
	A	B	C	Absolute error	R^2
PB 100	−22.48	0.132×10^5	-17.71×10^5	0.0380	0.975
PB 80	−22.86	0.132×10^5	-17.40×10^5	0.005	0.987
PB 60	−25.79	0.145×10^5	-18.87×10^5	0.000	0.992
PB 40	−38.25	0.218×10^5	-29.66×10^5	0.012	0.987
PB 20	−51.11	0.286×10^5	-38.55×10^5	0.043	0.993

Table 7 Regression parameters for Cottonseed oil biodiesel

Fuel type	Regression equation $\ln(v) = A + \frac{B}{T} + \frac{C}{T^2}$				
	A	B	C	Absolute error	R^2
COB 100	−23.49	0.138×10^5	-18.70×10^5	0.039	0.973
COB 80	−23.26	0.134×10^5	-17.65×10^5	0.007	0.990
COB 60	−25.49	0.142×10^5	-18.36×10^5	0.001	0.995
COB 40	−36.77	0.208×10^5	-27.97×10^5	0.006	0.988
COB 20	−55.67	0.314×10^5	-42.87×10^5	0.035	0.992

Table 8 Regression parameters for Soybean oil biodiesel

Fuel type	Regression equation $\ln(v) = A + \frac{B}{T} + \frac{C}{T^2}$				
	A	B	C	Absolute error	R^2
SOB 100	−23.37	0.137×10^5	-18.41×10^5	0.036	0.970
SOB 80	−23.92	0.136×10^5	-17.84×10^5	0.010	0.994
SOB 60	−24.15	0.133×10^5	-16.66×10^5	0.002	0.996
SOB 40	−34.34	0.191×10^5	-25.18×10^5	0.006	0.988
S0B 20	−63.78	0.366×10^5	-51.11×10^5	0.006	0.986

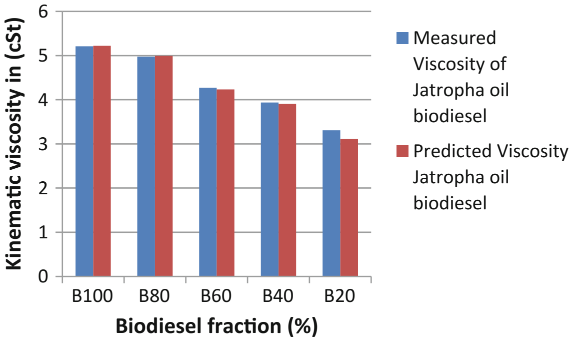


Fig. 5 Variation of measured and predicted kinematic viscosity of Jatropha oil biodiesel with % biodiesel fraction

Fig. 6 Variation of measured and predicted kinematic viscosity of Palm oil biodiesel with % biodiesel fraction

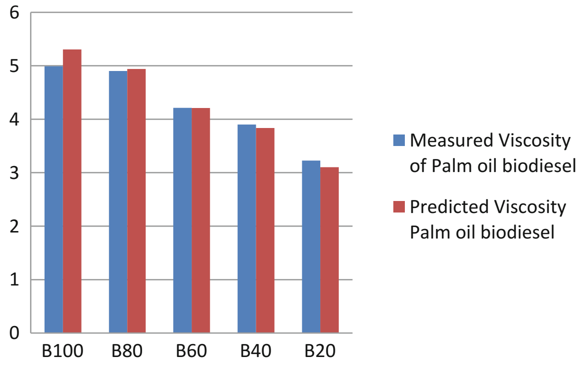


Fig. 7 Variation of measured and predicted kinematic viscosity of Cottonseed oil biodiesel with % biodiesel fraction

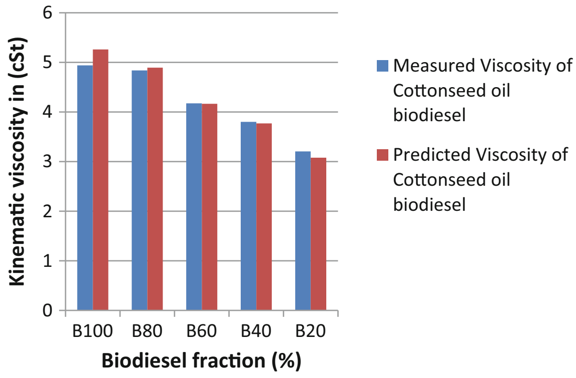


Fig. 8 Variation of measured and predicted kinematic viscosity of Soybean oil biodiesel with % biodiesel fraction

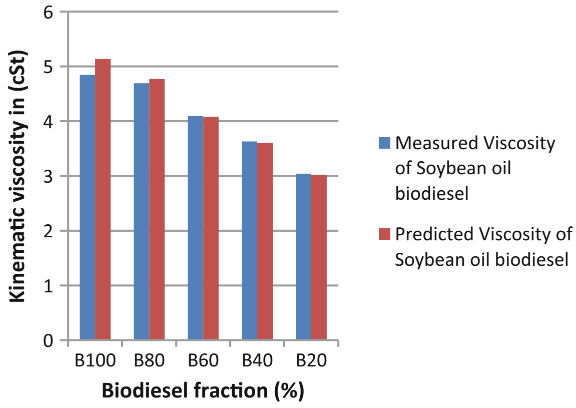
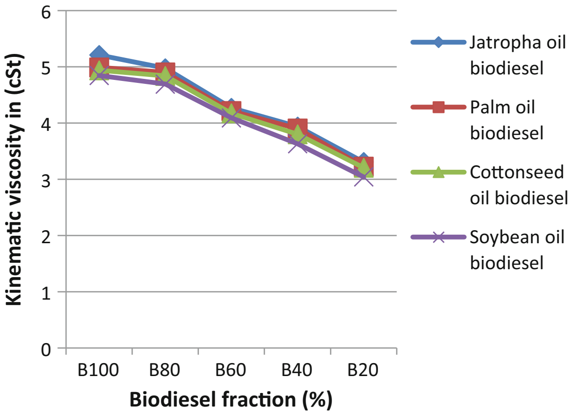


Fig. 9 Comparison of kinematic viscosity of blends of biodiesel with biodiesel fraction at 40 °C



5 Conclusions

The purpose of this study was to study variation of kinematic viscosity at different temperatures when the diesel fuel is blended with biodiesel. Four different biodiesels were blended with the diesel fuel and kinematic viscosities of the blends were determined. Generalized and empirical equations has been developed and, validated by using measured values, and were used for predicting the viscosities of the blend. All viscosities of blends, diesel and biodiesel decreased with increasing fuel temperature. An empirical equation to predict kinematic viscosities of blends of biodiesel as a function of temperature has been developed, and the predicted results are in very good agreement with experimental results. It is also recorded that the for all the blends of soybean oil biodiesel, the kinematic viscosities were found to be less than the palm, Jatropha and cotton seed oil blend of biodiesel. All blends of Jatropha oil biodiesel possesses the higher viscosities than blends of Palm, Cottonseed and Soybean oil biodiesel.

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Blending of Practices: A Study of Selected Biofuels Complex in India

Rahul Shukla and Sambit Mallick

Abstract Biofuels have caught the attention of the world as a source of renewable energy which can provide energy security, advance rural development, mitigate climate change, and foster international trade. India developed the National Mission on Biodiesel (NMB) as a rural development policy option to produce biodiesel from Jatropha and promoted it as a pro-poor and pro-growth initiative. The study will attempt to examine the emergence, trajectory, and the consequences of the NMB by examining the case of a public sector research institute involvement in developing and disseminating the technologies for sustainable energy in India. The study will also locate the trajectory of an object, which has been constructed into an industrial crop from a bush of semi-arid regions. What are the epistemic practices adopted by various actors in this construction? How is such knowledge diffused from laboratory to farmland? And, where does new cultivation get (the) space? These research questions will be examined within the theoretical framework of Science and Technology Studies (STS); where social, political, economic, cultural, institutional, ideological, etc. factors will account for production of knowledge, its accessibility, and application. To address the research objectives both primary and secondary sources has been used. The primary data is obtained by deploying in-depth interviews of the scientific community and the sources of secondary data viz. academic journals, books, policy documents.

Abbreviations

CSIR	Council of Scientific & Industrial Research
CSMCRI	Central Salt & Marine Chemicals Research Institute
GoI	Government of India
NMB	National Mission on Biodiesel
STS	Science and Technology Studies

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1 Introduction

The projection of World Energy Outlook [1] estimates the rise of 56% in global marketed energy consumption from 2010 to 2040. Owing to escalated demand of energy, social and political unrest unfolded in several Middle Eastern and African economies and insufficient oil supply response raised the price of oil in 2010 [2]. Another incident which preceded the surge in oil prices was in the decade of 1970–1980 when the several nations were in midst of the cold war. This lead to oil embargo, question of national security and emergence of environmental problems created the situation for the search for alternative fuels [3]. From the projected levels of energy demand and available resources it is increasingly apparent that new sources of science and technology should be tapped to meet the ever increasing demand for energy. Among the varying options being explored, biofuels have emerged as a viable option [4]. Biofuels have gained popularity as a global solution due to their potential to "reshape livelihoods, patterns of resource consumption, environments and agro-food production systems" [5].

India was among the countries who were advocating biofuels programmes, missions, and policies. Government of India (GoI) has been promoting renewable sources of energy production since 2002 and the National Mission on Biodiesel (NMB) aligned with the aims of the government to promote green sources of energy production. The NMB was publicised by the GoI as a development initiative and the objective of introducing a new technology/initiative was portrayed as an environmentally friendly method of producing energy domestically, in the process generating rural employment, improving the agriculture sector, and reducing oil imports [6]. It aimed at producing biodiesel from *Jatropha Curcas* (hereafter Jatropha), a non-edible oil seed, which would be cultivated on land under the scheme of Joint Forestry Management, hedges around agricultural land, 'culturable fallow lands', stretches of public land along railway tracks, highways, canals, and dry and marginal 'wastelands' [6].

2 Objectives of the Study

In this vein, the study concentrates on scientific practices employed for the construction of a biofuels plant and their impact on development discourse of an emerging economy—India. Specifically, the present study goes on to present the responses of scientific community of Council of Scientific & Industrial Research (CSIR) sponsored research institute namely Central Salt & Marine Chemicals Research Institute (CSMCRI)—Bhavnagar, India. The rationale for selection of the field site lies in the fact that CSMCRI has been engaged in research and development of renewable energy technologies, especially production of biodiesel from Jatropha. It is imperative to discuss the case of a public sector research institute involvement in developing and disseminating the technologies for sustainable energy in India. The objectives of this study are to:

(a) Understand the emergence of Jatropha as a source of ‘sustainable’ energy and its ability to grow on ‘wastelands’, and to locate its trajectory in the process of enrollment in biofuels network.
(b) Understand how biofuels have been popularised in India with manifold social benefits and to analyse the underlying assumption in discourses of scientific claim-making in promotion of biofuels in India.

3 Methodology

The methodology adopted to achieve objectives of the study is qualitative in nature. In-depth interviews have been conducted with scientists and engineers engaged in research and development of the sustainable energy sources at CSMCRI, especially in the field of biofuel production from Jatropha. The discussion is based upon the transcript obtained after the in-depth interviews. Content analysis has been deployed to examine information generated through secondary sources, including policy documents on biofuels, literature on science and technology studies, books and academic journals. The interview schedule broadly covered the following aspects of the study:

(a) The response of the scientific community in the issue of land-management
(b) The emergence of need for biofuels and construction of Jatropha as a source of sustainable energy source
(c) The response of the scientific community in the process of development of the variety and complexities they encountered
(d) The perception of stakeholders about the methods of the cultivation
(e) The role of the public research institution(s) vis-à-vis private institutions in the research and development of biofuels in India

4 Discussions

The following discussion will cover the responses of the scientific community over the adoption of Jatropha as biofuels crop. Furthermore, we shall discuss the emergence of the crop from a practice of land management to a potential source of biofuels. Here we will argue that the idea of “land improvement” [7] gave the passage for emergence of a biofuels crop in India, not the urge for biofuels itself. Then we go on to explore the various practices emerged in the midst of development narratives attached to Jatropha.

Initially Jatropha was adopted as a crop for ‘improvement’ of land by a research institute supported by the Indian state. Western part of India with lesser rainfall has very less intensity of vegetation and researches were trying to ‘improve’ the condition of landscape by adopting some measures. These measures were searching for the plant with specific characteristics which could sustain in semi-arid region with low water requirement; that could withhold soil from erosion; able to improve the nutrients level of soil; and have a considerable life span. This searching task was executed by Council of Scientific and Industrial Research (CSIR) sponsored Central Salt and Marine Chemicals Research Institute (CSMCRI)—Bhavnagar, India. Scientists in CSMCRI refer land management as:

> [Land management] is about selection of wasteland. There are various kinds of wasteland viz. saline wasteland, rocky wasteland, water-logged land, frosty land etc. Any sort of land with inherent problem or limitations where normal arable crop can not be grown.

Another respondent has the similar views on wasteland and an emphasis for plantation:

> We are targeting on the wastelands where nothing else grows. Jatropha has the capacity to grow in such lands, provided the soil is amended well before the plantation. A deep digging is required through heavy machinery once in a life-time. It will not bear expected quantity of fruits if no soil work will be done. Essential requirement is how to manage the root-zone.

The scientists identified Jatropha and Pongamia having the characteristics to grow in wasteland and simultaneously improve the land. Later, Jatropha planted in Gujarat—Western India, and Odisha—Eastern India with the funding of United Nations Development Program (UNDP) in 1996. The results of plantation were optimistic for future coverage on other part of semi-arid regions of India. Meanwhile, some State governments, oil marketing companies and research organizations started taking the interest in Jatropha promotion. Daimler-Chrysler used the oil in Mercedes Benz and ran about 10,000 km and was satisfied with engine performance; D1 oil, a UK oil firm, collaborated with CSMCRI and the government of Chhattisgarh for oil processing and distribution, and various other State governments proposed enthusiastic plans for the plantation, promotion, and distribution. CSMCRI received the funds from UNDP to cultivate Jatropha at modest scale. But, the intention of plantation was not for biofuels, rather to ‘improve’ coastal areas, sand dunes and ‘waste lands’. Later it was followed by appropriation of land after the improvement. Nonetheless, the fact that Jatropha lived up to its reputation as a shrub that could eke out a living on relatively ‘barren’ land piqued the interest of India’s Department of Biotechnology, which provided a modest funding for further exploration of biofuels possibilities using cuttings from three of the most productive plants in the UNDP trial. These developments also attracted the investors from outside India. A fund of US$1.9 million started research on Jatropha; which comprised of grants from Daimler-Chrysler AG, the German Investment and Development Company in Cologne, India’s Council of Scientific and Industrial Research and the University of Hohenhei [8].

There are over 400 species of trees bearing non-edible oilseeds in India [9]. The potential of all these species claimed to be considered—depending on their techno-economic viability—for production of biofuels. It has been possible to identify Jatropha among these as the "most suitable tree borne oilseed for production of bio-diesel in view of its ability to thrive under a variety of agro-climatic conditions, low gestation period and higher seed yield" [7, 9]. The fruits of Jatropha contain considerable quantity of oil but poisonous in nature for consumption by animals and humans. Though, industrial requirement for soap production and burning at domestic level have been the applications of Jatropha oil since a long time in India. It has long been used around the world as a source of lamp oil and soap, and as a hedging plant [3]. Scientists were aware of such property of Jatropha but oil extraction as a fuel for engines was not in their agenda at time of plantation for landscape development in India.

By the time Jatropha had been established as a renewable source of energy and as an instrument with manifold societal benefits. It was projected as hardy crop which doesn't require soil management, irrigation, fertilizers, and it is resistant to diseases. But, after the plantation it was observed that the plants survived without water and nutrients but could not bear fruits or had in lesser quantity than expected. The plants were also easily susceptible to various diseases as well viz. fungal, virus infection, pest, insect, etc. According to one of the respondents:

> Main problem with Jatropha is that it is not fully domesticated in our country (India). Though a lot of research has been done for its domestication, but still we do not have many good varieties of the plant. We are lacking in quality material for the plantation. If the seed from some unknown material, just for the purpose of growing somewhere in the fields, then it leads to difficulty in evaluating the performance of particular plant. We do not know how much yield would occur and how the plant would perform; the reason is the seeds are taken from unknown material.

Jatropha is a perennial plant, full cycle of crop does not complete within a year. It is imperative to observe performance of the plant year by year until it reaches in the stable condition. After four to five years of plantation it reaches at maturity level and then only yield from the plant gets stabilized. The scientific community [10, 11] emphasizes the need of selected genotypes for the plantation. They argue that plantation with unknown and undomesticated material leads to wastage resources and unexpected yield from the plant. Further they confirms that if the objective is to cover the unproductive area with green, unknown material can be planted; but, before taking the plantation at commercial level genotype of material genotype should be known. It is also necessary to that land must be fertile to some extent, to get considerable economic returns.

The constraints encountered by scientific community in development of the varieties are twofold; firstly, location/geographical factor, and secondly the issue of sustainability of the plant. One of the respondents admits that

> We do not have any established variety which can perform in all sorts of soil. Unlike crops viz. wheat, rice, corn etc. we have many varieties for various sorts of areas, soil and climate; but, this is not the situation with Jatropha.

Hence, so far developed varieties of Jatropha are restricted to specific areas only. The sustainability constraint could be surmounted when the plant can reproduce year after year without use of hybrid seeds; hybrids are limited to a generation only. Varieties are developed after monitoring generation after generation and it may take eight to ten years to develop a variety in case of Jatropha. Research and development is required in area of variety development for Jatropha.

Limitation to the scientific community are not limited to variety development, indeed they encountered resistance from the plant itself. Earlier it was assumed that the plant is resistant to disease, but now in different locations plants are found to be infested with various diseases. The respondent who develops tissue culture for the plant confirms that:

> Whatever we have researched on (the plant), and what we expect from a plant, it should behave consistently whether it is Jatropha or other plant. Basic problem for any plant is disease. Jatropha is also susceptible to different kind of disease viz. fungal collard, viral infection, and insects and pests are also friendly with this plant. Genetic engineering may help to develop some disease resistant germplasm.

On the employment of biotechnology for genetic modification of the plant, either for disease resistance or for the variety development, there is a lack of consensus among the scientists. As we have marked an inclination of the respondent in preceding view for the use of biotechnology, another scientist has apprehension about the same. She responds to the employment of biotechnology as a niche for the development of Jatropha:

> I go with traditional breeding. Science has some limitations. For some disease testing tools are available and for some are not. The introduction of a new gene definitely will work according to its function, but it also changes some function of organ(s) of plant, which can not be detected at the moment and cause some problem in the future. It is problem of jumping genes, they don't behave uniformly.

Aforementioned views, over use of biotechnology for the plant, emphasis on risk and uncertainty over politics of policy. Biofuels have been promoted and developed by the policy framers and biotech industry as an allegedly sustainable alternative to fossil fuels. However, during the past decade other actors have voiced their concerns about potentially detrimental social and environmental effects from large-scale biofuels [12, 13]. They argue in support of assessment of uncertainties associated with scientific and technological inventions and criticized the just acknowledgement and quantification of risk approach. In the case of Jatropha uncertainity is not centered at use of particular technology only, although it is spread over the method of plantation and expected yield after the plantation. According to the respondents:

> One should always plant cuttings not the seedlings. The seedlings have genetic variability. If you plant thousand plants, all will behave differently; whereas, the plants from cuttings and tissue culture will yield consistently. Other important point to consider that the cuttings and tissue culture plant should be from known varieties or from known plant of good history. Selection of germplasm is the most important criteria.

A few studies have been conducted on the yield of Jatropha and its economic viability [14–16]. It can be argued that the practices employed by the cultivators were different that resulted into varying yield of seeds. According to a respondent "what people did, they just got the hold of some seeds from forest for the plantation which resulted in no yield at all". The epistemic practices emerging from scientific knowledge and traditional/cultural knowledge system lead to employment of distinct cropping methods. The contrast between "technical rationality" and "cultural rationality" appears in outcome and process of decision-making [17]. Former's mindset puts her faith in empirical evidence, logical consistency, universality of findings and follow expert judgment in policy decisions; whereas, latter gives equal emphasis to personal and familiar experiences rather than depersonalized technical calculations, values the opinion of peer group with respect to their social standing and trusts process over outcome. People weigh evidences with their past experience and if there is possibility of deception or manipulation, they decide to go with cultural rationality. The incapability of technical experts to incorporate social factor leads to irrational decision and further in policy making. Universalistic findings of science may not be applicable to local community if those are not combined with socio-cultural perspective [18].

A few examples can also be drawn from the collabration between public and private intuitions, which show their respective interests in promotion of biofuels. Nexus between them resulted into a policy in line with earlier biotechnology policy to boost implementation of plans and setups for new technology [19]. Concessions in acquiring land, tax rebates for start-ups, low or nil tariffs in technology transfers are some examples which show the privileged status of businesses in biofuels. A few companies have taken up Jatropha and are developing the quality material for the plantation along with production of biodiesel. Indeed a few among them are providing the seeds to farmers at their own cost. But, these special treatments serve only commercial and political interests of a few; farmers had no voice in policy making so they were not on the pie of profit, rather their livelihood seems to be on stake and possibility of trapping by dependence over multinational organizations. These companies' benevolent approach of dissemination and diffusion of technology raises some question related to sustainability of the crop and dependence of the cultivators. According to one the respondents:

> As far as private companies are concerned they are developing only hybrids. Every year they are developing new hybrids and selling these to cultivators. They have resources and facilities and they can invest every year and develop a hybrid; whereas, In the case of public research institutions they can not invest in developing the hybrids on yearly basis. Our priority is to develop the verities which can be grown at varied location with generational consistency.

Nevertheless, considering the nature of agricultural pursuit in India, it may be observed that new technology enters farm economy through large size holdings. Large holdings have investment potential, capacity to bear risk and reasonable size of holding to afford the use of mechanical power, which is in variably raises the income of the farmers who employ new technologies [20]. The crop will not be profitable to farmers having small land holdings owing to expensive management. Farmers who are growing other crops and Jatropha as secondary crop can expect good returns. On the other hand the hype created for emergence of millions of rural employment could not withstand with reality. Only some skilled with new technology managed to get employment in laboratories or initiated own business. Knowledge economy in coming years will consume urban and rural workforce, is still an open question [19]. Scoones questions the above imaginations of planners by contextualizing the science, politics and policy in new economy of globalized and liberalized world. In doing so he does not subscribe the view of pro-biotechnology or anti-biotechnology. He only raises the questions pertaining to appropriate science and technology policy for India, changing pattern of ownership, control of technology and agriculture produce, participation, poverty, and vision of development. He compares the situations and approaches for green revolution and gene revolution in the era of new economy, new science and new policy. During the green revolution agricultural technology was based on field trials, research and developments activities was funded by state, and scientists and organizations were not concerned on profit making; on the other hand gene revolution intensively depends on laboratory experiments, funding in research and development is done through public-private or private organizations with profit laden motto supported by intellectual property rights regime.

Though there are varied perspectives on adoption of biofuels. A few perspectives focus on adverse consequences of biofuel on ecological cycle; others are in favour of biofuels as a product of biomass at rural level but not for mass production at industrial level [21]. And, a few have apprehensions over adoption of biofuels in either situation. In 2007 the 'fuel versus food debate' highlighted a link between the increased use of bioethanol in the USA and rising food prices in the world market [22]. That implies the shifting of resources from catering the need at subsistence level to commercial fuel production. It is claimed that the Indian approach to biofuels is somewhat different to the current international approaches which could lead to conflict with food security. "It is based solely on non-food feed-stocks to be raised on degraded or wastelands that are not suited to agriculture," thus avoiding a possible conflict of fuel versus food security [9(9)]. The Indian approach to biofuels is different. Where other countries are using food crops for biofuels production and diverting arable land for the production, India thrived for non-edible crop Jatropha at wastelands. Recent research suggests that while Jatropha plant can survive on degraded soil, they can only produce seeds in considerable quantity on fertile soil and with proper care/crop management. This takes us back to food versus fuel dilemma.

5 Conclusions

The aim of this study is to locate the trajectory of Jatropha and its construction as a biofuels crop in India. Biofuels as technology is promoted for manifold societal benefits. It is not possible to abandon the persuasion of technologies as policy instruments for the developments; therefore, the study has dwelled upon the role of a public sector institute as a promoter of biofuel technology and dissemination of the same as a sustainable source of energy. Findings of the study are based on responses of scientists associated with CSMCRI. Key recommendations based on the findings of the study are as follows:

(a) Recent studies have depicted some pessimistic experiences of cultivators where Jatropha programmes have failed. The reasons differ according to stakeholders' perspectives and range from lack of community commitment to shaky scientific facts. Being a perennial plant, Jatropha is expected to have a long productive life and it is prudent to invest generously in the initial phase so that the plantations remain productive. Rushing ahead with Jatropha cultivation on a large scale, without proven germplasm and agronomic practices, and without understanding of plant performance under different edaphic conditions, will inevitably lead to future disappointment.

(b) More research is required to develop the varieties which can flourish at varied location and have resistance towards disease. Biotechnology may help to develop some disease resistant germplasm and advances are already being reported. Scientists are trying to develop genetic markers for conventional breeding and molecular plant breeding. Unless more research takes care of disease and pests problem, it is not advisable to cultivate the genetically modified Jatropha. Indeed, other round of preliminary support is required in order to plant at commercial level.

(c) It could be attributed from the perspective of the scientific community that lack of proper agronomic understanding of the cultivators and exaggerated claims of productivity lead to inevitable backlash when reality failed to match expectations. Therefore, focus should be on primary data so that information can be responsibly disseminated.

(d) Cultivators and policy-makers must also be suitably educated on soil and weather conditions that must be avoided for the plantation. Jatropha is currently not suitable for saline, alkali soil, frosty soil, waterlogged conditions, and it is not frost tolerant. At the same time, research must be intensified both to improve yield and to make the plant more robust. This will open up further avenues for Jatropha cultivation. It is hoped that productivity will improve substantially in the future through inputs from biotechnology.

(e) While individual farmers with small land holding can cultivate in small patches of land; whereas the plant can be set up as part of a cooperative for the farming community with marginal land holding. The plantation takes four to five years to get into full bloom state. If the farming community adopts it, break-even is not achievable before seven to eight years. Some state support should be there for this period to encourage the cultivators.

(f) It has been discussed in the previous section that there is a gap in dissemination of technology from laboratory to field. The conflict between scientific knowledge system and cultural practices of cultivators resulted into varying and unexpected yield of the seed. Integration of knowledge system and better understanding of others' perspective may reduce the conflict.

In this backdrop the emergence of biofuels particularly Jatropha as a fuel can be conceptualized within the definition of fuel where “fuel is a […] peculiar technology nothing is inherently fuel. Fuel is simply a term for carrier of energy” [23 (422)]. The presence of socio-technological system at that time identified Jatropha as a carrier of energy and then it came into the ambit of fuel. Jatropha—or biofuels per say—as new carrier of energy compared and contested with fossil fuels irrespective of efficiency or other comparable parameters. There was nothing inevitable and natural in emergence of Jatropha as biofuels. It has been in application in rural areas for burning from long time. But, what was distinct in 2002, it was the global and local attributes imparted by socio-technical system placed in combination of state, research organizations, development and funding organizations, automobile sectors, and oil sectors. It does not imply that there no resistance were observed, rather initial oppositions were also emanating from same socio-technical system.

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Use of Vegetable Oil as a Fuel in Diesel Engine—A Review

Shiyasharan Patel and Nitin Shrivastava

Abstract It is an older practice to use vegetable oil as a fuel in diesel engine. Rudolf Diesel introduced vegetable oil as a fuel in compression ignition (CI) engine. In the past few decades' vegetable oils have emerged as an alternative fuel. Vegetable oils can either be non-edible or edible. Examples of Few of the edible oils are soya oil, peanut oil and cottonseed oil. The non-edible oils are mahua oil, jatropha oil, karanj oil, rubber seed oil, neem oil etc. The advantages of using vegetable oil at the place of diesel fuel in the CI engine are explained briefly. The use of vegetable oils as a fuel was found more important due to eco-friendly combustion characteristics and its agricultural origin. The current paper discusses the different steps for processing of vegetable oil, various properties and standards for vegetable oil, storage stability. The use of these vegetable oils into the diesel engine their performance, combustion and emission results reported by several researchers are presented.

1 Introduction

The present world has been modernized and industrialized, where the petroleum fuel resources have become necessary for automobiles and other purposes. Hence there is rapid consumption of petroleum resources which are very inadequate in quantity. Due to this, as compared to the past rate of fuel pricing, it is increasing continuously for regular retreating supply and for the fulfillment of the demand. So there is a need to discover new options and alternatives which are renewable, easily available and abundant in nature. So this is not a new idea that vegetable oils used in diesel engines.. Initially Rudolf Diesel supplied vegetable oil in diesel engine as a working fuel. In the past few decades it has already occupied an alternative place. Vegetable oils have similar properties to that of fossil fuels such as physical

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composition and combustion characteristics. The most favorable thing about vegetable oils is their renewable and eco-friendly behaviors as well as the fact that they are obtained from different plants and seeds which can be easily cultivated in our rural areas. Vegetable oils can both be edible and non-edible. Some of the edible oils include palm oil, sunflower oil, rice bran oil, and cottonseed oil and non-edible oils include mahua oil, jatropha oil, rubber seed oil etc. However the vegetable oil is directly used in the diesel engine because it creates some durability and operational problems. However due to poor volatility, cold flow nature and high viscosity of the vegetable oils, some run time complications like fuel nozzle chocking and piston ring sticking occurred [1]. To reduce the high viscosity and to increase the volatility of the vegetable oils, they are pre- heated [2, 3]. The emission of some harmful gases such as CO (carbon monoxide), CO_2 (carbon dioxide), un-burnt hydrocarbons, NO (nitrogen oxides) and smoke can be controlled by replacing the diesel fuel by vegetable oil as a fuel [2–5]. The injection timing and pressure of diesel engine should be modified to overcome some performance difficulties occurred due to the mismatch of chemical structure of diesel fuel and vegetable oil. A few researchers have suggested that-the fuel injection timing should be advanced, when vegetable oil is instead of diesel fuel in diesel engines. Also due to high bulk modulus of vegetable oils, the injection pressure and valve timing should be more advanced to make the proper burning of fuel [6, 7]. Pumping and fuel spray characteristics of vegetable oil ranges between 30 and 200 at 40 °C due to higher viscosity. When compared to diesel fuel 4 at 40 °C. For long running, preheated vegetable oils are appropriate as fuels for diesel engines.

2 Processing of Vegetable Oils

Vegetable oils are obtained from oil-bearing seed and fruit after processing under a certain number of operations. An installation for the extraction of vegetable oils which consists of seed storage, seed clearing, and grinding, pressing, degumming, filtration and oil storage tanks. All impurities have to be removed from the raw material, which can be done by two operations: either decanting in successive tanks, or direct filtering through a filter. For each stage in the production chain, a certain number of factors may modify or influence the quality of the oil obtained downstream. Consequently, a certain number of precautions have to be taken at each stage of the process (Fig. 1).

2.1 Seed Storage

Seeds can be stored more than few months for the process planning. These have to be regularly aired to prevent heat build-up and acidification [9]. The moisture

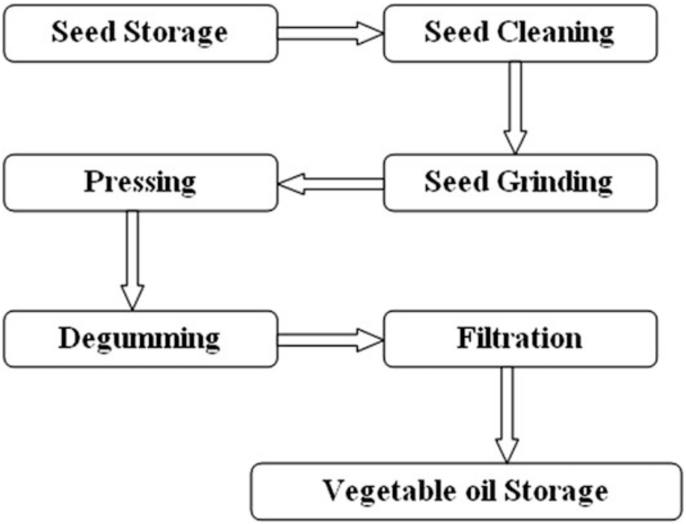

Fig. 1 Vegetable oil quality in relation to the production process [8]

content in the seeds should be below 9% in weight and then only the batches are held to be stabilized [10]. This is the highest seed moisture content which must be present for pressing operation which is currently available on the market to operate efficiently [11].

2.2 *Seed Cleaning*

The elimination of impurities such as soil, stones, metallic objects etc. in the seed must be done up to a maximum of 2% [10] by weight. The impurities when improved in their levels in oil reason wear in the press. This is due to the thermal rupture of oil cell walls at temperatures above 100 °C [11, 12]. Clogging in diesel engine is due to raised level of impurities which in turn increase phosphorus concentrations in the oil [8, 13].

2.3 *Seed Grinding*

The seed grinding process is the most important step. The preheated seeds are grind on the roller mill. Clean seeds are crushed to the right constituent by Mechanized grooved rollers and hammer mills. The seeds are grinded in the form of powder. Seed powder is then heated to help the extraction of the oil. More impurities are free with the oil when the seed are grinded although this procedure allows more oil to be pressed out. These impurities must be removed before the oil can be deemed edible [14].

2.4 Seed Pressing

Fuel vegetable oil is obtained by simple cold pressing of oil bearing seeds and fruits. The oils extracted from various seed and fruits may vary in quantity and quality. Some of the basic variable in seed pressing are type of press, moisture content, seed variety, heating or not, and the cleanliness of seed [15]. Generally, two types of press are used [15]: "whole cylinder or ring" presses for capacities under 100 kg of seeds processed per hour and "strainer", which presses up to 2 tons of seeds per hour. To improve the oil extraction rate they are pre heated to 20 °C [16]. The seed temperature should not exceed the temperature 80 °C inside the press, Higher the temperature higher more the phospholipids content. Hence, the cold pressing is recommended [15, 17]. The extraction rate lies within a range of 80–85%, which mainly varies due the outside temperature and seed moisture content [17, 18].

2.5 Degumming

The mixing of vegetable oil with high temperature water is called degumming. Where the phospholipids of vegetable oils are hydrated and some particles are formed. The drying process of vegetable oil takes place after centrifugation and removal of solid particles. Which makes them extremely energy-intensive and dissipate water [19]. Degumming is the first step in processing for vegetable oil which contain amount of hydra table phosphatides. This steps help in production of the lecithin and reduce the phosphatide removal load in neutralization. Degumming is an important part of processing which is used for the removal of fatty acids. Phosphatides are another material which includes glycerol, metals, resins, protein meal and carbohydrates.

2.6 Filtration

The better quality oil fuel may be obtained by removing entities such as solid particles, phospholipids and waxes through some chemical processes. Oil purification is most important and necessary steps for using vegetable oils sustainably in engines [15, 17]. Filtration can be done directly in vegetable oils by pressing through a plate filter press. Filtration must be done about temperatures of 20–60 °C to remove every soluble element [17]. Above 60 °C, there is a high risk of oil oxidation, which reduces shelf life. Direct filtration is used with the plate filter. In fact, friction insides the press heats the oils to the temperature 60 °C for filtration. The vegetable oils must be filtered at 10 mm for the prevention of impurities and any pollution in the oil [20].

2.7 Oil Storage

Improper storage of vegetable oils can result in oxidation and acidification, which leads to higher viscosity and result in engine filtration problems. So vegetable oils must be stored in clean, air-tight containers in a cool and dark storage area, after filtration [15].

Light is conducive to oil oxidation and acidity. Storage period should be minimized and analyzed before the start of each processing run to establish proper processing conditions. Storage of oils more than a long duration causes oil oxidation. Hence causes high viscosity and filtration problems in the engine.

3 Properties of Vegetable Oil

The vegetable oil and diesel fuel have similar characteristic. Density, flash point, pour point, fire point, net calorific value, cetane number and kinematic viscosity are several of the properties. The usable capacities of vegetable oils similar to diesel fuel are its density, viscosity, flash point, pour point and cetane number. Properties of a fuel can be determined by quality. These properties also indicate performance of engine and its emission. The different types of standard which are used to define the limit of the fuel properties are ISO, ASTM, ENs, etc. The most extensively followed standard is ASTM. The value to the fuel properties must be laid in the range for the satisfaction of the standard engine emission and its performance. The most important part to use any liquid as fuel is to study its fuel properties.

3.1 Kinematic Viscosity

The kinematic viscosity of vegetable oils varies in the range 30–40 centistokes at 38 °C. Their molecular weights are in the range of 600–900 g/mol [21], which are about 3 times higher than those of the diesel fuels [21–23]. Lubricating oil has its most important property of viscosity. The process of a fluid film of a lubricant between the friction surface and the frictional heat generation particular conditions of load, bearing spread and lubricant supply mostly depend upon the viscosity of the lubricant and also on its oiliness at some extent. When large working clearances exist between the friction surfaces, high viscosity oil is generally recommended cushioning the intermediate application of load. The viscosity of oil decreases with increase of temperature as a result of decrease in intermolecular attraction due to expansion. Hence it is always necessary to state the temperature at which the viscosity was determined. Viscosity affects diesel engine operation, mainly due to reduction in the maximum injection by major pressure drop in the injection pump and in the filters, injectors or nozzles, and poor atomization and vaporization, hence incomplete combustion [24–29]. Lubrication problems are regularly observed at low temperature in a few injection pumps, resulting in substantial mechanical losses [22, 23, 27, 30–32]. Preheating the oil prior to starting up the engine can be a solution [31, 33, 34]. Another solution consists in mixing the oil with diesel oil [24, 34–38] or starting up the motor with pure diesel oil before switching to vegetable oil.

3.2 Density

Density is another most important property of the vegetable oil. Density is a measure of the amount of oil contained in a given volume. The mass per unit volume is called density. The diesel fuel has its density 10% less than that of vegetable oils. This needs to be taken into consideration to regulate fuel flow rates. Density is considered at 15.5 °C. Vegetable oil has densities range 900–930 at 15.5 °C.

3.3 Flash Point

These of oils are defined as the lowest temperature at which the vapor pressures of the oils are sufficient to maintain the flame. These are noticeably lower for diesel fuels than for vegetable oils (+100 °C) and its rate has no particular influence on engine performance and combustion efficiency. It is more of a safety parameter for storage. The usual precautions for the storage and handling of petroleum products therefore go beyond what is needed for vegetable oils [22]. The flash point shows, the volatility of the vegetable oils.

3.4 Net Calorific Value (NCV)

The net calorific value of a fuel is the amount of net heat obtainable by the complete combustion when unit quantities of the fuels are completely burnt. Higher calorific value for fuel is desired because it facilitates the heat release during combustion and improves engine performance. The net calorific value of vegetable oils is lower than that of diesel oil. The difference between the mass net calorific value of vegetable oils and that of diesel oil is around 10–15% [23, 24]. However, the volumetric net calorific value of vegetable oils is about 5–6% less due to high density, on average, than that of diesel oil. Combined with the density, the net calorific value is used to determine the volume flow rate for vegetable oils compared to diesel oil, so as to inject identical energy [39]. The consequences of the low net calorific value of vegetable oils compared to that of diesel oil are around 8% extra consumption of vegetable oil, a drop in engine power and a drop in thermal efficiency [23, 25, 28, 33, 40–42].

3.5 Cetane Number

Cetane numbers are a main indicator of the quality of fuel used in compression ignition (CI) engines. As it regulate the timing of injection and combustion. The higher it is, the more flammable is the fuel [9]. Then cetane number of a vegetable oil is defined as the percentage by volume of cetane in a mixture of cetane and naphthalene which exactly matches its knocking characteristics with the vegetable oil under test. The cetane number of the vegetable oil can be improved by adding substances such as ethyl nitrite, is amyl nitrate and acetone peroxide. The cetane numbers of low speed, medium speed and high speed diesel engines should be at least 25, 35 and 45 respectively (Tables 1 and 2).

4 Standards for Vegetable Oil

4.1 History

Firstly Gaupp studied about the use of vegetable oils in diesel engines as an alternative fuel, in 1937 [44]. He highlighted only physical properties of different vegetable oils such as viscosity, pour point, iodine value and their effects of diesel engines. His study was not concerned about the effect of vegetable oil contaminations like water and phosphorus on the diesel engines [45]. Later, in 1982 pryde stated his first tentative vegetable oil standard during the International Conference on Plant &Vegetable Oils as Fuels [46]. Because of law petroleum oil prices in the 1980s the work initiated by Pryde was not taken seriously. Shortly Germany made the great research about vegetable oils and proposed a draft quality standard for rapeseed as fuel in 1994. This proposal was successfully improved in 1996, then in 2000 and become the Weihenstephan Quality Plan [47]. Finally in 2006, the Weihenstephan Quality Plan was reviewed and converted into pre-standard DIN V 51605 for rapeseed oil as a fuel [45]. In this standard, special attention was paid to phosphorus because of foemation of deposits and its poisonous behavior towards

Table 1 Description of the main chemical and physical properties of vegetable oils [43]

Property	Description	Comments
Viscosity (V)	Resistance between the adjacent layers of a fluid, which hinders the sliding of one over the other	Important for the fuel and injection supply of the engines
Density	Mass of the unit of volume	Influences the performance of the oil in the injectors
Flash point	The minimum temperature at which the vapors of a fuel catch fire if in contact with a flame	The higher this value is, the safer storage, transport and manipulation of the product will be
Calorific value (CV)	The energy released by a fuel during the combustion process. Higher calorific value (HCV) indicates all the energy produced by the fuel, lower calorific value (LCV) on the contrary does not consider the latent heat of the vaporization of water produced by the chemical reaction of hydrogen with oxygen	Influences specific consumption
Cetane number	Indicates performance on ignition	Influences cold start, combustion and noise of the engine
Melting point	Indicates the temperature at which the transformation from solid to liquid state can be observed in standard conditions	High melting point values can cause problems on flow in the fuel supply
Oxidation stability	Indicates the quantity of gum and macromolecules which are formed when subjecting a sample to certain conditions of pressure in the presence of oxygen	The compounds generated cause an increase in viscosity
Phosphorus content	Measures the phosphatide content	Phosphatides may form gum in the tanks, in the feed pipes and the filters
Carbon residue	Measures the presence at high temperatures of some natural compounds with high molecular weight	At high temperatures some compounds decompose giving rise to carbon residues
Water content	Measure the water content	The water can shorten filter life or plug fuel filter and promote fuel corrosion and microbial growth

catalysts used in exhaust mufflers. Although, the modern catalysts can be deactivated by earth alkali metals like Ca & Mg and the commission has been working for Na & K specifications currently [45, 48] (Table 3).

4.2 Pre-standard DIN V 51605

People interested to use vegetable oil as a fuel, refer Pre-standard DIN V51605 as a base [49]. Some authors suggested to use rapeseed oil as a fuel in commercial

Table 2 Specifications and technical regulations of vegetable oil [43]

Parameter	Unit	Low speed	High speed	DIN 51605
Viscosity (V)	10^{-6} m^2/s	2.0–100	<38	<38
Density	kg/m^3	<991	900–930	900–930
Flash point	°C	>100	>220	>220
Calorific value (CV)	kJ/kg	–	>35,000	>35,000
Cetane number	–	30-40	39	39
Melting point	–	–	–	–
Oxidation stability (110 °C)	H	–	>5	>5
Phosphorus content	mg/kg	<80	<15	<12
Carbon residue	%m/m	<0.3	<0.48	<0.48
Water content	%m/m	<0.2	<0.075	<0.075

engines, with the recommendation of either changing the engine in a dual-fuel mode with fuel preheating as using it as a mixture of diesel fuel and vegetable oil [48, 50]. The pre-standard DIN V51605 shows following limitation; the pre-standard do not allow the rapeseed oil. The kinematic viscosity and cetane number are also restricted specifications of vegetable oils to be used in stationary diesel engines. Palm oil cannot be used because of the above mentioned restriction [51–54]. Since testing methods are not designed foe vegetable oils but for diesel fuel or biodiesel. The applicability of vegetable oils needs to be evaluated [50]. The analytical tools used to evaluate the characteristics of petroleum-derived fuels can also be useful foe vegetable oil but however they will not be affordable to small scale laboratories in developing countries. Pre-standard DIN V 51605 recommended 15 parameters which are not of practical use in case of stationary applications.

5 Diesel Fuel Standards

The diesel fuel standards are affecting on the diesel engine performance and emissions. From the refining of crude oil, Diesel fuels are obtained. Diesel fuel is a mixture of different petroleum components like paraffin’s, naphthenic and olefins, each with its own physical properties and chemical properties. For giving acceptable performance, the properties of diesel fuel should be balanced. These components also can be used as fuel in diesel engines [55]. Normally this fuel might be containing amounts of select cracked distillates [56]. Diesel fuel is used in weighty vehicle like buses, trucks and cars etc. [57, 58]. This standard at present covers different grades of diesel fuel. The grades are scheduled in order of increasing viscosity and density. The ASTM standards guarantee satisfactory fuel quality. Diesel fuel must at a standstill meet the standard recognized by ASTM. All fuel standards are related to the performance, operability, fuel, economy durability and

Table 3 Evolution of oil quality standards from 1982 to 2006 [8]

	Unit	E. H. Pryde (1982) [46]	Draft of quality standard (1994)	Weihenstephan quality plan (2000)	Pre-standard DIN V 51605 (2006)	Pre-standard DIN V 51605 (2006)
Characteristic feature						
Specific gravity at 15°	kg/m^3	0.91–0.93	0.91–0.93	0.91–0.93	900–930	DIN EN ISO 3675/12185
Iodine value	g I_2/100 g	80–145	<115	100–120	95–125	DIN EN 14111
Viscosity at 40 °C[a]	cst	30–50[b]	<80[a]	<38	<36	DIN EN ISO 3104
Flash point, min	°C	300	55	220	220	DIN EN 2719
Carbon residue, max	% (m/m)	–	0.5	0.4	0.4	DIN EN ISO 10370
Heat value, min	kJ/kg	–	35,000	35,000	36,000	DIN 51900-1, -2, -3
Combustibility (cetane number)	–	30–40	39	–	>39	IP 498
Sulphur content, max	mg/kg	–	300	20	10	DIN EN ISO 20884/20846
Variable features						
Total contamination (insolubles) max	mg/kg	10	–	25	24	DIN EN 12662
Water content karl fisher max	% (m/m)	0.2	0.1	0.075	0.075	DIN EN ISO 12937
Phosphorus ma	mg/kg	200	30	15	12	DIN EN 14107
Free fatty acid max	mg KOH/g	–	1.5	2	2	DIN EN 14104
Ash content max	mg/kg	500	200	100	100	DIN EN ISO 6245
Oxidation stability min at 110 °C	h	–	–	5	6	DIN EN 14112
Ca + Mg content, max	mg/kg	–	–	–	20	DIN EN 14538

[a] Viscosity at 20 °C
[b] Viscosity at 38 °C

emissions. Gummy residual fuel oil is used in diesel engine and marine engine. The diesel fuel chemical composition is changeable depending on the nature of the refining processes and original crude oil.

6 Oxidation Stability of Vegetable Oil

For the storage the Oxidation stability of vegetable oils is the most important issue. The vegetable oil has high stage of polyunsaturated fatty acids. These polyunsaturated fatty acids can polymerize into insoluble particles such as other deposits, Sediments, gums, sediments, oxygen and high storage temperature [59, 60]. The iodine value is much closer to oxidation stability [61]. The Oxidation stability of vegetable oils plays an important role in determining the quality. The Oxidation stability is defined as the resistance of the oil and fats to degradation. The Oxidation stability is illustrious from storage stability. Oxidation may occur also during production and usages. The oxidation stability of vegetable oils is measured to the degree of double bond. The fuel instability is proportional to the number of double bond. The vegetable oils Oxidation stability also depends on the oil refining process, the presence of natural antioxidants and fatty acids distribution. The oxidation stability of vegetable oils reduces as the un-saturation of the fatty acids increases. The un-saturated fatty acids are most susceptible to oxidation than fatty acid having one or more double bond [62]. The vegetable oil can be preferred for breeding programs and genetic modification due to its improved oxidation stability. The suggested oxidation stability experiment methods of American standards [63] and European standards [64] are contentious. The vegetable oil has oxidized for the period of improper storage. Sharma and Jain stated that there are different types of stabilities such as thermal; storage and oxidation in produce the fuel unstable [65]. The volatile acid attendance is reduced by the raise in conductivity. The oil stability index or induction time is time to reaction products appear [66]. The oil molecule is the presence of water [62]. The researchers have growth a method for the determinant of oxidation stability of vegetable oils [67].

7 Performance of Vegetable Oil

The brake-specific fuel consumption and brake thermal efficiency are the most important performance parameter of the vegetable oils. These performance parameters are analysis with vegetable oils and orderly diesel fuel. The engine load extensive from 18 to 90% in steps of 18%. The performance parameters and fuel inlet temperatures was determined and compared.

7.1 Brake-Specific Fuel Consumption

A main performance parameter of the vegetable oil is Brake Specific fuel consumption. The mass fuel consumption per unit brake power is called brake-specific fuel consumption. It defines consumption by unit of power and unit of time. The Specific fuel consumption generally lowers with the higher engine load for every fuel. The Specific fuel consumption is higher with vegetable oil than that of diesel fuel in diesel engines. Brake- specific fuel consumption is increased for a given load at decreased inlet fuel temperature for vegetable oil [20, 25, 27, 31, 33, 41, 68–71]. The vegetable oils have high specific fuel consumption as compared to diesel fuel because of their low net calorific value, high viscosity and high density [72].

7.2 Brake Thermal Efficiency

The brake thermal efficiency of vegetable oils as fuel is lower than diesel fuel [41]. The ratio of brake power to fuel supply is brake thermal efficiency. The brake thermal efficiency of the vegetable oils is low due to poor combustion characteristics [25, 41]. The brake thermal efficiency may be improved by enhancing fuel atomization by preheated vegetable oils which results in reduced fuel viscosity and increase volatility [35]. The brake thermal efficiency of vegetable oils is relatively higher than that of diesel oil [20].

8 Combustion Characteristic of Vegetable Oil

The high compression ratios (14:1–20:1) of CI engine make the pressure and temperature of the intake air extremely high. Then the Fuel is injected through one or more jets into this highly compressed air and form a spray envelope in the combustion chamber. This spray envelope is created both by atomization and volatility of the fuel. A mixture of air and fuel forms at some location in the spray envelope and oxidation starts. The time lapse between the start of injection and begin of combustion is called ignition delay. It is the research time on the air-fuel mixture previous to combustion. The ignition delays of vegetable oils are longer than that of diesel fuel. The cetane numbers of vegetable oils are lower than that of diesel fuel. [22, 26, 71]. However, in ignition delay there is not major difference between the vegetable oil and diesel fuel, whereas the variation between cetane numbers is repeatedly substantial. Fort et al. [73], like Jalinier [74] published work in the 1980s in which these found that the ignition delay of vegetable oils was shorter than for diesel oil. These disagreements in the results may be due to the conditions under which ignition delays were determined. Vaïtilingom (1992) [22] showed that, with an air inlet temperature of 100 °C; the same ignition delays have the diesel fuel and vegetable oils, and ambient temperature of diesel fuels at 500 °C the same evaporation characteristics as vegetable oils.

9 Emission Characteristic of Vegetable Oil

The emissions exhausted into the surroundings pollute the atmosphere. Dissociation of nitrogen, combustion and impurities in the fuel and air are the major causes of this emission. Un-burnt hydrocarbon, oxides of nitrogen, carbon monoxide, Carbon dioxide and smokes are major things responsible for emissions. Which are mainly responsible for air pollution? These pollutants are known to cause serious health problems. Therefore there are laws on emission standards, which limit the amount of each pollutant in the exhaust gas emitted by an automobile engine. The exhaust gas emissions of vegetable oils are lower than that of diesel fuels. Vegetable oil mainly emits unburned carbon monoxide (CO), oxides of nitrogen (NO_X), hydrocarbons (HC), and smoke emissions. These pollutant's emissions are generally described less when engines fueled with vegetable oil.

9.1 Carbon Monoxide (CO) Emission

The highest carbon monoxide emissions are fond at rated power. Carbon monoxide is colorless but a poisonous gas. The carbon monoxide emissions with vegetable oils are higher as compared to diesel fuel. It decreases as the engine loads increases. The high viscosity of vegetable oil causes poor mixture, incomplete combustion and poor spray characteristics can also be the source for carbon monoxide emissions. Preheating of vegetable oil affects positively the result the carbon monoxide (CO) emission. The carbon monoxide emission can be lowered by means of preheating due to the progress in better fuel mixing and sprays characteristics. The cause given is the poor combustion of vegetable oils, which is due to their higher viscosity and little volatility.

9.2 Carbon Dioxide (CO_2) Emission

The unheated vegetable oils emit more carbon dioxide when burnt in a diesel engine as compared to diesel fuel, but it may be controlled to some extent by preheating it. However, the emission of carbon dioxide from vegetable oil does not add into greenhouse gases in the atmosphere as it is absorbed by the plants growth in crop cycle. Carbon dioxide (CO_2) emission from vegetable oils is higher than from diesel oil due to poor vegetable oil combustion [25]. However, the problem for this case is that the performance from the engine was particularly poor, even with diesel fuel.

9.3 Nitrogen Oxides Emission

Nitrogen oxides commonly called NO_X, the corresponding fact to a mixture of NO and NO_2. Oxides of nitrogen are present in exhaust gases of engine rotating about 2000 ppm. Exhaust gases of engine mostly contain nitrogen oxide with a small amount of nitrogen dioxide. NO_X is very undesirable. Oxide of nitrogen (NO_X) is created mostly by reaction of nitrogen present in the air. Regulating to reduce nitrogen oxide emission continue to become more and more stringent year by year. Nitrogen can also be found in fuel blends. NO_X emissions are often lower with vegetable oils compared to diesel oil (20, 25, 27, 33, 42, and 68). The cylinder temperature should be reduced in order to decrease Nitrogen oxides emission.

Cetane number improvers are different type of additives which are used to reduce the NO_X emission from vegetable oil combustion. The vegetable oil having lower heating value and used as a preheated vegetable oil to reduce the NO_X emission significantly. The cetane number improver is used to decrease engine ignition delay. At a 100% engine load, the reduction in emissions reaches 40.3% [43]. The lower NO_X emissions for vegetable oils than for diesel oil are due to the low net calorific value of vegetable oils [24, 27], with lower temperature peaks in the combustion chamber [75, 76]. However, several researchers have established a raise in Nitrogen oxides emissions by means of vegetable oils compared to diesel oil [18, 77]. These attributed their Nitrogen oxides emissions to the formation of deposits in the combustion chamber, causing a higher temperature inside the chamber. However, acknowledge that NO_X emissions increase in line with engine load.

9.4 Un-Burnt Hydrocarbon Emission

Exhaust gases leaving the combustion chamber of a diesel engine contain hydrocarbon particles. Hydrocarbon emissions will be different for each vegetable oil blend, depending on the original fuel components. Combustion chamber geometry and engine operating parameters also influence the hydrocarbon spectrum. When hydrocarbon emissions get into the atmosphere, they act as irritants odorants; a few are carcinogenic. The vegetable oil produce lesser hydrocarbon emissions compared to diesel fuel [20, 27, 42]. These reductions show a more complete combustion of the fuel takes place and thus Hydrocarbon level decreases considerably. An investigational work on a few compression ratio and injection timing for vegetable oil blended diesel shows that improved compression ratio reduced the Hydrocarbon emissions compared with ORG CR. The increased injection timing reduced the Hydrocarbon (HC) emissions compared to ORG IT.

9.5 Smoke Emission

Smoke emission of vegetable oil was greater than that of diesel oil. Preheating the vegetable oil result in lower smoke emission compared to unheated vegetable oil yet it is still higher than diesel [4]. For preheated vegetable oils blend the smoke emission's decrease with the preheating. The smoke density is high at higher loads due to more fuel being injected into the combustion Chamber resulting in incomplete combustion. Smoke emissions with vegetable oil are higher due to poor atomization, injection of larger droplets causing more over rich zones in combustion chamber.

10 Conclusions

Vegetable oils can be used to replace diesel oil, the main agricultural fuel, in diesel engines. They can be directly produced locally in a short supply chain and offer the extra fuel needed to increase agricultural production. They do not generate any extra amount of unwanted waste, indeed there by-products can be used in agriculture and livestock production [78].

(i) The brake thermal efficiency better with preheated vegetable oil as a fuel as compared to unheated vegetable oil as a fuel.
(ii) Thermal efficiency was lesser for unheated vegetable oil compared to preheated vegetable oil and diesel fuel. Thus far, preheating the blend increases the thermal efficiency.
(iii) The brake specific energy consumption with blends is lesser as compared to vegetable oil on account of improved atomize-blends resulted in lesser brake specific energy consumption. As discussed on the vegetable oil, these are the better option for the substitute of fuel for the diesel engine.
(iv) The carbon dioxide, carbon monoxide, hydrocarbon and smoke cloudiness were lesser for vegetable oil compared to that of diesel.
(v) The temperature of exhaust gas is lower with pre-heated vegetable oil as a fuel due to improved combustion.
(vi) CO (Carbon monoxide) emission is lesser with vegetable oil (unheated or pre heated) as compared to diesel.
(vii) Un-burnt HC (hydrocarbon) emissions are lesser with pre-heated vegetable oil as a fuel and higher with unheated vegetable oil as a fuel at full load as compared to diesel due to lower combustion temperature.
(viii) Nitrogen oxide emission is lower with vegetable oil on account of lower combustion temperature.
(ix) Smoke opacity is lower with pre-heated vegetable oil.

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Manufacturing of Biodiesel from Mahua (Madhuca Indica) Oil

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Abstract In recent years, increased environmental awareness and energy shortages have encouraged researchers to investigate the possibility of using alternate fuels which are environment friendly and renewable such as vegetable oils or animal fats instead of fossil fuels. Vegetable oils have considerable potential to be considered as appropriate alternative as they possess fuel properties similar to that of diesel oil. The major problem associated with direct use of vegetable oil is their high viscosity and gum content. One possible method to overcome the problem of high viscosity is the transesterification of potential vegetable oils to produce biodiesel (esters) of respective oils. This interest is because biodiesel is biodegradable, sulphur free, oxygenated and renewable alternative diesel fuel derived from vegetable oils or animal fats. In the present investigation, Mahua oil ester (biodiesel) was prepared from non-edible feedstock of Mahua raw oil. Raw Mahua oil as obtained from the market has very high value of FFA (free fatty acid) i.e. around 19%. Different samples of Mahua oil biodiesel were obtained through Transesterification process using Potassium Hydroxide (KOH) as a base catalyst, Sodium Hydroxide (NaOH) as a base catalyst and through a Two-Step Esterification & Transesterification process using Sulphuric Acid (H_2SO_4) and Potassium Hydroxide (KOH) as acid-base catalyst. Among the above three different methods/process, the process which reduces the FFA level to minimum was selected for further characterization and comparison of fuel properties were made for further use in C.I. Engines. In the investigation it was observed that the Two-Step Process of Esterification & Transesterification reduces the FFA level to 0.40% which was the least among other processes of transesterification which was having FFA level of 2.04% (using KOH) and 1.44% (using NaOH) respectively. The optimum process for reducing the FFA level to less than 1% was carried out with 0.33 v/v (methanol/Mahua oil) ratios and with 1.30% v/v (H_2SO_4/Mahua oil) ratios for acid catalyst in the first

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step. The above mixture of methanol and acid was mixed with preheated Mahua oil for about 1.30 h's reaction time and at 60 °C. After completion of the first step i.e. esterification process, the mixture was allowed to settle for 1–2 h. Methanol water and biodiesel layers were formed at the top and bottom respectively and the top layer of methanol water was removed. The bottom layer was collected and the second step i.e. Transesterification was carried out with 0.25 v/v (methanol/Mahua oil) ratio and 0.75% w/v KOH as base catalyst for 1 h at 60 °C. The produced mixture was kept for settling for about 24 h and after removing glycerol from the separated layers, pure biodiesel with 98.4% yield was obtained which was washed and dried later to get pure and clean biodiesel that was found to have properties comparable to Diesel.

1 Introduction

With the fast pacing world, fossil fuels and petroleum products will be exhausted and costlier to produce. Due to its excessive use, world is facing problems of Pollution and Global Warming. Among the conventional fuels, diesel fuel plays an important role in industrial economy of a country. It is being used in public transports like buses, locomotives, heavy trucks, generators, farming equipments, mining machineries, defense etc., so the demand for it is touching heights but due to excessive emissions from its combustion, it is being terminated in highly scaled polluted cities by the government. Therefore there is a need to prevent the world from this crisis by finding an alternative to diesel fuel which is environment friendly and renewable. Vegetable oils are among one of the alternatives existing to be used as a fuel in Diesel engines. India being essentially a net importer of edible vegetable oil, that's why it is essential that only non-edible vegetable oil sources which are locally available be used for production of biodiesel. Biodiesel production from non-edible sources like Karanja (*Pongamia Glabra*) [1], Pine (*Pinus Sylvestris*) [2] and Jatropha (*Jatropha Curcas*) [3] have already been studied. Mahua (Madhuca Indica) is also non-edible oil obtained from seeds of Mahua tree with 4 00,000 tons as an annual production in India [4].

Use of vegetable oils in diesel engine is associated with problems like high viscosity, higher free fatty acids, density and non-volatility. These problems affect pumping, atomization and combustion when used as a fuel in diesel engines. High viscosity is the main factor which leads to gumming, sticking and contamination problems. So to reduce the viscosity and FFA, several methods are used as; Direct use & blending (preheating), Micro emulsification, Thermal Cracking and Transesterification. The first two methods effectively reduce the viscosity but the chemical structure of the oil remains the same and affects the life of the engine on prolong use. Thermal cracking changes the chemical structure of the oil but it is costly and increases the ash content in the oil that creates the problem. Transesterification involves chemical change in the structure of oil by reaction of triglyceride molecule of raw vegetable oil with alcohol (methanol,

ethanol, propanol, or butanol) in presence of catalyst to form methyl or ethyl esters of oil (biodiesel) and glycerol as byproduct. Transesterification is the most preferred method among all methods as it is potentially less expensive way of transforming large branched molecular structure of bio-oils into smaller straight chain molecules of the type required as per specification in regular diesel combustion engines and are also found in literature [5–7]. Transesterification depends on alcohol and catalyst amount, reaction time, temperature and FFA content. For high FFA oil the conversion via transesterification is difficult and results in low yield and soap formation [8]. High FFA Mahua oil (19%) is processed using base catalyst with Two-Step pretreatment process to reduce FFA to less than 1% [5].

From the above facts, present investigation was undertaken at Birla Institute of Technology, Mesra, Ranchi (India) to find the best suitable method with least FFA content, reduced Viscosity and higher yield for biodiesel production and to determine its suitability when compared as a substitute for diesel.

2 Materials and Methods

2.1 Materials

Mahua oil was obtained from local oil industry i.e. R.K. Oil Products, Indore (M.P). The chemicals including methanol (Emplura Grade, 98%, Merck Millipore), sulfuric acid (Emplura Grade, 99%, Merck Millipore), sodium hydroxide (Emplura Grade, 98%, Merck Millipore), potassium hydroxide (Emplura Grade, 84%, Merck Millipore) and distilled water (Emplura Grade, Merck Millipore) were procured from chemical stores at Ranchi. The KOH and NaOH were used as base catalyst in Transesterification reaction.

2.2 Experimental Set-up

The Esterification and Transesterification were conducted in a conventional laboratory set up, which consisted of 500 milliliters and 2 L flat bottom flask (Borosil), a thermometer graduated up to 360 °C, a magnetic stirrer with hot plate (Remi—2 MLH) for constant stirring and heating of mixture in flask, a magnetic bead (Fisher Scientific) for mixing, a water cooled condenser (Riviera—750 ml) fitted on the neck of flask to prevent methanol evaporative loss, measuring cylinders and beakers (Borosil—10 ml, 25 ml, 50 ml, 500 ml, 1 L) for chemical addition and for taking samples. The flask with mixture was placed on a hot plate magnetic stirrer keeping constant temperature of 60 °C i.e. below boiling point of methanol and 1600 rpm speed for proper mixing controlled by regulator on it. After the reaction, a separating funnel for settling of mixture (Borosil—500 ml and 1 L), an air pump for bubble washing with wooden bubbler and a glass bottle (Borosil—4 L) for storing pure biodiesel is needed.

2.3 Methodology

The high FFA level (about 19%) of crude Mahua oil with a small quantity of moisture leads to a formation of soap and decrease the percentage yield during the transesterification reaction. Therefore, transesterification reaction was conducted in presence of both KOH and NaOH to see the effects and to obtain the biodiesel from it for comparison in terms of FFA level and yield. A Two-Step pretreatment process of esterification and transesterification was employed because of high FFA content of the oil and to reduce the probability of soap formation with higher yield compared to using base catalyst either KOH or NaOH. The two-step pretreatment process reduces the FFA to less than 1%. [5].

A. Transesterification (using KOH as catalyst)
   This process involves heating of 1000 ml Mahua oil to a temperature of 100–110 °C in a broad open beaker to remove moisture or water content present in the oil if any. Then the preheated oil was processed under transesterification (Base catalyzed) which was carried out with 0.70–0.75 v/v methanol-to-oil ratio in the presence of 4.0% w/v KOH as base catalyst in 1.5–2.0 h reaction time at a temperature of 60 °C. The KOH was present in form of pellets. After the completion of reaction, the mixture was allowed to settle down in separating funnel for about 24 h to obtain biodiesel and glycerol. The biodiesel obtained in the process is further washed with distilled water for 2–3 times for removal of excess methanol and catalyst and then it is heated above 100 °C to separate the moisture present in the biodiesel.
B. Transesterification (using NaOH as catalyst)
   This process involves heating of 1000 ml Mahua oil to a temperature of 100–110 °C in a broad open beaker to remove moisture or water content present in oil if any. Then the preheated oil was processed under transesterification (Base catalyzed) which was carried out with 0.25–0.30 v/v methanol-to-oil ratio in the presence of 1.0% w/v NaOH as base catalyst in 1.0–1.5 h reaction time at temperature of 60 °C. After the reaction, it was allowed to settle down in separating funnel for about 24 h to obtain biodiesel and glycerol. The glycerol obtained in this process is in the form of gel and NaOH takes more time to dissolve in methanol as compared to KOH. The biodiesel obtained in the process was further washed with distilled water for 2–3 times for removal of excess methanol and catalyst and then it is heated above 100 °C to separate the moisture present in the biodiesel.

C. Two-Step Pretreatment Process (using H_2SO_4 & KOH as catalyst)
This process involves heating of 1000 ml oil in an open beaker to a temperature of 100–110 °C to remove moisture or water content present in oil if any. The process was progressed in two steps and is known as Two-Step Pre-treatment Process. In the first step of esterification, preheated oil was processed with 0.33 v/v (methanol/Mahua oil) ratio in presence of 1.30% v/v (H_2SO_4/Mahua oil) ratio as an acid catalyst for 1.30 h reaction time at 60 °C in flat bottom flask. After the completion of reaction, the mixture was settled down in a separating funnel for 1–2 h and after that the methanol water mixture was separated from the top. In the second step of transesterification, the pre-treated oil (separated in bottom after settling in first step) was again processed with 25% methanol and 0.75% w/v KOH as base catalyst for 1 h reaction time at 60 °C reaction temperature. The produced mixture was kept for settling for about 24 h and after removing glycerol from the separated layers, pure biodiesel with 98.4% yield was obtained. The fuel properties of Mahua biodiesel produced were found to be comparable to those of diesel.

D. Settling Process
The prepared mixture after the reaction is transferred to separating funnel and allowed it to settle for about 24 h. After the settling process, one can visualize the layer of glycerin being separated at the bottom of funnel and biodiesel at the top. Glycerin layer was removed carefully and stored in a container which is a useful by-product of the transesterification reaction.

E. Washing
Biodiesel obtained from above methods are not suitable enough to run on engine because of impurities, so washing of biodiesel is a very necessary step. Bubble washing method is generally used to wash where the aquarium air pump with wooden bubbler is used to create bubbles in distilled water which is poured in biodiesel (1/2 the volume of biodiesel). The bubble collides with impurities and gets mixed with water which is removed later by separating funnel. The washing is done till the biodiesel obtained appears clear with no impurities and when it reaches 7 pH. Water removed after washing is stored in container as it can be used for cleaning purpose.

F. Heating
The washed biodiesel obtained is heated to 110 °C in an open beaker and maintain this temperature for about 10–15 min as shown in figure. This process eliminates the possibility of water particles in biodiesel. The process should be done with nonstop stirring and allow the biodiesel to cool slowly. Measure the biodiesel quantity and store in a clean and dry container. The biodiesel obtained after washing and drying results in yield of 97.6%.

Flowchart of Biodiesel Manufacturing

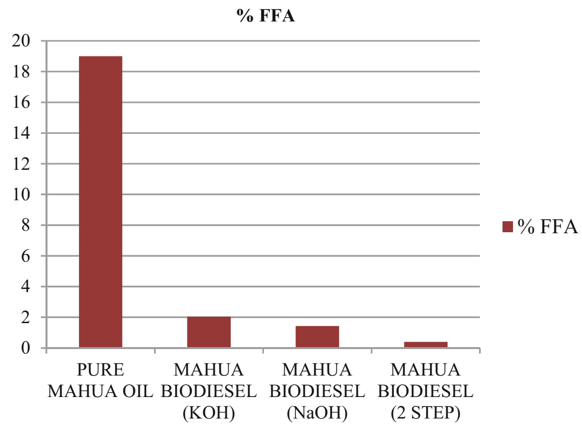
3 Results and Discussions

A. The following results were obtained in the production of Mahua biodiesel using KOH as base catalyst in transesterification process;
   FFA content of the biodiesel: 2.04%
   Yield of biodiesel: 84%
   The FFA content of the obtained biodiesel is significantly high and the yield is quite low.
B. The following results were obtained in the production of Mahua biodiesel using NaOH as base catalyst in transesterification process;
   FFA content of the biodiesel: 1.44%
   Yield of biodiesel: 89%
   The FFA content of the obtained biodiesel is still on the higher side and the yield is high.
C. The following results were obtained in the production of Mahua biodiesel using two step pretreatment processes with KOH as base catalyst and H_2SO_4 as acid catalyst in transesterification process;
   FFA content of the biodiesel: 0.40%
   Yield of biodiesel: 97.6%
   The FFA content of the obtained biodiesel is significantly low and the yield is quite high.

Thus two step pretreatment process of Transesterification is quite effective for production of Mahua biodiesel in terms of both FFA content as well as in terms of yield (Graphs 1 and 2).

The fuel properties of pure Mahua oil, Mahua biodiesel and diesel are summarized in Table 1. It can be observed that Mahua biodiesel obtained from this process had comparable fuel properties as that of diesel (Graphs 3, 4, and 5).

Graph 1 % FFA of pure mahua oil and biodiesel obtained from different processes



Graph 2 % Yield of biodiesel obtained from different processes

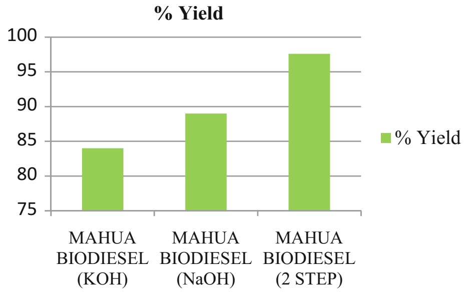
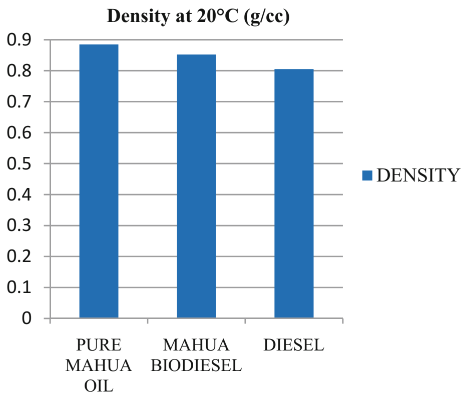


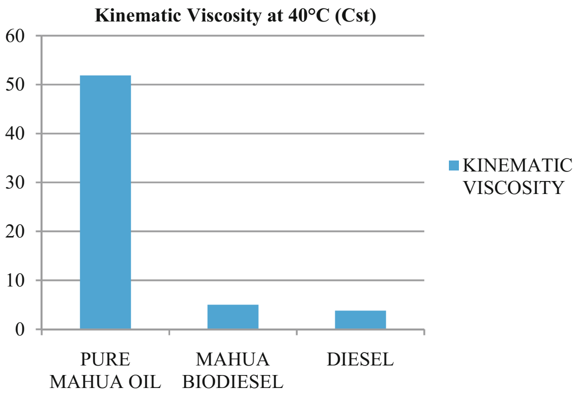
Table 1 Properties of pure mahua oil, mahua biodiesel and diesel

Property	Unit	Pure mahua oil	Mahua biodiesel	Diesel
Density at 20 °C	g/cc	0.885	0.852	0.805
Kinematic viscosity at 40 °C	Cst	51.850	5.032	3.805
Calorific value	MJ/Kg	38.62	40.20	42
Flash point	°C	360	280	68
Fire point	°C	368	287	73
Pour point	°C	13	8	−18
Cloud point	°C	12	6	−15
Free fatty acid	%	19	0.40	0.17

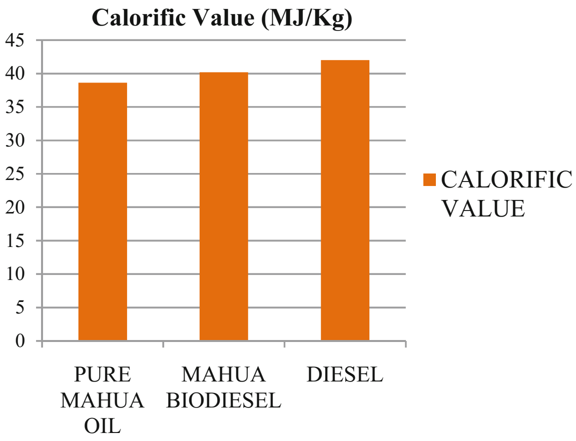
Graph 3 Density of pure mahua oil, mahua biodiesel and diesel at 20 °C



Graph 4 Kinematic viscosity of pure mahua oil, mahua biodiesel and diesel



Graph 5 Calorific value of pure mahua oil, mahua biodiesel and diesel



4 Conclusions

The success of Transesterification process is always reflected in terms of FFA content of the biodiesel obtained and the % yield of biodiesel. As evident, the two step pretreatment process of Transesterification is the most effective way to produce biodiesel. It is highly preferable especially if the feedstock oil used for biodiesel production has initially very high value of FFA content.

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Influence of Intake Air Pre-Heat on a Diesel Engine Operating on Ethanol in Dual Fuel Mode

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Abstract The lavish consumption of energy have not only resulted in global energy crisis but also aggravated the climatic conditions by the emissions of greenhouse gases and consequently global warming. The effects of global warming includes the rise of sea level, frequent wildfires, drought and floods. Internal combustion engines have also contributed significantly in the degradation of the environment. The researchers have therefore focussed on not only the development of alternative fuels, especially bio-fuels but also have shown interest in the domain of fuel-related techniques. Alcohol, especially ethanol which is renewable in nature and may be derived from crops is one of the promising alternative fuel. In the presented paper, the effects of intake air pre-heat on the performance and emissions of compression ignition engine operating on ethanol in dual fuel mode have been investigated. The improved vaporisation of ethanol due to increased intake air temperature evinces the slightly enhanced brake thermal efficiency. Moreover, preheating the intake air lowers carbon-mono-oxide and unburnt hydrocarbons, whereas, increases the oxides of nitrogen.

1 Introduction

Owing to their excellent drivability, high energy conversion efficiency and robustness, diesel engines are widely used in various sectors such as agriculture, transportation and industry. However, the depleting reserves of crude oil and their spirally increasing prices along with strict policy regulations on exhaust emissions motivates extensive research for the search for alternative fuels, with particular emphasis on the bio-fuels that possess the added advantage of being renewable fuels.

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Though various engine-related technologies [1] like common-rail systems, fuel injection control strategies, exhaust gas recirculation, exhaust gas after-treatment, etc. have been fostered, thus making headway for the development of cleaner diesel engines and addressing the challenges of deteriorating environmental conditions. However, the realm of fuel-related techniques, such as the use of renewable fuels in fumigated form has attracted increasing attention, thus necessitating only minor modification in the engine.

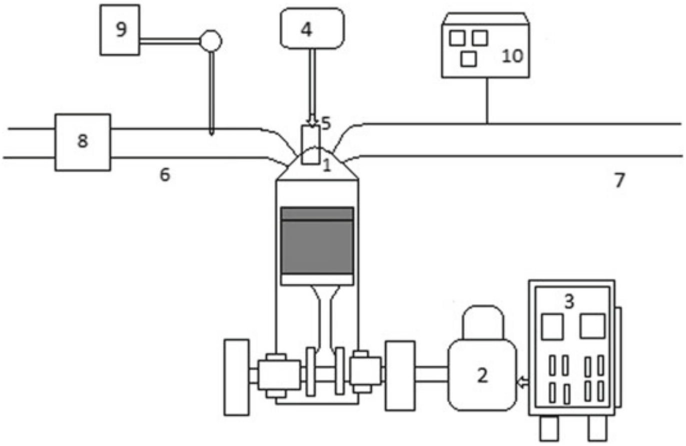
Ease of storage and handling and the abundance of alcohol producing resources are few positive aspects that render alcohol as most attractive alternative fuel [2, 3]. Among alcohols, lower alcohols viz., methanol and ethanol are distinguished as potential renewable fuels for automotive applications. Disadvantages such as, low calorific value and toxicity restrains the wide application of methanol as fuel. On the other hand, ethanol is a biomass based renewable fuel, which can be produced from a wide range of carbohydrate containing plants, such as sugar cane, sugar beets, sorghum, wheat, corn, barley and cassava, forestry product and grasses.

The utilisation of ethanol as an alternate fuel can enhance agricultural economies because it can be produced indigenously from many kinds of agricultural products and result in significant savings in carbon dioxide emissions. Solution, fumigation [4–7], dual injection, blending [8–11] and ignition improvement are the techniques to use ethanol in diesel engines in dual fuel mode. Limited miscibility of ethanol in diesel restricts the use of ethanol/diesel solutions to small percentages which otherwise offers the advantage of being easiest one among all the above-mentioned techniques of using ethanol in CI engines. Emulsions may accommodate larger percentages but the cost of the emulsifiers and the poor low temperature properties restricts its application. The introduction of ethanol at the engine-intake may permit large percentages of ethanol. Since ethanol have high vaporization energy requirements, one way to vaporize ethanol is to preheat intake air.

Alcohol fuels are significantly affected by intake air temperature and would affect engine performance and emissions. In the present study, ethanol at the flow rate of 2, 4 and 6 ml/min were investigated in a diesel engine at ambient (30 °C) and preheated (70 °C) intake air temperatures. It was shown that HC and CO emissions decreased with elevated intake air temperature as compared to ambient conditions. The diesel and ethanol flow rates of 2, 4 and 6 ml/min at ambient temperature of 30 °C are designated as E0T30, E2T30, E4T30 and E6T30, whereas, same flow rates of ethanol are represented by E2T70, E4T70 and E6T70 at intake air temperature of 70 °C in the following text. The engine load up to 1 kW is referred as low load, whereas loads greater than 1 and 3 kW respectively are termed as medium and high loads in the following text.

2 Experimental Set up

The experimental set-up used for investigation, as shown in Fig. 1, consists of a single cylinder, water-cooled, four-stroke stationary diesel engine (Kirloskar, AV1 model, rated power 3.7 kW at 1500 rpm) coupled to an AC alternator. The speed governor regulates the amount of diesel sprayed in the cylinder in accordance with the engine-load applied. The requisite quantity of ethanol is introduced at the intake. The temperature at principal points, viz., cooling water inlet and outlet, induction and exhaust manifold are noted with the help of K-type thermocouples. ARAI certified gas analyser and diesel smoke-meter, both of i3sys make are used to measure exhaust emissions. Gas analyser is used to measure NOx, CO and HC, whereas smoke meter is capable of measuring smoke opacity. The values of HC and NOx emissions are provided in ppm, whereas that of CO in % (by vol.). Intake air was preheated using an electric heater which was located at the air inlet. Preheated air was approximately 70 °C with a deviation of about 2 °C due to thermocouple precision, while ambient air was approximately 30 °C. The detailed technical specifications of the engine and gas analyser respectively, are given in Tables 1 and 2.



1. Engine 2 Alternator 3. Resistance load bank 4. Diesel fuel tank 5. Diesel fuel injector 6. Intake manifold 7. Exhaust manifold 8. Electric heater 9. Ethanol fuel tank and pump 10. Gas analyser

Fig. 1 Schematic diagram of experimental set up

Table 1 Specifications of diesel engine

Details	Specification
Model	Kirloskar-AV1
Type of engine	Vertical/single acting, 4 stroke, water cooled, totally enclosed, high speed compression ignition diesel engine
Rated power and speed	5.0 H.P. (3.7 kW) at 1500 RPM
Bore × stroke (mm)	80 × 110
Compression ratio	16.5:1
Cubic capacity	0.553 Litres
Type of governor	Mechanical centrifugal type
Fuel injection timing (degree)	23 °bTDC
Fuel injection pressure (bar)	200

Table 2 Specifications of exhaust gas analyser

Details	Specifications
Make	i3sys
Gases measured	CO, CO_2, O_2, HC & NOx
Principle	Non-dispersive infrared for CO,CO_2 & HC, electrochemical sensor for O_2 & NOx
Measuring range	CO: 0–15% vol, O_2: 0–25% vol, CO_2: 0–20% vol HC: 0–30,000 ppm,, NOx: 0-5000 ppm
Data resolution	CO, O_2, CO_2: 0.01%, HC & NOx: 1 ppm
Accuracy	±3% Relative, ±0.02% Absolute

3 Results and Discussions

3.1 Brake Thermal Efficiency (BTE)

Figure 2 shows brake thermal efficiency of pure-diesel and various ethanol flow rates in dual fuel mode at ambient and increased intake air temperatures. In case of preheated air, improvement in the BTE was evident almost for all the ethanol flow rates due to better vaporization as compared to those evaluated at ambient temperature. For different ethanol flow rates, BTE increases up to maximum of 3.7, 2.2 and 1.3%, respectively at low, medium and high loads for intake air temperature of 70 °C when compared to corresponding ethanol flow rate at 30 °C.

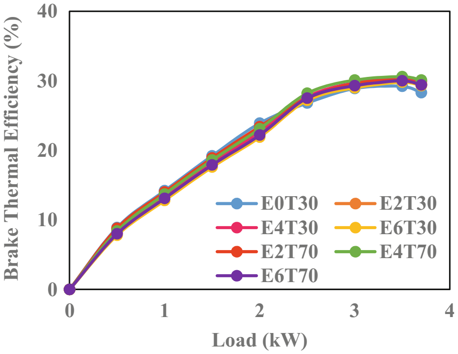


Fig. 2 Variation of brake thermal efficiency with load, ethanol flow rate and intake air temperature

3.2 *Exhaust Gas Temperature (EGT)*

It is seen in Fig. 3, that exhaust gas temperature increases as the load increases. At part load, exhaust gas temperature for preheated air case was found to be sufficiently higher than its corresponding value for all ethanol rates when intake-air is at 30 °C. At full load, slight change in exhaust temperature was observed. Also, the exhaust gas temperature increases as ethanol flow rate increases at high loads. Ethanol, being oxygenated fuel may result into the improved combustion and consequently, higher heat release rate thus resulting higher exhaust gas temperature with the substitution of ethanol. Slight improvement in EGT with pre-heat of intake air is probably due to better vaporization of ethanol fuel leading to improved mixing of air-ethanol vapour with diesel.

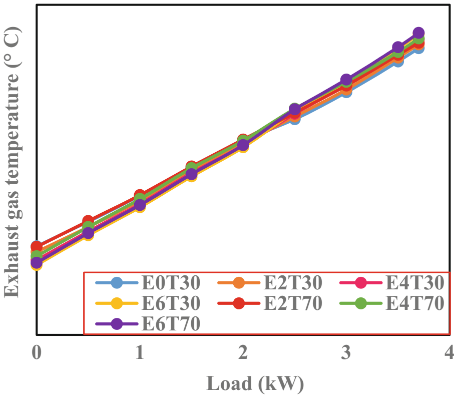


Fig. 3 Variation of exhaust gas temperature with load, ethanol flow rate and intake air temperature

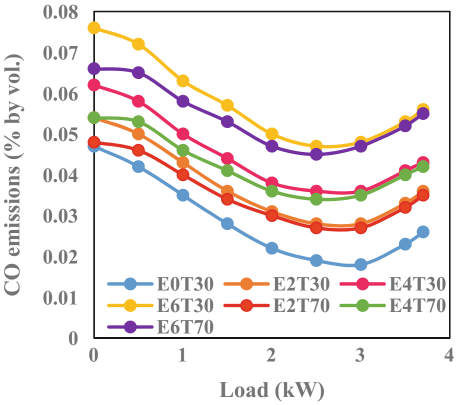


Fig. 4 Variation of CO emissions with load, ethanol flow rate and intake air temperature

3.3 Carbon Monoxide (CO) Emissions

CO emissions decrease as the load increases as shown in Fig. 4. However, at high loads, large amount of diesel fuel injected may lead to poor mixing thus increasing CO emissions moderately. For different ethanol flow rates, CO decreases up to maximum of 13.2, 7 and 3.6%, respectively at low, medium and high loads for intake air temperature of 70 °C when compared to corresponding ethanol flow rate at 30 °C. As indicated in the figure, increasing ethanol content in dual fuel mode increases CO emission as compared to pure diesel case. The charge cooling due to higher latent heat of vaporization increases CO emissions. Moreover, lower cetane number of ethanol and consequently increased ignition delay inhibits combustion, thus increasing CO emission. At elevated air intake temperature, CO emission reduces for various ethanol flow rates as compared to those in case of intake air temperature of 30 °C. Overall, preheating air, increasing engine load (except at higher loads) and decreasing ethanol flow rates indicate lower CO emissions. The improved vaporization due to preheating and thus enhanced combustion reduces CO emissions.

3.4 Oxides of Nitrogen (NOx) Emissions

As the ethanol concentration increases, various ethanol flow rates result in lower NOx emissions as shown in Fig. 5. It is apparent that the high latent heat of vaporization may induce cooling in the combustible mixture thus reducing NOx emissions. Maximum increment of 9.6, 6 and 3.1% in NOx emissions were observed at low, medium and high loads respectively for E2T70, E4T70 and E6T70 in comparison with corresponding ethanol flow rates at intake air temperature of 30 °C. Thus, preheating intake air augments the combustion temperature as well as NOx emissions. Also, at full load, insignificant difference in NOx is evident. This is

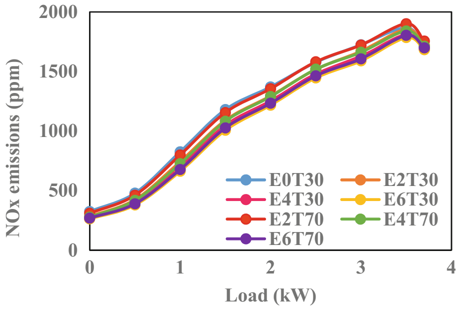


Fig. 5 Variation of NOx emissions with load, ethanol flow rate and intake air temperature

due to the fact the cooling effect of alcohols is less pronounced and heat release rate enhances at higher loads.

3.5 Hydrocarbon (HC) Emissions

As shown in Fig. 6, unburned HC emissions that increases with increasing ethanol concentration are observed to decrease with the preheating of air. Maximum decrement of 24.8, 13.7 and 7% in HC emissions were observed at low, medium and high loads respectively for E2T70, E4T70 and E6T70 in comparison with corresponding ethanol flow rates at intake air temperature of 30 °C. It is explained by the fact that HC is product of incomplete combustion and induction of ethanol in intake reduces the combustion temperature which leads to incomplete combustion and higher HC emission. But, the quenching of charge is outweighed by preheating air and thus, the ignition delay is shortened and more complete combustion occurs with less HC emission.

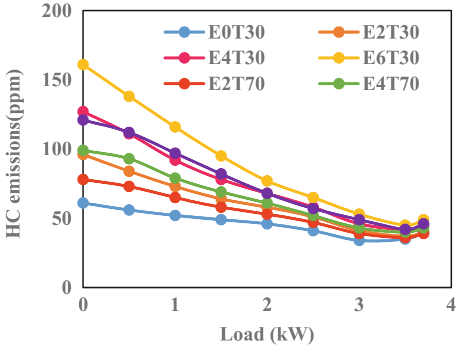


Fig. 6 Variation of HC emissions with load, ethanol flow rate and intake air temperature

4 Conclusions

It was demonstrated in this investigation that elevated intake air temperature affects utilization of ethanol in compression ignition engines. Brake thermal efficiency and exhaust gas temperature increased by increasing intake air temperature due to better vaporization and in-cylinder combustion. As a consequence of enhanced combustion due to intake air preheat, reduction in CO and HC emissions whereas increase in NOx emission was noticed.

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Experimental Investigation of the Performance and Emission Parameters of Stationary CI Engine Using Methyl Esters of Karanja and Fumigated Ethanol

D.K. Jamuwa, D. Sharma, S.L. Soni and Amit Sharma

Abstract The scarce and rapidly depleting conventional petroleum resources have alarmed the researchers around the globe, for the search of the alternate fuel, which not only possess the advantage of availability in abundance but also check the menace of environmental degradation and climate change, to a considerable extent. Among various possible options, bio-diesel and alcohols, especially lower alcohols not only reduce diesel fuel requirements and environmental pollution but strengthen agricultural economy and provide rural employment. Methyl esters of vegetable oils, which possesses improved properties viz., reduced viscosity and free fatty acid content, mitigate exhaust emissions and offers to strengthen India's energy security and lessen reliance on oil imports. Lower alcohol, such as ethanol is also a renewable fuel and can be obtained from perennial sources viz., plants and livestocks and thus help to achieve energy security and sustainability. Among the most common techniques for using alcohol in dual fuel mode, fumigation is the simplest and inexpensive as it requires no modification in the engine. In the present research, performance and emission characteristics of single cylinder, four stroke, constant speed, water cooled, direct injection CI engine using methyl esters of Karanja and ethanol fumigation are investigated.

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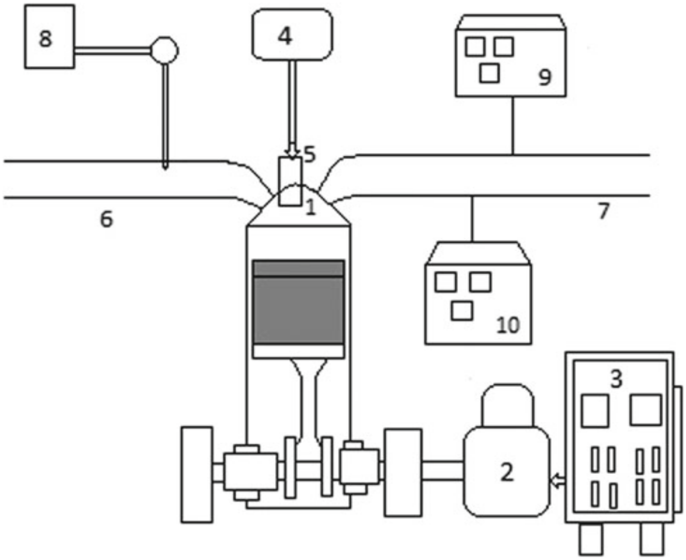
1 Introduction

Scientists have expressed concerns that global temperatures will continue to rise for decades to come, largely due to greenhouse gases produced by human activities. The rise of urbanism laden with lavish lifestyle has brought not only energy crisis across the globe but a concomitant risk of global warming. Moreover, the indiscriminate exploitation of crude-petroleum has brought their reserves to extinction. The effect of rising temperatures includes the melting of glaciers and sea ice, shifting precipitation patterns and shift of animal ranges. In the coming decades, storm surges and high tides could combine with sea level rise and may cause large scale devastation.

Alternative fuels, especially renewable ones [1–3] can play a significant role not only in strengthening India's energy security and reducing reliance on oil imports but also in lowering greenhouse gases' emissions and enhancing the prospects of rural employment as well as agrarian-economy thus achieving the objective of sustainability. Among the renewable fuels, considerable work has been undertaken in the domain of bio-diesel in recent years. Biodiesel [4–8] or straight vegetable oils cannot be used directly in internal combustion engine due to its high viscosity. Higher viscosity of vegetable oils as compared to that of diesel fuel can cause problem in fuel handling, pumping, atomization and fuel jet penetration. Transesterification [2] of oil with alcohol reduces the viscosity and other properties which have been evaluated to be comparable those of diesel. Certain characteristics of vegetable oil like safe storage and transportation due to higher flash point or ignition temperature and its less knocking tendency due to good cetane number render safe operation of CI engines. The success of the use of vegetable oil faces several challenges such as economic feasibility in absence of subsidies, utilization of cultivable wasteland and identification of the potential markets to facilitate its availability. Among alcohols, which are also known as renewable fuels, the lower alcohols, viz., methanol and ethanol [9–12] are considered for automotive application. Methanol has certain disadvantages, such as its low calorific value and toxic effects. Ethanol is a biomass based renewable fuel that can be produced by alcoholic fermentation of sugar from vegetable materials, such as corn, sugar cane, sugar beets, barley, sweet sorghum, cassava, molasses etc. The objective of this paper is to investigate the optimum blend of methyl esters of Karanja oil, K20 with fumigated ethanol in dual fuel mode and to compare the various performance and exhaust emission parameters with that of pure diesel case. In the present work, methyl esters of Karanja oil were prepared by single stage esterification process using sulphuric acid and methanol. The product thus obtained from this stage was subjected to base transesterification to produce biodiesel. High content of free fatty acid (FFA) in Karanja oil was reduced from 9.4 mg KOH/g to 0.14 mg KOH/g by two stage esterification process. When compared to the different blends of Karanja bio-diesel, K20 recorded higher brake thermal efficiency and lower emissions. Pure diesel and Karanja oil (20% vol by vol) is designated as D100 and K20, whereas, ethanol flow rates of 2 ml/min and 4 ml/min in dual fuel mode with K20 are denoted by K20E2 and K20E4 in the following text. The loads ranging from zero to 1, 1.5 kW to 2.5 kW and 3 to 3.7 kW respectively are referred as low, medium and high loads in the entire manuscript.

2 Experimental Set Up

A single cylinder, water-cooled, four-stroke stationary diesel engine (AV1 model of Kirloskar with rated power 3.7 kW at 1500 rpm) coupled to an AC alternator, as shown in Fig. 1 has been selected for the investigation. The engine used in the present study was a constant speed engine and speed governor adjusted the quantity of diesel or bio-diesel injected to keep the engine speed constant at different load conditions. The quantity of diesel/bio-diesel injected to the engine varied with load and ethanol at constant rate is fed at the intake. K type thermocouples and multi-channel digital temperature indicators (not shown in figure) are used to measure and display the temperature at the salient points of the test rig viz., inlet and outlet of the cooling water; exhaust gas and intake air. ARAI certified 5 gas analyser of make i3sys is used to analyze NO_x, CO and HC. The values of HC and NO_x emissions are provided in ppm, whereas that of CO in % (by vol.). Smoke in exhaust is measured in Hartridge Smoke unit (in %) with the help of ARAI certified smoke meter of i3sys make.



1. Engine 2 Alternator 3. Resistance load bank 4. Diesel fuel tank 5. Diesel fuel injector 6. Intake manifold 7. Exhaust manifold 8. Ethanol fuel tank and pump 9. Gas analyser 10. Smoke meter

Fig. 1 Schematic diagram of experimental set up

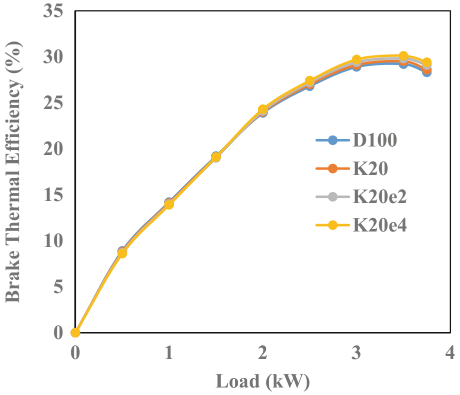


Fig. 2 Variation of brake thermal efficiency with load for different test fuels

3 Results and Discussions

3.1 *Brake Thermal Efficiency*

Diesel or biodiesel is injected into the engine cylinder directly through the fuel injector, while a mixture of ethanol and air is introduced through engine-intake. It was observed that BTE of engine increased with increasing engine load, which is due to increased fuel quantities and thus enhanced energy release. Figure 2 portrays the variation of brake thermal efficiency with engine-load for all the tested fuels. BTE was observed to be almost similar for K20 and pure diesel at all loads. For blending higher than 20%, BTE decreased with increased percentage of biodiesel in the test blend. For K20e2 and K20e4, BTE decreased by 2.2 and 3.4% at low loads, whereas it increased 2.8 and 3.9% at high loads, as compared to that in case of D100. When the engine is operating with constant flow rate of ethanol at low engine load, the fumigated ethanol and the intake air form a mixture which might be too lean to support combustion, resulting in deterioration in the combustion efficiency. At medium to high engine loads, the mixture will be rich enough to support combustion, resulting in better combustion because the mixture burns in the premixed mode.

3.2 *Exhaust Gas Temperature*

From Fig. 3, it can be observed that the exhaust gas temperature increased with increasing load for all test fuels under investigation. Insignificant change or slight decrease in exhaust gas temperature was evidenced at low loads. At full load, the exhaust gas temperature is found to be 521, 535, 546 and 551 °C, respectively, for

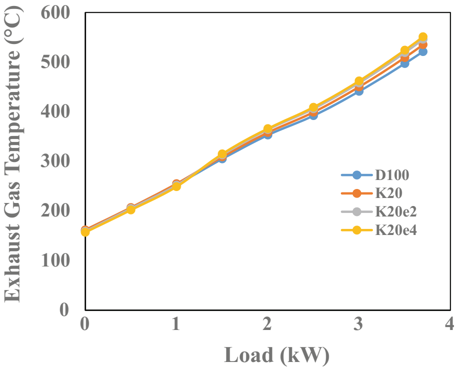


Fig. 3 Variation of exhaust gas temperature with load for different test fuels

D100, K20, K20e2 and K20e4. The higher exhaust gas temperature at higher loads is attributed to greater number of oxygen molecules due to addition of Karanja oil and/or ethanol thus resulting into improved combustion.

3.3 NO_x Emissions

The important factors that affect the formation of NO_x in CI engines are combustion temperature, availability of oxygen and its residence time. NO_x increased slightly, ranging from 1.9% at low loads to 4.8% at high loads with K20 as compared to D100. For K20e2 and K20e4, NO_x emissions decreased by 12 and 18% at low loads, whereas it increased 5.9 and 6.2% at high loads, as compared to pure diesel case. Due to high latent heat of vaporisation of ethanol, the cooling of combustion charge may take place, which decreases NO_x values, particularly at low loads, as noticed in Fig. 4. But, at high loads, the increased heat released rate predominates the quenching factor thus increasing NO_x emissions.

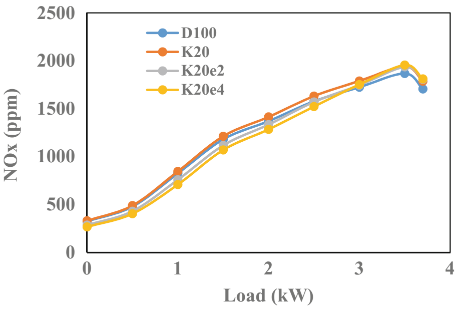


Fig. 4 Variation of NO_x emissions with load for different test fuels

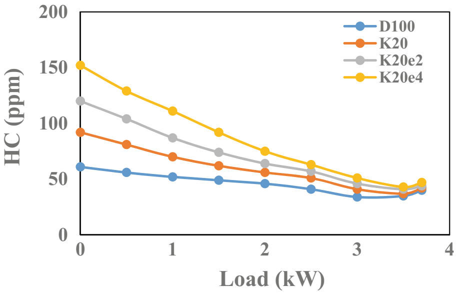


Fig. 5 Variation of HC emissions with load for different test fuels

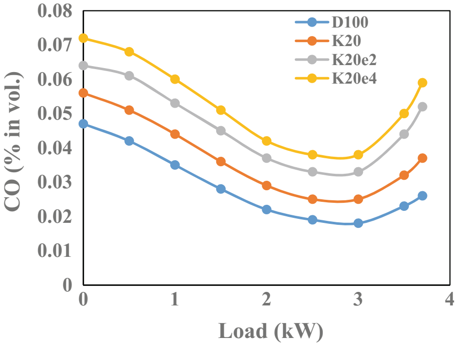
3.4 HC Emissions

Hydrocarbon emissions were determined with the help of exhaust analyser in parts per million (ppm). HC emission were relatively higher at lower engine loads and decreased with increasing engine loads for all test fuels. Overleaning of fuel injected during the delay period and the overfuelling condition resulting into the under-mixing with air are the two major causes of HC emissions in diesel engine under normal operating conditions. At low engine loads, poor availability of air leads to deteriorated combustion resulting in higher HC emissions, as evident in Fig. 5. However, with increasing load, HC emission reduced drastically due to improved atomization and availability of sufficient air. As compared to D100, maximum increase in HC emissions of 50.8, 96.7 and 149.2% at low loads, 26.5, 51 and 87.8% at mid loads and 20.6, 35.3 and 50% at high loads for K20, K20e2 and K20e4 respectively were observed.

3.5 CO Emissions

The presence of fuel-rich zones in the combustion chamber and lower combustion temperature at low engine load may result into higher CO emissions. It is observed from Fig. 6, that CO emissions decreases with increasing load, because at higher loads improved mixing and higher temperature and pressure conditions enhances combustion. But at loads ranging from about 80% of rated load to the full load, CO emission increases further which is attributed to the reduced availability of air at higher loads. CO emissions increased by 25.7, 51.4 and 71.4% at low loads, 31.6, 73.7 and 100% at mid loads and 42.3, 100 and 126.9% at high loads for K20, K20e2 and K20e4 respectively as compared to that in case of D100.

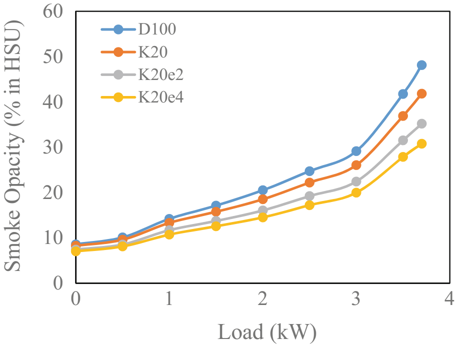
Fig. 6 Variation of CO emissions with load for different test fuels



3.6 Smoke Opacity

As shown in Fig. 7, it can be observed that smoke opacity increases with the increase of engine-load, for all the tested fuels. Fuel quantity increases with increasing engine load thus resulting in higher smoke opacity. It is an indication of presence of unburnt soot particles generated from fuel pyrolysis in the engine exhaust. It is evident that K20 produces less smoke compared to pure diesel for same load conditions. Lower soot formation and carbon residue for methyl-ester blends as compared to pure diesel causes reduced smoke density. Smoke opacity further reduced with increasing ethanol content for the entire load range. As compared to D100, maximum reduction in smoke opacity of 6.3, 17.6 and 24.5% at low loads, 10.2, 22.2 and 30.3% at mid loads and 13.1, 26.9 and 36.1% at high loads for K20, K20e2 and K20e4 respectively were observed.

Fig. 7 Variation of smoke opacity with load for different test fuels



4 Conclusions

The present work investigates the performance and exhaust-emission in single cylinder, water-cooled, four-stroke stationary diesel engine K20 with fumigated ethanol in dual fuel mode and to compare the various performance and exhaust emission parameters with that of pure diesel case. BTE increased up to 3.9% at high loads with K20 and ethanol fumigation, as compared to pure diesel case, but decreased at low loads. NO_x emissions decreased up to 18% at low load and increased up to 9.4% at high load conditions, respectively, as compared to pure diesel operation. As compared to baseline diesel case, maximum increase in HC and CO emissions of 149.2% and 71.4% at low loads whereas increase up to 50% and 126.9% at high loads for K20, K20e2 and K20e4 respectively were observed. Smoke opacity decreased significantly at all loads for Karanj-biodiesel and ethanol fumigation.

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Biogas Quality Upgradation Using *Musa bulbasiana*: A Study on Domestic Biogas Plant

Pinak Pani Baruah, Plaban Bora and Dhanapati Deka

Abstract This study highlights an alternative route of biogas quality upgradation by absorption of CO_2 using *Musa bulbasiana* stem (an agrowaste). The variations in percentage of CO_2 absorption were investigated for different concentrations of ash (produced from *Musa bulbasiana* stem) in water and for different scrubber bed heights. Experimental results showed reduction in CO_2 up to 20% from biogas, which also contributed to subsequent improvement in fuel quality with the increase in gross calorific value (GCV) of the gas. The activity period of the absorbents present in ash was also theoretically determined as 19 days (approx.). This approach of CO_2 absorption from biogas using waste banana stem may be an economically favourable and attractive option with regards to domestic biogas production plants.

Abbreviations

GCV	Gross calorific value
CO_2	Carbon dioxide
H_2S	Hydrogen sulphide
K	Potassium
Ca	Calcium
Na	Sodium
KOH	Potasium hydroxide
$Ca(OH)_2$	Calcium hydroxide
NH_3	Ammonia

These authors contributed equally in designing, conducting experimental work and writing the manuscript.

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NaOH	Sodium hydroxide
MEA	Mono-ethanolamine
MMTPA	Million metric ton per annum
$\mathbf{l}_{\mathrm{CO2}}$	Amont of CO_2 passing through the scrubber per day
v	Gas flow rate in the scrubber
x	Percentage of CO_2 absorbed
t	Daily hours of cooking
D	Activity period (in days) of the absorbents

1 Introduction

Biogas exhibits incredible potential as gaseous biofuel and can substantially meet conventional fossil fuel demand. In terms of process economics and energy conservation, production of biogas by anaerobic digestion of organic material is one of the most beneficial options. Utilization of biogas can contribute to waste management and reduction of greenhouse gas emission [1–8]. The feedstock for biogas production mainly includes waste, energy crops, or landfill sites.

Biogas usually contains 45–70% of methane (CH_4) and 30–45% of carbon dioxide (CO_2) [8]. Trace amounts of hydrogen sulphide (H_2S), ammonia (NH_3), hydrogen, nitrogen, saturated or halogenated carbohydrates and oxygen are also present in biogas depending on the nature of feedstock. Biogas is saturated with water vapour and may also contain dust particles and organic silicon compounds (e.g.: siloxanes) [1–8].

Biogas exhibits high gross calorific value (15–30 MJ/Nm^3). The fuel quality such as gross calorific value of biogas mainly depends on the percentage of CH_4. However, the major demerit of biogas is that its second largest constituent carbon dioxide (CO_2) does not have any contribution to heating value. The gross calorific value of biogas containing 65% methane and 35% CO_2 was 6.5 kWh/nm^3 and that of natural gas containing 91% methane was 10.89 kWh/nm^3 [9]. Moreover, the flame speed was 25 cm/s for biogas as against 38 cm/s for LPG. Presence of incombustible gases such as CO_2, H_2S and water vapor unnecessarily increases the volume of the plant and make the biogas uneconomical to compress and transport, besides reducing calorific value, flame velocity and flammability range [1–8].

There are various methods to reduce the quantity of CO_2 in biogas, namely: water scrubbing, polyethylene glycol scrubbing, carbon molecular sieves, membrane separation, high pressure gas separation, gas-liquid absorption membranes etc. [1–6]. However, these methods involving high cost are suitable for industrial scale production and become very expensive in the case of domestic level production.

On the contrary, alkaline solutions such as potassium hydroxide (KOH), sodium hydroxide (NaOH), calcium hydroxide ($Ca(OH)_2$) and mono-ethanolamine (MEA) were found to be very good absorbents of CO_2 [8]. Significant amount of potassium (K), calcium (Ca) and sodium (Na) is also present in different plant species such as banana, potato, beets etc. [4]. Previous studies also confirmed the presence of 9.4–33.4% of K and 7.5–32.3% of Ca (on dry ash basis) in different morphological parts of banana plants e.g. pseudostems, petioles/mid rib, leaf blade, floral stalk, leaf sheaths and rachis [10–13], from which respective alkaline solutions (KOH and $Ca(OH)_2$) may be prepared. India, being the largest producer of banana in the world with a production capacity of 29.8 MMTPA (million metric tons per annum), banana stems (often called pseudostem) are generally discarded as a postharvest measure [14]. However, these enormous quanta of agro-waste generated from banana stem contribute to environmental pollution. Therefore, exploration of newer processes involving efficient utilization of these agro-wastes would undeniably serve as an incremental step for material and energy recovery, besides contributing to environmental upgradation and partially towards alleviating global warming via waste management [14].

This study deals with absorption of CO_2 from biogas using the ash of *Musa bulbasiana* (banana tree species locally known as 'Bheem Kol') stem. The idea behind the present investigation was also drawn from a popular Assamese food item named '*kolakhar*' which is prepared from the ash of banana peels. The peels are first burnt followed by the mixing of ash with water. This mixture is very alkaline in nature and used as an alternative for salt.

2 Materials and Methods

2.1 Feedstock Selection and Preparation

In our investigation stems were extracted from the *Musa bulbasiana* plants collected from Napaam, Tezpur, India (Sampling point/Co-ordinates 26° 42′ 19″N to 92° 50′ 21″E). Gas was collected from a domestic fixed dome type biogas plant of 2 m^3 over a period of seven days.

The extracted stems were cut down into small pieces followed by drying under sunlight for one week and removal of mud attached to them. The pieces were then burnt and the produced ash had been collected. Different steps of scrubbing material preparation are presented in Fig. 1.

2.2 Scrubber Design

2.2.1 Packing Material Selection

Small pebbles were used as packing material as it can provide relatively a greater pressure drop in a small volume.

Fig. 1 Different stages of scrubbing material preparation

2.2.2 Gas Flow Rate

Absorption of gas depends on the pressure drop, gas flow rate and packing density of the scrubber. The gas for the present investigation was collected from a fixed dome type plant where the gas flow rate varies proportionately with temperature. Thus, the gas flow rate in summer is generally greater than in winter. This variation of gas flow rate greatly influences the scrubbing process and hence a design that will suit both in summer as well as in winter is required. To measure the gas flow rate (in m/s) an anemometer was used. Each of the reading (m/s) was then multiplied by the cross-section area of the pipe to obtain the gas flow rate. The minimum gas flow rates of both summer and winter were used as the main design parameter of the scrubber. The optimum height of the scrubber for which the outlet gas flow rate equals the minimum required gas flow rate in the burner was estimated by using three model scrubbers of same cross-section area (with diameter of 12 cm) and varying bed heights (b.h.): 20, 30, 40 and 50 cm.

2.3 Collection of Biogas

Gas was collected from a domestic biogas plant of 2 m^3 sizes over a period of seven days and the initial CO_2 percentage was measured in the Orsat Analyzer (Apex Instruments VSC-33). Owing to the difficulties in onsite characterization of the biogas, the gas was collected in two bags made out of circular rubber tubes used in car wheels (Fig. 2). A gate (on-off) valve was also attached with the bag for controlling the gas flow rate.

Fig. 2 Biogas collection in rubber tubes

2.4 Absorption of CO_2

The gas bag was connected to the scrubber containing different quantity of ash mixed in 1000 ml water. The outlet of the scrubber was connected to the other gas collecting bag (empty). The gas was forced inside by applying weight over the bag connected to the inlet of the scrubber. For removing the preoccupied air remained inside the scrubber, some amount of gas was allowed to leave the outlet before connecting with the second bag (empty). After mixing the gas for few minutes' final percentage of CO_2 was measured. The amount of ash for which the absorption percentage was highest, had been selected for further experiments.

The outlet pipe was not inserted inside the cylinder and the gap of around 4 cm was provided between the pebble bed and the top so that the scrubbing material does not flow out through the outlet pipe. The graphical representation of the arrangement used for biogas purification is presented in Fig. 3.

2.5 Measurement of CO_2 Percentage at the Scrubber Inlet and Outlet

The percentage of CO_2 at the inlet and the outlet of the scrubber were also measured using an Orsat Analyzer (Apex Instruments VSC-33). A solution of 400 gm/1000 ml solution of KOH was used in the Orsat Analyzer to absorb the CO_2 from a sample of 100 ml biogas.

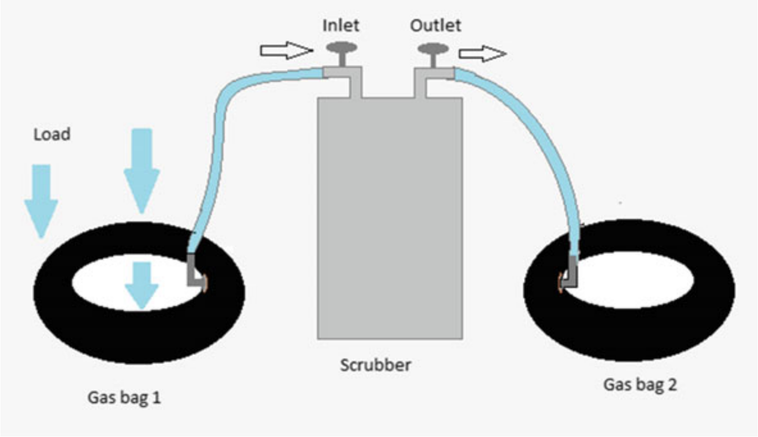


Fig. 3 Graphical representation of the biogas purification process

2.6 *Measurement of Gross Calorific Value*

The gross calorific value (GCV) of the scrubbed biogas was measured using a Junker's Gas Calorimeter.

2.7 *Theoretical Validation of Absorbing Material*

The activity period for the absorbents is also estimated (theoretically) as follows:

Theoretically, one moles of K reacts with one moles of water to give one mole of KOH (1). Similarly one mole of Ca reacts with two moles of water to give one mole of $Ca(OH)_2$ (2).

$$K(s) + H_2O(l) \rightarrow KOH(l) + 1/2H_2(g) \tag{1}$$

$$Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(l) + H_2(g) \tag{2}$$

The quantity of main absorbents K and Ca present in the dry ash sample are assumed as 33.4 and 7.5%, respectively, based on previous studies [11–13]. Therefore, the amount of ash containing one mole of K would be 116.77 gm (=39/0.334 gm) and one mole of Ca would be 533.33 gm (=40/.075). This means, the amount of ash required to form a 1 N solution of KOH and $Ca(OH)_2$ in 1000 ml water would be 116.77 and 533.33 gm, respectively (assuming 100% conversion).

This means, 'm' gram of ash in 1000 ml solution produces a solution with normality $= m\left(\frac{1}{116.77} + \frac{1}{533.33}\right)$ N. In the absorption process, KOH and $Ca(OH)_2$ first absorb CO_2 to form K_2CO_3 and $CaCO_3$, respectively, according to (3) and (4).

$$2\mathrm{KOH} + \mathrm{CO_2} \rightarrow \mathrm{K_2CO_3} + \mathrm{H_2O} \tag{3}$$

$$\mathrm{Ca(OH)_2} + \mathrm{CO_2} \rightarrow \mathrm{CaCO_3} + \mathrm{H_2O} \tag{4}$$

K_2CO_3 and $CaCO_3$ further absorb CO_2 to form their bicarbonates (5) and (6), although these reactions proceeds with much slower rates.

$$\mathrm{K_2CO_3} + \mathrm{H_2O} + \mathrm{CO_2} \rightarrow 2\mathrm{KHCO_3} \tag{5}$$

$$\mathrm{CaCO_3} + \mathrm{H_2O} + \mathrm{CO_2} \rightarrow \mathrm{Ca(HCO_3)_2} \tag{6}$$

Combining (3)–(6), we obtain (7) and (8), respectively.

$$2\mathrm{KOH} + 2\mathrm{CO_2} \rightarrow 2\mathrm{KHCO_3} \tag{7}$$

$$\mathrm{Ca(OH)_2} + 2\mathrm{CO_2} \rightarrow \mathrm{Ca(HCO_3)_2} \tag{8}$$

Therefore, 1 mol of KOH is equivalent to 1 mol of CO_2, i.e. a solution of 1 N KOH absorbs 22.4 L of CO_2. Similarly, 1 mol of $Ca(OH)_2$ is equivalent to 2 mol of CO_2, i.e. a solution of 1 N $Ca(OH)_2$ absorbs 44.8 L of CO_2. Therefore, if 'm' gram is the amount of ash used in 1000 ml water for the process then the amount of CO_2 absorbed in liters will be,

$$\begin{aligned} \mathrm{l} &= \mathrm{m}\left(\frac{22.4}{116.77} + \frac{44.8}{533.33}\right) \\ = &> \mathrm{l} = 0.2758\mathrm{m} \end{aligned} \tag{9}$$

However 'l' greatly depends on the solubility of K and Ca in water.

Generally, biogas contains approximately 40% of CO_2, Assuming the gas flow rate to be 'v' l/hr and the daily hours of cooking to be 't' hr, the amount of CO_2 passing through the scrubber per day is,

$$\mathrm{l_{CO2}} = \mathrm{v} \times \mathrm{t} \times 0.4\ \mathrm{l/day} \tag{10}$$

If '*x*' is the percentage of CO_2 absorbed by the scrubber, then the amount of CO_2 absorbed per day is,

$$= \mathrm{v} \times \mathrm{t} \times 0.4 \times x\ \mathrm{l/day} \tag{11}$$

Therefore, total number of days for which the absorbents of amount 'm' remain active is,

$$\mathrm{D} = \frac{0.2758\mathrm{m}}{\mathrm{v} \times \mathrm{t} \times 0.4 \times \mathrm{x}} \tag{12}$$

3 Results and Discussions

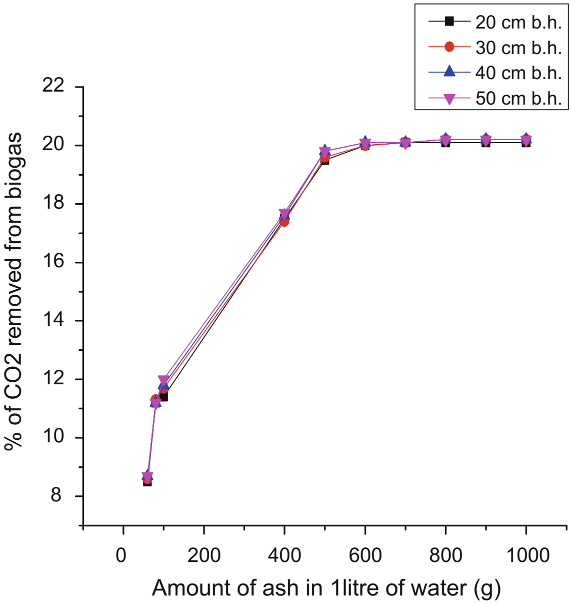
3.1 Gas Flow Rate

Gas flow rate for the summer was very high in comparison to the gas flow rate during winter. The gas flow rate measured for 2–3 cooking hours without connecting the burner was in the range 137.64–231.14 cm^3/s in the month of June (summer) and 75.66–125.73 cm^3/s in the month of January (winter).

3.2 Optimization of Absorbing Material (Ash)

The optimum CO_2 absorption was observed for a mixture of varying concentration of ash in 1 l of water and is presented in Fig. 4. The investigation was carried out for the scrubbers with bed heights of 20, 30, 40 and 50 cm and the inlet flow rate was maintained at 175.11 cm^3/s. The amount of CO_2 removed from the biogas increased with the increasing concentration of ash in water and it attained a maximum value (around 20%) at 600 gm ash/1 l of water. However, no momentous variations were observed for further increase in ash concentration for the scrubbers with different bed heights. Therefore, the remaining investigations were carried out for a mixture of 600 gm of ash in 1 l of water.

Fig. 4 Percentage of CO_2 absorption at various concentrations of ash in water



3.3 Absorption of CO_2 from Biogas at Different Gas Flow Rates

The percentage of CO_2 removed from the biogas was studied by varying the inlet gas flow as well as for different scrubber bed heights namely 20, 30, 40 and 50 cm and presented in Fig. 5. Even though no significant variation in absorption was observed for different scrubber bed heights, generally absorption percentage remained higher for the longer bed heights. The percentage of CO_2 removal increased up to around 20% until the inlet gas flow rate reached 180 cm^3/s (approx.). However, further increase in gas glow rate decreased absorption percentage of CO_2.

3.4 Gross Calorific Value

The inlet gas (containing 60% methane) exhibited GCV of 23.88 MJ/m^3. The inlet gas flow rate for which the maximum absorption was observed (for different scrubber bed heights) was selected for determining the GCV of the biogas (gas coming out from the outlet) and presented in Table 1. The outlet gas showed

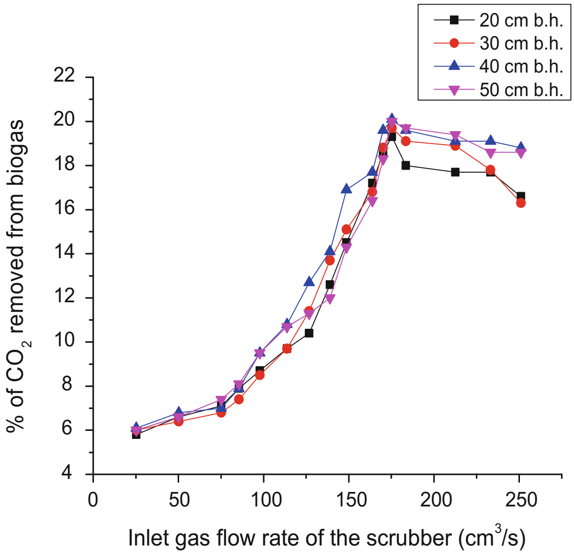


Fig. 5 Percentage of CO_2 absorption at different inlet gas flow rate

Table 1 GCV of the biogas after CO_2 absorption

Bed heights (cm)	GCV (MJ/m^3)
20	25.91
30	26.02
40	26.51
50	26.54

increase in GCV (25.91–26.54 MJ/m^3) in comparison to the inlet gas. This also confirmed the removal of CO_2 from the biogas.

3.5 Activity Period of the Absorbents

The gas flow rate through the burner (when connected) was found to be 13.33 cm^3/s (0.8 l/min) and the daily cooking period was assumed to be 2.5 h. Therefore, number of days till the absorbents remain active for a gas flow rate of 0.180 l/hr and ash content of 600 g/1 l of water is,

$$D = \frac{0.2758 \times 600}{0.0133 \times 3600 \times 0.4 \times 0.180 \times 2.5} = 19.20 \sim 19\,\text{days}.$$

4 Conclusions

Biogas from a domestic fixed dome type plant was upgraded via absorption of CO_2 using ash of *Musa bulbasiana* stem. This investigation highlighted an alternative route of CO_2 removal from biogas, which can be a cost effective option in comparison to other methods. The absorbents such as K and Ca present in significant quantity in the ash of 'banana' stem effectively contributed to remove CO_2 from biogas. The change in absorption percentage of CO_2 with ash content and bed height of scrubbing material was investigated in the study and up to 20% of CO_2 could be absorbed. CO_2 removal form biogas subsequently contributed to increase the GCV of the biogas. However, greater research capacity like addition of a blower of suitable range which would further contribute to increase the absorption rate by a greater pressure drop inside the scrubber and better arrangement for resisting the influence of climatic changes is necessary for further upgradation of the investigated method of CO_2 removal.

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Structural and Optoelectronic Properties of Nano Carbons Synthesized by Simple Pyrolysis of Bamboo

Bhagyashree Pani, Puspalata Pattojoshi and Udai P. Singh

Abstract Nano carbon today is an attractive material with excellent optoelectronic and thermal properties. It has found huge interest in electronic industries. This study reports the synthesis of nano carbon from two different bamboo precursors; Bambora arundi nacfau and Bambosa nafau, available in Indian forests. Synthesis of nano carbon materials have been carried out by simple pyrolysis technique by carbonizing the bamboo pieces in a furnace at 600 °C in atmospheric condition with heating rate of 10°/min and stand at this temperature for 30 min. Different properties were investigated by means of X ray diffraction, UV-VIS Spectrophotometric and Hall Effect measurements. Absorbance was found to be below 20% for dispersed nano particles. From crystallographic analysis (XRD) formation of graphite was observed only in Bambosa nafau. Apart from these three prominent peaks at 28.13, 40.34 and 50.08° were observed that could be attributed to residual matrix. The nano carbons synthesized from two different bamboos were compared in terms of their structure, light absorption in UV-VIS region and electrical properties. The as grown carbons showed resistivity in the range of 10^4–10^5 Ω-cm.

1 Introduction

Nanocarbons are carbon based materials bonded at the molecular level in different ways to achieve unique properties. Because of its' excellent optoelectronic and thermal properties, it is being used as an important material for several applications [1]. For meeting the increasing demand as well as for environment concerns, presently, biomass sources are being explored as a potential alternative for sources of nanocarbons. Use of biomass derived materials from different sources such as

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plants, wood, waste materials, coconut shells, rice husks, bamboo etc. are increasingly being discussed and researched because of their abundance, low cost, renewability and non-toxicity [2].

This study presents synthesis of nanocarbon materials from bamboo charcoal, by simple pyrolysis of bamboo, a commonly available grass all over the globe. In recent years, bamboo charcoal has attracted much attention due to its' widespread potential applications. Here, results of synthesis of nanocarbon from two different bamboo precursors: Bambora arundi and Bambosa nafau is presented.

2 Problem Identification and Basic Principle

Nanocarbons are normally synthesized from hydrocarbons over metal/alloy catalysts. Hence for obtaining metal catalyst nanoparticles for synthesis of nanocarbons consumes precious mineral resources as well as energy. Environmental degradation is associated with the above operations. Hence, increasing use of biomass resources [3] are being explored for synthesis of nanocarbons to meet the demand. Among various biomass resources cited in previous section, advantages of using bamboo charcoal used in this study is manifold. First, bamboo grows very rapidly, a few days or weeks harvest being equivalent to an entire season's harvest of cotton. It does this with far less irrigation, making it less of a drain on our resources [4].

Compared to trees, which when cut, take decades to regrow, whereas for bamboo, the renewability is even more apparent. Bamboo stabilizes the earth through it's roots much more, preventing erosion, and produces 35% more oxygen than the same sized stand of trees. Hence, with proper application areas being identified, bamboo cultivation can also be promoted, especially in developing countries for improving the socio-economic conditions of people [5].

What really makes bamboo charcoal interesting is that the process of carbonization creates nano particles with an enormous surface area to mass ratio and the ability to attract and hold (adsorption) a wide range of chemicals, minerals, radio waves, and other harmful substances.

3 Methodology

Experimental: Fresh bamboo cuttings were collected from the forests and its' variety was identified by the Forest department experts. It was cleaned thoroughly and left to dry in open fields for about a week. Then it was cut into small sizes in the workshop and again left to dry for around two days to get rid of moisture, if any.

Dried specimen were placed into a horizontal tube furnace and then sealed. The temperature was raised to 600 °C with heating rate of 10°/min and rests at this temperature for about 30 min.

It was allowed to cool down for about 6–8 h and charcoals obtained were removed from the furnace. The charcoal pieces were powdered in a mortar and pestle and then stored in moisture free condition to be analysed without any further treatment.

Characterisation: Different properties were investigated by means of X ray diffraction studies, UV-VIS spectrophotometer, photoluminescence and Hall effect measurements.

X-ray diffraction powder patterns (XRD) were measured with Shimatzu-6100 X-ray diffractometer (Cu Kα = 0.154 nm, 2° incidence angle, 2θ range 20–60°). X-ray diffraction of the as synthesized powder was taken at a step size of 0.02°.

An Hitachi U 3010 double beam spectrophotometer was used for absorbance measurements.

For investigation of electrical properties, Hall Effect measurement was carried out by means of Ecopia HMS 3000 system. Magnetic field of 0.5 T and current of 5 nA was employed.

4 Results and Discussions

4.1 Structural Analysis

Figure 1 shows XRD patterns of as synthesized charcoal obtained by the pyrolysis of Bambora arundi and Bambosa nafau. From crystallographic analysis (XRD) we found formation of graphite indicated by the peak at 26.53° which was attributed to graphite only in Bambrsa nafau [1]. Apart from these three prominent peaks appeared for both the samples at 28.13, 40.34 and 50.08° could be attributed to residual matrix. Crystalline structure was found better in powder obtained from Bambrsa nafau, confirmed from sharper and intense diffraction peaks.

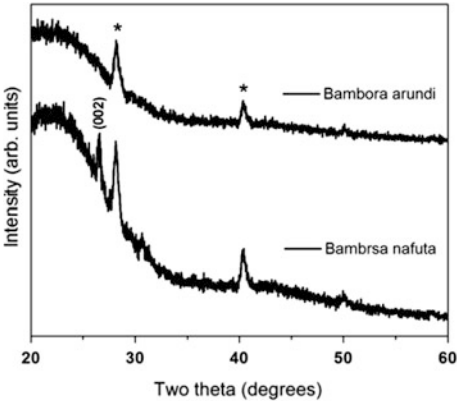

Fig. 1 XRD patterns of as synthesized charcoal

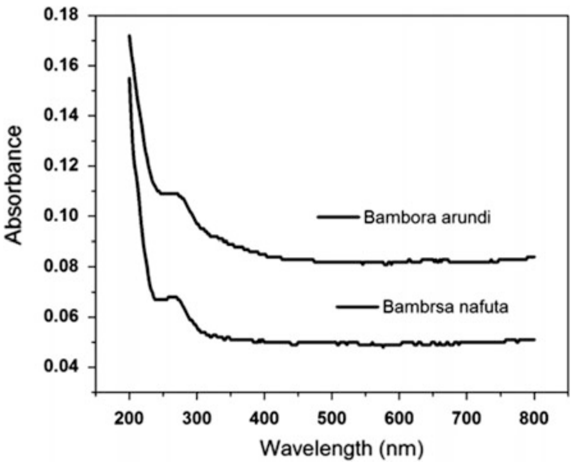

Fig. 2 Absorbance spectrum of as synthesized bamboo charcoal

Absorbance was found to be below 20% for dispersed nanoparticles. The relative percentage of absorption from the measured extinction spectrum depends on the size, shape, and composition and aggregation state of the sample [6]. As a general rule, smaller particles will have a higher percentage of their extinction due to absorption (Fig. 2).

4.2 Electrical Properties

The grown carbons showed resistivity in the range of 10^4–10^5 Ω-cm, measured from Hall Effect (Table 1). The higher resistivity could be related to presence of residual matrix in the pyrolysed product [7]. It is expected that by employing higher temperature, electrical properties could be improved. Charcoal prepared from Bambosa nafau exhibited comparatively higher carrier conc., mobility and lower resistivity.

Table 1 Hall effect measurement

Sample name	Carrier conc. (cm^{-3})	Mobility (cm^2/Vs)	Resistivity (Ω-cm)
Bambora arundi	1.29E+11	0.14	5.6E+07
Bambosa nafatu	7.5E+11	1.35	3.5E+05

5 Conclusion

Nano carbon was synthesized by carbonising bamboo pieces in a laboratory furnace in limited supply of oxygen at a temperature of 600 °C. Different properties of the charcoal yield were investigated.

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A Review on Vermicomposting of Different Leaf Litters

Rajesh Babu Katiyar, S. Suresh and A.K. Sharma

Abstract This study focuses on the review of vermicomposting of different leaf litters such as forest litters, polyalthia longifolia, mango, eucalyptus, neam, and water hyacinth with vegetable, agro-residues, kitchen and mixed liquor suspended solid wastes, institutional and industrial (sludge and fibres) waste and Rice husk. Leaf litter accumulating in the urban and suburban locations such as sidewalks and roadside which adds to the overall problem of municipal solid waste disposal. In India and other several countries, leaf litter is often piled-up and set on fire which adds to air pollution. Vermicomposting is the best known process for the biological stabilization of solid organic wastes. Vermicomposting involves the use of earthworms to mix, fragment and aerate organic waste material, making it more conducive to microbial activity and results highly humified product which contains most nutrients in plant-available forms such as nitrates, phosphates, and exchangeable calcium and soluble potassium and also reduction of pathogens.

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1 Introduction-Vermicomposting

Vermicomposting is being considered as a potential option in the hierarchy of integrated solid waste management that involves the stabilization of organic material by the joint action of earthworms and microorganisms [1, 23]. Vermicomposting as a practice started in the middle of 20th century and the first serious experiments were established in the Netherlands in 1970, and subsequently in England, and Canada. Later vermiculture practices were followed in USA, Italy, Philippines, Thailand, China, India, Korea, Japan, Brazil, France, Australia, and Israel [4]. Several other research studies have demonstrated the ability of some earthworm species to consume a wide range of organic wastes such as sewage sludge, animal dung, crop residues and industrial wastes which have been already vermicomposted and turned into nutrient rich manure include paper waste, textile mill sludge, guar gum industrial waste sugar industry wastes, distillery sludge, leather industry and beverage industry sludge, agro industrial sludge, primary sewage sludge and tannery industries. Several earthworm species are suitable for the treatment of municipal solid market, with *Eisenia andrei* and *Eisenia fetida* being the most commonly used [14]. The vermicast obtained at the end of the process is rich in plant nutrients and is free of pathogenic organisms [23]. Some of the important parameters affecting vermicomposting are discussed below.

(i) Moisture: Water constitutes 75–90% of the body weight of earthworms, so prevention of water loss is important for earthworm survival [5]. Earthworms also need a moist skin in order to breathe and therefore a moist environment is required for their growth and survival. Edwards and Fletcher [4] found the optimum moisture conditions for *E. fetida* to be 80–90% with a limit of 60–90%. However, in an earlier study, Reinecke and Viljoen [21] observed that earthworms have different moisture requirements at different stages of growth. **(ii) Temperature**: Temperature just like moisture content of organic wastes is also a major factor in determining the growth of earthworms. The activity, metabolism, growth, respiration, and reproduction of earthworms are all greatly influenced by temperature [3]. The temperature limit for survival of earthworms varies between species [15]. *Eisenia fetida* thrives well in at temperatures of between 25 and 30 °C but can tolerate temperatures ranging from 0 to 35 °C [4]. Reinecke et al. [22] found *E. fetida* to be more suited for vermiculture in Southern Africa compared to two other species they tested because it had a wider temperature tolerance. During the reproductive stages of earthworms require lower temperatures of less than 25 °C which are less than those required for rapid growth. **(iii) Worm stocking density**: Neuhauser et al. [20] studied effects of population density on growth and reproduction of *E. fetida* and showed that the earthworm growth decreased with increased population density. Using regression analysis they estimated the ideal stocking density for *E. fetida* to be approximately 0.8 kg-worms/m^2 on horse manure and 2.9 kg-worms 17-2 on activated sludge. Later, Domínguez and Edwards [2] working with *Eisenia andrei* concluded that, whereas individual worms grew more and faster at the lowest population density, the total biomass production was maximum at the highest population density. They observed that at higher densities, the worms sexually matured faster than at lower stocking densities. In a related study, Ndegwa et al. [19] reported that density of 1.60 kg-worm/m^2 resulted in the highest bioconversion of biosolids into earthworm biomass and also produced the best vermicompost though at a lower feeding rate. From the above it is clear that a high stocking rate is to be preferred if rapid turnover of materials is desired. **(iv) pH**: The distribution, numbers, and species of earthworms that live in any particular environment are limited by the pH of the environment. Edwards and Fletcher [4] found the optimal pH for *E. fetida* to be a pH of >5 and <9. However, Edward (6) found that when given a choice in a pH gradient, *E. fetida* tended to move towards the more acid materials with a pH preference of 5.0. According to Reed (1996), the pH of a growing medium is a measure of the concentration of hydrogen ions (H^+) found in the media solution. The pH influences the availability of nutrients in the medium solution. For this reason, plants usually grow best in a medium with a pH of 5.5–6.5. Although studies have suggested that worms perform best in neutral pH. The alteration of pH in the bedding is due to the fragmentation of the organic matter under series of chemical reaction. **(v) C: N ratio**: Organic carbon and inorganic nitrogen are important for cell synthesis, growth and metabolism in all living organisms including earthworms [18]. Aira et al. [1] reported that low C: N ratio materials resulted in an earthworm population that consisted mainly of mature adults with a higher mean individual weight than in high C: N ratio. However, in high C: N ratio materials the population consisted of mainly juveniles and hatchlings. A suitable C: N ratio is, therefore, required for the different materials used in vermicomposting that will allow for high earthworm growth and reproduction rates in order to accelerate waste breakdown and stabilization. **(vi) Electrical conductivity**: Electrical conductivity (EC) is used as an indication of the salt concentration in a growing medium. Considering that a medium is expected to supply plants with nutrients, and nutrients appear in solution as mineral salts, the electrical conductivity should not be too low. It should also not be too high, because plants have difficulty in extracting water from solutions with a high salt concentration. **(vii) Feedstock**: When the material with high carbon content is used with C/N ratio exceeding 40:1, it is advisable to add nitrogen supplements to ensure effective decomposition. All organic matter should be added only as a limited layer as an excess of the former may generate heat (Edward et al. 6). From the waste eaten up by the worms 5–10% are being assimilated in their body and the rest are being excreted in the form of a nutrient rich cast. They are no known stimulants which will force the earthworms to breed but fairly fresh manure or other nitrogen rich green organic matter seems to be the best stimulant to rapid breeding.

2 Literature Discussions

Gajalakshmi and Abbasi [9] investigated that vermicomposting of neem (*Azadirachta indica A. Juss*) was accomplished in ‘high-rate’ reactors operated at the earthworm (*Eudrilus eugeniae*) densities of 62.5 and 75 animals per litre of reactor volume. Experiments on the growth, flowering, and fruition of brinjal (*Solanum melongena*) plants with and without fertilization with vermicompost, revealed that the vermicompost had a significantly beneficial impact. Litter of the mango (*Mangifera indica*) tree leaves was composted and then converted into vermicast by the action of the earthworm *Eudrilus eugeniae* Kinberg. After over nine months of continuous operation the vermireactors with 62.5 animals/l generated ~13.6 g vermicast per litre of reactor volume (l) per day (d) whereas the reactors with 75 animals/l produced ~14.9 g vermicast/l d. Different earthworm species exist in almost all regions of the world except those with extreme climates, such as deserts and glaciers. These species have quite different life cycles, behaviours and environmental requirements. They are classified into three major ecological categories based primarily on their feeding and burrowing strategies: epigeic, endogeic and anecic [26]. Only epigeic earthworms seem to be relevant for vermicomposting [7]. About 8000 species of earthworm worldwide have been described as epigeic from ~800 genera belonging to the order Oligochaetae. Of those, seven earthworm species are used in vermicomposting, namely *Eisenia fetida*, *Dendrobaena veneta*, *Dendrobaena rubida*, *Lumbricus rubellus*, *Perionyx excavatus*, *Eudrilus eugeniae* and *Pheretima elongata* [7, 26]. These species show good growth on organic wastes compared with other species. Edwards [7] provides a comparative summary of the life cycle and cocoon production of the seven earthworm species suitable for vermicomposting (Fig. 1). Table 1 shows the literature survey of vermicomposting and its parameters, remarks.

In India million tons of livestock excreta, agro and kitchen wastes are produced every year which are serious problems for society. Nath et al. (17) evaluated potential of an epigeic earthworm *Eisenia fetida* to convert the different combination of variety of wastes into rich nutrient vermicomposts/vermiwash and pre and post chemical analysis of feed mixtures. Nath et al. (17) indicated that

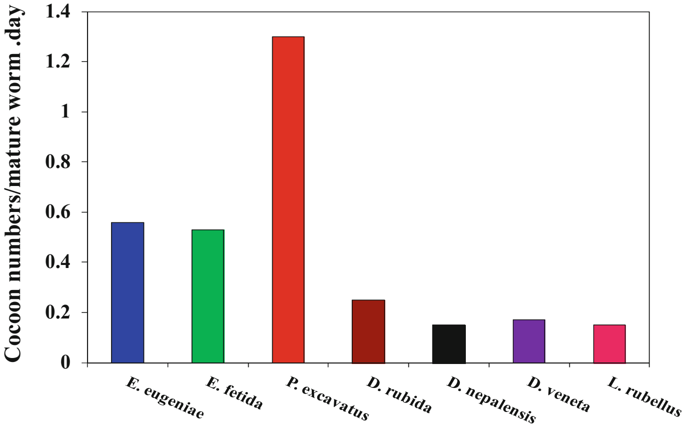

Fig. 1 Mean cocoon production of the seven earthworm species suitable for vermicomposting (adopted from Edwards [7])

Table 1 Literature survey of vermicompositng and its paramerters, remarks

S. No.	Organic waste	Amendment or bulking material	Parameters	Earthworms species	Composter	Vermireactor	Remarks	References
1	Water hyacinth	Cowdung	Temp = 31–60 °C, 50, 62.5, 75, 87.5, 100, 112.5, 125, 137.5 and 150 animals/l, 50% moisture content, 5 weeks	*Eudrilus eugeniae*	50l wooden box (10 & 5 cm thickness, 1 cm soil)	4l circular plastic container (1 cm saw dust, 2 cm river sand, 4 cm garden soil)	–	Gajalaskmi et al. (10)
	Forest litters	Decomposed farmyard manure	–	*Eisenia fetida Perionyxexcavatus and Dicogaser*	65–75%	Open permanent pits 4 m and 3 m x 1 m deep were constructed under the tree leaf shade which was about 2.4 m above ground to avoid entry of rainfall into the pits	Application of all three vermicomposts to forest trees significantly improved their heights and diameters over those of control trees, although the increases were lower than those resulting from the chemical fertilizer applications	Manna et al. [16]
5	Household waste containing green waste and shredded	Mixed woodchips of depth 20 cm	Temperature = 20 ° C, density 2 kg earthworms/m^2 of bed	*Dendrobaena veneta*	Pre-treating the material for 7-day	Five vermireactor of 10–15 cm depth and 10 m^2 bed area	–	Hobson et al. (11)

(continued)

Table 1 (continued)

S. No.	Organic waste	Amendment or bulking material	Parameters	Earthworms species	Composter	Vermireactor	Remarks	References
9	Vegetable waste (HP-heterogenic plant waste, p-tomato plant waste, t-tomato fruit waste)	Cow dung, wheat straw	Five non-clitellated earthworm weighing between 0.17 and 0.13 gm. Sample kept dark at 24 °C for 12 week. Moisture content 80–85%	*E. andrei*	Waste were oven dried at 25 °C and chopped	500 ml glass pots areated for a week to eliminate substance toxic to the earthworm	Chemical and enzymatic analyses and germination index show that vermicomposting was effective in bistabilization of greenhouse vegetable waste where salt content was the main factor restricting earthworm development	Fernandez-Gomez et al. (8)

vermicomposting of animal, agro/kitchen wastes not only produced a valuable vermicompost/vermiwash but also increased level of plant growth supplements in final vermicompost.

Suthar [24] studied vegetable solid waste (VW) amended with wheat straw (WS), cowdung (CD), and biogas slurry (BGS) into vermicompost using earthworm *Eisenia fetida*. VW was mixed in bulky materials (WS, CD, and BGS) in different ratios to produce eight different combinations for laboratory screening of wastes for 15 weeks. The vermicomposting caused a decrease in organic C (12.7–28%) and C: N ratio (42.4–57.8%), while increase in total N (50.6–75.8%), available P (42.5–110.4%), and exchangeable K (36.0–78.4%) contents. The results indicated that vermicomposting can be an efficient technology to convert negligible vegetable-market solid wastes into nutrient-rich biofertilizer if mixed with bulking materials in appropriate ratios. Wani et al. (25) found that moisture content, total organic carbon, humus, nitrogen, phosphorous and potassium was high in cow dung, followed by kitchen waste and garden waste. This study clearly indicates that vermicomposting of garden waste, kitchen waste and cow dung can not only produce a value added produce (vermicomposting) but at the same time reduce the quantity of waste.

Katiyar et al. [12] studied that vermicomposting of the different leaf litter and solid wastes at MANIT campus, Bhopal. The electric conductivity (EC) of Institutional and Vegetable market waste materials does not appear to be a toxic factor for *Eisenia fetida* and *Eudilius eugeniae*. The earthworms seem to be rather tolerant in a solution which has EC of up to 3 dS/m. pH levels in the range 5.0–8.0 have no negative effect on *E. fetida* and *E. eugeniae*. Many of waste materials seem to be converted to mature vermicomposts with low C/N ratio (<11) after the 48-days composting-vermicomposting treatment. Mixtures of DBS and Hostel kitchen waste and palash leaf litter with C: N ratio of 30 was more suitable for composting as this produced more mature and humified compost and vermicompost with higher N, P, K contents. High temperature attained during the thermophilic stage of composting could have been responsible for pathogen elimination. A temperature of 55 °C must be maintained for 15 consecutive days for efficient composting and pathogen reduction. A pre-composting period of 24 days was found to be suitable for a combined system for stabilizing digested biogas slurry-hostel kitchen waste and palash leaf litter. Pre-composting of waste for 24 days reduced fecal coliforms, below 100 MPN per gram after composting and was thus ideal for combining composting-vermicomposting waste mixtures.

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Hydrogen Gas Generation from Enzymatic Hydrolysis of Pre-Treated Rice Straw by Bacteria Through Dark Fermentation

R. Singh, C. Srivastava and M. Srivastava

Abstract Hydrogen is an eco-friendly, clean, sustainable and high energy fuel. It does not contribute to global warming and is a promising alternative to fossil fuel. Rice straw, a ligno-cellulosic material is economical, renewable and easily accessible and can be used as feed stocks for hydrogen production, through enzymatic hydrolysis. During this process sugar is released from rice straw hydrolyzate which is converted to hydrogen gas by bacteria via dark fermentation. It is a two-stage approach. In present research work, pretreatment with hydrogen peroxide, sulphuric acid and sodium hydroxide was persuaded to increase the fermentability of rice straw which was used as a substrate for hydrogen. Under dark fermentation, bacterial strains were able to procreate hydrogen gas from rice straw hydrolyzates of different pretreatments for delignification. Maximum reducing sugar was attained through H_2O_2 pretreatment (1453 µg/ml) compared to H_2SO_4 pretreatment (1376 µg/ml) and NaOH pretreatment (1334 µg/ml) under optimum conditions. Hydrogen gas is generated maximum during H_2O_2 pretreatment (46.99%).

1 Introduction

Presently, fossil fuels fulfilled the energy demands of the world, many efforts are being made to produce energy from renewable feed-stocks. Bio-hydrogen production is a promising technology for producing renewable energy from cellulosic waste materials. Molecular hydrogen is an attractive energy vector and as an energy carrier hydrogen offers the simplest way to reach zero emission. It is the cleanest fuel with high energy content of 122 kJg^{-1} and can be easily produced from biomass. Hydrogen is easily ignited, stored, transported, burns smoothly both on small

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domestic appliances and on large industrial units. Only water vapour is released when hydrogen gas is utilized and hence, reducing greenhouse effects, whereas fossil fuels emitting CO_2, CO, SO_x, NO_x and other harmful gases into the atmosphere [1]. Hydrogen is recyclable, efficient and can be used in fuel cells to directly generate electricity [2]. An important component of anaerobic digestion is hydrogen generation and its net evolution into the digester atmosphere is negligible [3]. Hydrogen has gained importance as a clean fuel for the future [4]. But, high production cost, low hydrogen yields and its formation rates [1, 5–7] create major obstacles in its production and commercialization and thus, it is necessary to develop some strategies which could make it economically feasible. By exploiting, ligno-cellulosic materials the cost of bio-hydrogen production could be minimized as they are cheap, renewable, abundant and sustainable. Due to the presence of higher amounts of monomeric sugars (mainly glucose and xylose); ligno-cellulosic hydrolysate can be used for the production of hydrogen, ethanol and other high valuable chemicals [8]. Ligno-cellulosic materials are utilized for the production of liquid or gaseous fuels in the second generation of bio-fuels [9]. Hydrogen has been obtained from various raw materials including corn stover [9, 10], wheat bran [11], wheat straw [12], rice straw [13], sweet sorghum [14], potato steam peels [15], cassava stillage [16], sugarcane bagasse [17] and beer lees [18]. The most abundant components of agricultural waste which have the potential for bio-fuel production are rice straw, wheat straw and corn stover. The hydrogen production processes from ligno-cellulosic biomass is found to be more cost-effective and commercially feasible as it is one-stage hydrogen production. The porosity and crystallinity of ligno-cellulosic and lignin content are the factors affecting enzymatic hydrolysis. The activity of all microorganisms was inhibited below pH 4.0 and for the hydrogen production pH 4.0 was regarded as the operational limit. Biological pretreatment are eco-friendly, safe and have low chemical and energy requirement. Saccharification is the rate limiting step in bio-fuel production. Waste can be degraded to CH_4 and CO_2 through the action of H_2 producers and utilizes [3, 19]. Hydrogen and methane production from CHO-rich wastes by various microorganisms has been observed [20]. Biogas production from many plant wastes has been demonstrated [21–23]. Hydrogen is better fuel in comparison to methane [4, 24, 25]. Hydrogen is produced by electrolysis of water, which can be achieved by microorganisms. The photosynthetic machinery of green plants i.e. chlorophyll helps in trapping solar energy in the form of photon, which is converted into ATP. Photolysis of water leads to splitting of water molecule into oxygen, electron and hydrogen ions [H^+]. Hydrogen ion is converted into hydrogen gas by enzyme hydrogenase and nitrogenase. Hydrogenase is sensitive to oxygen which is produced during photolysis of water. Nitrogenase is the main hydrogen producing enzyme in cyanobacteria and it is less sensitive to oxygen. Nitrogenase is reduced to ammonia with release of hydrogen gas in the presence of nitrogenase enzyme. The biological processing to obtain bio-hydrogen is an attractive way of producing clean fuel [6]. Glucose [26], Sucrose [27] were used as substrate and hydrogen yield was improved remarkably. A complete conversion of the organic matter to hydrogen can be realized by decoupling hydrogen production from methane production. Pure cultures of microorganisms are used to evolve bio-hydrogen. Bacteria convert organic matter to lower metabolites like organic acids, carbon-dioxide and hydrogen. The efficient production of very pure hydrogen from wet biomass is the distinctive merit of biological conversion. All over the world, the biological production of hydrogen represents on emerging area of technology development. During anaerobic process, when glucose is completely metabolized to acetate or acetone, the hydrogen yield is 4 mol H_2/mol glucose. An important parameter affecting the rate and yield of hydrogen gas production is the composition of mixed cultures. Due to the ubiquitous nature of hydrogen consumers and inter-species hydrogen transfer reactions, the mixed microbial community and wastes as a raw material produce only traces of hydrogen. The main objective of this study is to determine the highest yield of bio-hydrogen production through rice straw by using specific bacterial strain.

2 Materials and Methods

2.1 Feed Stock Material

Rice straw named Pusa Sugandh was used in this experiment. It was obtained from Indian Agriculture Research Institute (IARI). Firstly, rice straw was cut to approximately 1–2 cm length and washed thoroughly with tap water until the washings were clean and colorless. The rice straw was air dried before any pretreatment. The range of chemical composition of rice straw was determined and reported in Table 1.

2.2 Pretreatment of Rice Straw

For alkali, acid and peroxide pretreatment, chopped rice straw was soaked in 2% of sodium hydroxide (NaOH), sulphuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2) respectively. After that, it was washed with distilled water to remove chemicals and soaked in 0.1 M tris-acid buffer to neutralize the pH at 7. The pretreated rice straw was then oven dried overnight prior to use.

Table 1 Chemical composition of Rice straw

S. No.	Characteristics of rice straw (%)	%
1	Cellulose	35.33–39.04
2	Hemi-cellulose	20.11–21.64
3	Lignin	15.28–16.40
4	Ash	16–18.3
5	Silica	8.25–10.6

2.3 Enzymatic Saccharification of Pretreated Rice Straw

Saccharification or hydrolysis of the wet pretreated paddy straw samples was carried out using E-CELAN, an endo-1, 4-β-glucanase from *Aspergillus niger* supplemented with EBGLUC (endo-β-glucosidase), a β-glucosidase from *Aspergillus niger* (Megazyme International and Genecor) [28]. Enzymes were selected by studying various research papers. All other chemicals employed in this study were of reagent grade. 10 units of E-CELAN and 5 units of EBGLUC were used and volume of reaction mixture was made 10 ml with citrate buffer (pH 4.8). It was kept at 50 °C and 150 rpm in a constant temperature shaker water bath for 6 h.

2.4 Hydrogen Producing Bacterial Strain

In this study, *Bacillus coagulans* 2323 was selected for production of hydrogen. Under anaerobic conditions, the pure culture of strain was pre-cultured on the medium consists of K_2HPO_4 (0.15 g/l), NH_4Cl (0.05 g/l), NaCl (0.025 g/l), Na_2HPO_4 (0.3 g/l), 1 M $MgSO_4$ (1 mg/l), 0.1 M $CaCl_2$ (1 mg/l) and Glucose 25% (250 g/l).

2.5 Hydrogen Production from Pretreated Rice Straw

All the experiment was done in 300 ml BOD bottles which were fitted with a B-19 ground- glass stopper with a gas outlet Kumar et al. [29]. Alkali, acidic and peroxide pretreated rice straw samples released sugar through enzymatic saccharification under optimum conditions. *Bacillus coagulans* 2323 was able to produce hydrogen gas from different rice straw hydrolysate through dark fermentation. 250 ml of media was added to the BOD bottles. The pH of BOD media was adjusted to 7. BOD bottles were then fitted with a B-19 ground-glass stopper. Rubber tube was attached to the gas outlet of B-19 whose other end was inserted inside the silicon tube which was kept in the beaker filled with water (pH-2). The pH of water was adjusted at 2 to avoid CO_2 dissolution. Argon was used as carrier gas. Argon gas was passed for about 1–2 min at a pressure of 1 cubic m^2 to create an anaerobic condition. After this, the outlet of silicon tube and B-19 was closed by the stopper. The level of water was raised till the end of silicon tube. Incubation of the experimental set up was done at 37 °C for 24 h. Note down the level of water of silicon tube for total biogas production and gases were collected by water displacement method for analysis of Hydrogen, methane and carbon dioxide. The level of water displaced indicated the amount of biogas produced. Record the pH of BOD media and again adjust the pH to 7 with 2 N NaOH. The bottles were re-flushed with argon (Fig. 1).

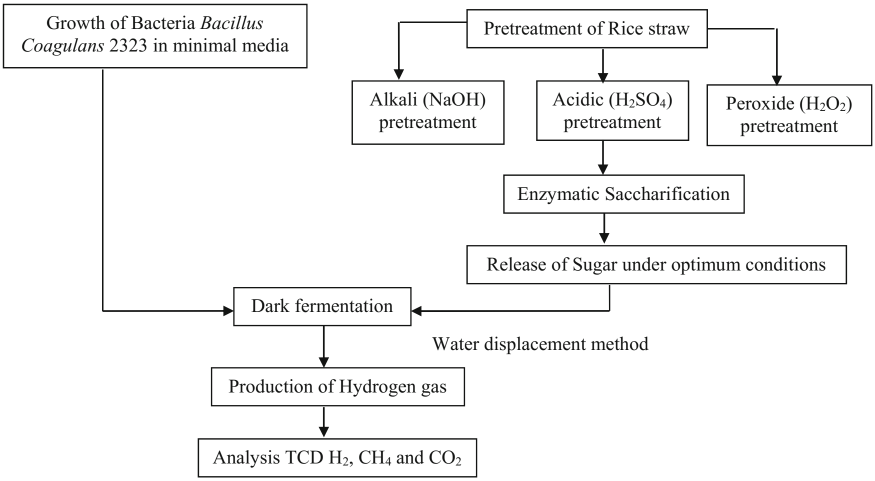

Fig. 1 Methodology of the process showing production of hydrogen gas

2.6 Analysis of Sugar

The concentration of reducing sugar was measured through DNS method [30, 31]. One unit of enzyme activity was defined as the amount of enzyme releasing 1 µmol of reducing sugars per minute.

2.7 Analysis of Gases

Gases were collected over water (pH was adjusted to 2) in syringes. Hydrogen, methane and carbon-dioxide were analyzed by standard GC procedures on a GC 5700 (Nucon Engineers, New Delhi). Argon was used as the carrier gas. Every time, samples were also analyzed for methane and carbon dioxide. Gas standards of Hydrogen methane and carbon dioxide were also run before each set up of analysis.

3 Results and Discussion

Maximum reducing sugar was attained through H_2O_2 pretreatment (1453 µg/ml) compared to H_2SO_4 pretreatment (1376 µg/ml) and NaOH pretreatment (1334 µg/ml) under optimum conditions. The hydrogen gas was evolved maximum in all the pretreatment methods as compared to untreated rice straw sample. Hydrogen gas was highest in hydrogen peroxide (H_2O_2) (46.99%) pretreated rice

Table 2 Production of hydrogen gas continued for 5 days

S. No.	Pretreatment Methods	Hydrogen gas (%)
1	Sodium hydroxide (NaOH)	43.98
2	Sulphuric acid (H_2SO_4)	44.56
3	Hydrogen Peroxide (H_2O_2)	46.99
4	Untreated sample	40.25

straw sample than those of sulphuric acid (H_2SO_4) and sodium hydroxide (NaOH) pretreated rice straw samples. Production of hydrogen gas continued for 5 days i.e. 120 h and there after it ceased down (Table 2).

4 Conclusion

Hydrogen is a clean, efficient, sustainable and eco-friendly fuel. Hydrogen production from rice straw under dark fermentation is most cost-effective and commercially feasible process. Rice straw, is an economical, renewable and easily accessible ligno-cellulosic material that can be utilized as feed stocks for hydrogen production. *Bacillus coagulans* 2323 was able to produce hydrogen gas from different rice straw hydrolysate through dark fermentation. The current study showed that hydrogen gas is evolved maximum during hydrogen peroxide (H_2O_2) (46.99%) pretreatment as compared to acidic and alkaline pretreatment process.

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Review on Microbial Fuel Cell Energy Enhancement Using Nano Materials

Samatha Singh and S. Suresh

Abstract The microbial fuel cell (MFC) is a very promising technology for generating electrical energy from anaerobic fermentation of organic and inorganic matter in wastewater using microorganisms as biocatalysts while simultaneously treating the wastewater or industrial waste water. However, the overall low performance of the MFC compared to other more established fuel cell technologies and the high cost of its components compared to the low value of the wastewater it treated, are the two major barriers to commercialization. On the other hand nano materials are to be the soul of the next technological development in all spheres of science. When these two latest technologies clubbed together wonders will happen, Nano-structure electrode has potential to enhance the MFC performance. MFC's performance can be improved by cheaper nano-composite materials such as nano-structured carbon in the electrodes that are more conductive and mechanically stabile with larger surface area and higher electrochemical catalytic activity compared to the conventional Pt on carbon. MFCs, especially nano scale materials that have high potential for enhanced power production. The objective of this research is to review and address some of the problems surrounding the current state of microbial fuel cells, such as inefficient electron transfer, low currents, and lack of modularity by using suitable nano materials.

1 Introduction

In recent years, energy needs in the world continue to increase and in an effort to achieve energy independence, research initiatives are focused on alternate, renewable and pollution free energy sources. Past few decade introduced us with a variety of new sources of alternate sources of energy. A few of which are hydroelectricity, geothermal energy, wind energy, tidal energy, solar energy and many

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more. But still we could not meet our energy requirements. A similar source of energy came into light i.e. Microbial Fuel Cell which produces electrical energy using microorganisms, it is one such renewable and sustainable technology that is considered to be one of the most efficient energy sources. The fact that bacteria can oxidize the substrates to produce electricity makes MFCs an ideal solution for wastewater treatment and domestic energy production. "Microbial fuel cells (MFCs) are electrochemical devices that use the metabolic activity of microorganisms to oxidize fuels, generating current by direct or mediated electron transfer to electrodes" [1].

The microbial fuel cell consists of simple yet vital components to effectively harness the energy are as follows:

- Electrodes—both in the anode and cathode chambers
- Proton Exchange Membrane—Nafion as the least resistive membrane
- Substrate—any organic matter used as source of energy for microorganisms i.e. wastewater
- Bacteria—exoelctrogens, most suited for MFC applciations

Latest MFC developments focus on optimising each aspect in order to increase the overall efficiency of the electrochemical device.

MFC is a highly promising device which can produce energy with low or zero emission of greenhouse gases but it still has some drawback which makes it unable to be operated on a large scale successfully. One of the major drawback is that, it have very low power output. The main reason of low power is that the electron that are emitted by microbes are not captured by the electrode. This drawback can be minimized by applying a coating of nanocomposite material on the electrodes which will result in high surface area of the electrode and help capture more electrons.

2 MFC and Nano Technology

After the consumption of organic substrate by microbes, Carbon-dioxide is expelled out and formation of H^+ ions takes place along with release of e^-. These e^- released are utilized for electricity generation.H^+ ions after passing from PEM, gets mixed up with oxygen to form water.

Overall Reaction

$$C_{12}H_{22}O_{11} + 13H_2O \rightarrow 12CO_2 + 48H^+ + 48^{e-}$$

AtAnode

$$e^- + O_2 + H_2 \rightarrow H_2O$$

AtCathode

A nanocomposite material is a multiphase solid material where one of the phases have one, two or three dimensions of less than 100 nm. Various nanomaterial for electrodes are

- Polypyrole coated carbon nanotube
- Polyaniline carbon nanotubes composite
- Activated carbon nanofiber, etc.

3 Methodology

3.1 Polyaniline/Titanium Dioxide Composite

Qiao et al. [1] used Nanostructured Polyaniline/Titanium Dioxide Composite Anode for Microbial Fuel Cells with *Escherichia Coli*. It was found that the composite with 30 wt% PANI gives the best bio and electro catalytic performance.

Current and potential measurements on the MFC were carried out by using a benchtop digital multimeter (ESCORT 3146A) during discharge in constant-load mode with an external resistance of 1.95 kΩ. Figure 6 shows that, after bacteria enrichment for about 48 h, the power density rises to a plateau and remains there for about 450 h without addition of glucose or other nutrition. After 500 h from inoculation, the power density drops sharply as glucose is depleted in the anodic compartment.

3.2 Polypyrrole (PPy) Coated Carbon Nanotubes (CNTs) Composite

Zoua et al. [2] constructed a MFC using polypyrrole (PPy) coated carbon nanotubes (CNTs) composite as anode material with *Escherichia coli*. The power output of the MFC increased along with the increase of the composite loading. In the absence of exogenous electron mediators, the MFC with the composite modified anode contained 5 $\mathrm{mgcm^{-2}}$ PPy-CNTs exhibited a maximum power density 228 $\mathrm{mWm^{-2}}$ with a cell voltage of 0.18 V. These results provide significant prospects for developing low cost and effective anode of MFC.

The electron mediators used in MFC are poisonous and high cost, and many kinds of microbes cannot realize the direct electron transfer with the electrode because the membrane of the bacteria is nonconductive. Considering the fact that the MFC used here does not include any such electron mediators, PPy-CNTs is a promising material for electrode of MFC.

3.3 Polyaniline Hybridized 3D Graphene

Yong et al. [3] constructed a MFC that has an anode based on polyaniline hybridized three dimensional (3D) graphene. It outperforms the planar carbon electrode because of its abilities to three-dimensionally interface with bacterial biofilm and facilitate electron transfer, and provide multiplexed and highly conductive pathways.

3.4 Ni Nanoparticles Dispersed Carbon Nanofibers

Singh et al. [4] constructed a nickel (Ni) nanoparticles dispersed web of carbon micro-nanofibers (ACFs/CNFs) was fabricated as the electrode of a MFC with *Escherichia coli* [3]. The prepared electrode material having significant mesoporosity, electrical conductivity, and dispersed Ni NPs facilitated electron transfer to the anode and the catalytic reduction of oxygen at the cathode. The MFCs were stable and had small internal resistances [3].

3.5 PEM in MFC

Protons and electrons were generated via biochemical reactions in an anaerobic anode chamber of MFC. Protons must travel to cathode via one PEM. At the first step, Nafion 117 was used as PEM in dual chamber of MFC and the performances of cells were considered by polarization curve. The polarization curve and power density versus current density are shown in Fig. 1. The maximum power and current density with is membrane were 15.4 $\mathrm{mWm^{-2}}$ and 112 $\mathrm{mAm^{-2}}$, respectively [5] (Fig. 1).

4 Characterization Techniques for Nanoparticles

Different techniques are available for the characterization of nano materials designed with specific properties and applications as per requirements. They are:

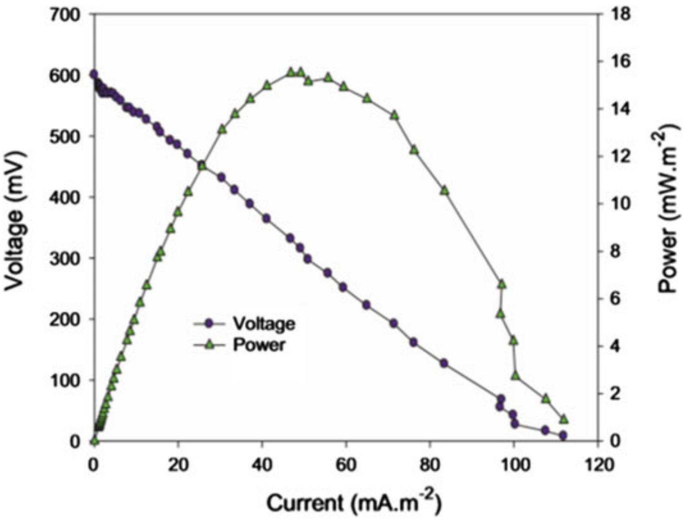

Fig. 1 Polarization curve with nafion 117 as PEM [5]

4.1 Transmission Electron Microscopy (TEM)

Transmission electron microscopy is a powerful characterization tool that provides information regarding the morphology, crystallography and elemental composition for advanced materials [6].

4.2 Scanning Tunneling Microscope (STM)

Scanning Tunneling Microscope allows for the imaging of the surfaces of metals and semiconductors at the atomic level. It provides atomic-scale resolution of surfaces and is also being developed to move atoms on surfaces. According to its inventors, G. Binnig and H. Rohrer of IBM Zurich, it was operational in 1981. They won the 1986 Nobel Prize for this work.

4.3 Atomic Force Microscopy (AFM)

The AFM differs from the STM in that what is being measured is the force between the sample and the tip. Since no electric current is involved, the tip/sample does not have to be metallic. The AFM operates like a record player except that it has flexible cantilevers, sharp tips, and a force feedback system. It is ideally quantitatively measuring nano scale surface roughness and for visualizing surface nano-texture on many type of material surface including polymer and nano composites.

4.4 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) uses a focused electron probe to extract structural and chemical information point-by-point from a region of interest in the sample. The high spatial resolution of an SEM makes it a powerful tool to characterize a wide range of specimens at the nanometer to micrometer length scales.

4.5 X-Ray Diffraction (XRD)

X-ray diffraction (XRD) is one of the most important non-destructive tools to analyze all kinds of matter ranging from fluids, to powders and crystals. From research to production and engineering, XRD is an indispensible method for structural materials characterization and quality control which makes use of the Debye-Scherrer method. This technique uses X-ray (or neutron) diffraction on powder or microcrystalline samples, where ideally every possible crystalline orientation is represented equally.

5 Conclusion

The distinctiveness of bio-electrochemical systems comes from their ability to simultaneously take on two ecological vices with: sustainable energy production, and waste-water treatment. The basics of how bacteria in a MFC produce electricity are understood. Proper enhancement can be done by coating Nanomaterials and thereby increasing e^{-} transfer and hence electricity generation. Further ahead, MFC will be made and bacteria's such as Escherichia Coli will be employed for the use to generate electricity. Different kinds of Nano materials and their characterization techniques explained.

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