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Research Paper

Characterization of jatropha oil for the preparation of biodiesel

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Abstract

There has been greater awareness on biodiesel in developing countries in the recent times and significant activities have picked up for its production especially with a view to boost the rural economy. In the present investigation ***Jatropha curcas* Linn.** seed oil (non-edible) and its methyl ester have been chosen to find out their suitability for use as petro-diesel. Experimental investigation has been done to find out the different properties of jatropha oil. Theoretical equation has been developed to find out the properties and they have been compared with the experimental values. Biodiesel was prepared from jatropha oil, through esterification followed by trans-esterification; former was performed using acid catalyst (5% H_2SO_4) and methanol (20% of oil). The trans-esterification reaction was carried out for 2 hrs keeping the molar ratio of methanol to oil at 6:1 and sodium hydroxide concentration of 0.7 weight percentage of oil. The yield of jatropha oil methyl ester was about 97% .The properties of biodiesel depends on the nature of the vegetable oil to be used for preparation of biodiesel and if the developed process is scaled up to commercial levels then excellent business opportunity will be offered by the biodiesel obtained from jatropha oil methyl ester and it could be a major step towards the creation of an eco-friendly transportation fuel that is relatively clean on combustion and provides farmers with substantial income.

Keywords: Seed oil, Extraction, Jatropha oil, Esterification, Transesterification, Methyl ester, Biodiesel, Catalysts, *Jatropha curcas*.

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Introduction

Due to gradual depletion of world petroleum reserves and the impact of environmental pollution, there is an urgent need for suitable alternative fuels for use in diesel engines. In view of this, vegetable oil is a promising alternative because it is renewable, environment-friendly and produced easily in rural areas, where, there is an acute need for modern forms of energy[1-5]. In recent years systematic efforts have been made by several research workers to use vegetable oils as fuel in engines[6-9]. Seeing the cost and edible oils consumption, the use of non-edible oils compared to edible oils is very significant. ***Jatropha curcas* Linn.**, tree or shrub grows practically all over India under a variety of agro-climatic conditions and it is commonly found in most of the tropical and subtropical regions of the world. Thus it ensures a reasonable production of seeds with very little inputs. It is evident that there are various problems associated with straight vegetable oils being used as fuel in compression ignition engines, mainly caused by their high viscosity[10-12]. Although short term tests using neat vegetable oil showed promising results, longer tests led to injector coking, more engine deposits, ring sticking and thickening of the engine lubricant. These experiences led to the use of modified vegetable oil as a fuel. Although there are many ways and procedures to convert vegetable oil into a diesel like fuel, the transesterification process was found to be the most viable oil modification process[13]. It is the process of using an alcohol, in the presence of a catalyst, such as sodium hydroxide or potassium hydroxide, to break the molecule of the raw renewable oil chemically into methyl or ethyl esters of the renewable oil, with glycerol as a by product. Both the acid as well as alkaline esterification were subsequently performed to get the final product. NaOH

was found to be a better catalyst than KOH in terms of yield[14].

Biodiesel, defined as the mono-alkyl esters of fatty acids derived from vegetable oil or animal fat, has demonstrated a number of promising characteristics, including reduction of exhaust emissions[15]. Transesterified, renewable oils have proven to be a viable alternative diesel engine fuel with characteristics similar to those of diesel fuel. In the present investigation ***J. curcas*** seed oil, non-edible oil and its methyl ester has been chosen to find out its suitability for use as fuel oil. The oil content of jatropha seed ranges from 30 to 35% by weight and common byproducts produced while processing the biodiesel are glycerol and oil seed cake. During oil expelling, about 65-70% of the seed kernel is obtained as de-oiled cake. Glycerol is a byproduct of transesterification process. As jatropha oil cake contains nitrogen, phosphorus and potassium, it can be used as organic manure. After extraction of oil from seed the detoxification of the seed cake is necessary so that the seed cake can be used as cattle feed. The type of toxic component present in the seedcake varies from seed to seed, but for jatropha seed cake detoxification is highly essential. It is found that de-acidification and bleaching could reduce the content of toxic phorbol esters up to 55%[16, 17]. The fatty acid composition of jatropha oil[18] consists of myristic, palmitic, stearic, arachidic, oleic and linoleic acids. The jatropha cultivation is useful as renewable energy source, erosion control and improves soil and generates employment and economy.

A very large number of potentially useful catalysts have been investigated as a means to enhance the reaction rate. Without added catalysts some degree of rearrangement can be obtained but only under extreme conditions of temperature and time, leading to undesirable effects such as isomerization, polymerization and decomposition. Apart from the now generally preferred catalysts, e.g. sodium methoxide and alcolates, alkali metal alkoxides are found to be more effective transesterification catalysts compared to acidic catalysts. Sodium alkoxides are the most efficient catalysts, although KOH and NaOH can also be used. Transmethylation occurs in the presence of both alkaline and acidic catalysts. As they are less corrosive to industrial equipment, alkaline catalysts are preferred in industrial processes. A concentration in the range of 0.5-1% (w/w) has been found to yield 94-99% conversion to vegetable oil esters and further increase in catalyst concentration does not affect the conversion but adds extra cost, as the catalyst needs to be removed from the reaction mixture after completion of the reaction. Transesterification of vegetable oils using methanol and alkaline catalyst is the most commonly used processes for manufacture of methyl esters. This catalyst has the advantages, e.g. short reaction time and relatively low temperature can be used with only a small amount for catalyst and with little or no darkening of colour of the oil.

The most important variables which influence the transesterification reaction are: reaction temperature, ratio of alcohol to vegetable oil, catalyst mixing intensity and purity of reactants. Yield of biodiesel is affected by molar ratio, moisture and water content, reaction temperature, stirring, specific gravity, etc.[19].

The literature has revealed that the rate of reaction is strongly influenced by the reaction temperature. However the reaction is conducted close to the boiling point of methanol (60-70°C) at atmospheric pressure for a given time. Such mild reaction conditions require the removal of free fatty acids from the oil by refining or pre-esterification. Therefore, degummed and deacidified oil is used as feedstock[20]. Pretreatment is not required if the reaction is carried out under high pressure (9000 kPa) and high temperature (240°C), where simultaneous esterification and transesterification take place with maximum yield obtained at temperatures ranging from 60-80°C at a molar ratio of 6:1 [20-22]. A molar ratio of 6:1 is normally used in industrial processes to obtain methyl ester yields higher that 98% (w/w)[20-23].

It has been observed that during the transesterification reaction, the reactants initially form a two-phase liquid system. The mixing effect has been found to play a significant role in the slow rate of reaction. As phase separation ceases, mixing becomes insignificant. The effect of mixing on kinetics of the transesterification process forms the basis for process scale-up and design.

Impurities in the oil affect the conversion level considerably. It is reported that about 65- 84% conversion into esters using crude vegetable oils has been obtained as compared to 94-97% yields refined oil under the same reaction conditions[18]. The free fatty acids in the crude oils have been found to interfere with the catalyst. This problem can be solved if the reaction is

carried out under high temperature and pressure conditions.

Materials and Methods

Experimental set-up

The reactor used for experiments was a 1000ml three-necked round-bottomed flask (Fig.1). The flask is placed on a water bath. The center neck is fitted with a stirrer. One of the two side necks is equipped with a condenser and the other is used for thermo-well and for sample collection. A thermometer is placed in the thermo-well for temperature measurement inside the reactor. The motor is connected to a speed regulator for adjusting and controlling the stirrer speed.

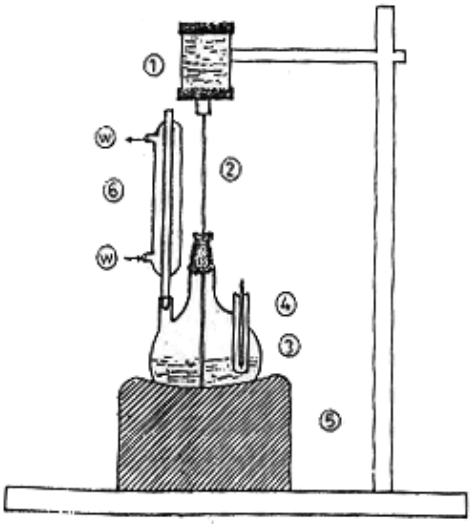

Fig. 1: Experimental set-up for preparation of methyl esters from jatropha oil —
1. Electric Motor; 2. Stirrer;
3. Three-necked Round Bottom Flask;
4. Thermo-well with thermometer;
5. Water bath; 6. Condenser

Esterification

A known amount of jatropha oil was taken in the three-necked round-bottomed flask. Heat was supplied to the setup using a heating mantle. A known amount of sulfuric acid in methanol was added to the oil and stirred continuously maintaining a steady temperature of 65°C. Reaction continued for two hours. Under optimal condition esterification was performed using acid catalyst (5%H_2SO_4) and methanol (20% of oil). Intermittently samples were collected at regular intervals (30 min) and acid values were determined. Esterification was continued till the acid value reduced to <1. The excess methanol from the reaction was distilled out and total mass was further dried under vacuum to remove the moisture present in the sample. The organic layer after neutralizing with 10% NaOH solution, the excess methanol present in the reaction was distilled out. The methyl ester was refined with NaOH solution the reaction temperature was maintained at 65°C for 25 minutes. The refined sample was further cooled and centrifuged to remove residual soap. The oil after esterification undergoes transesterification to obtain methyl esters.

Transesterification

In a typical experiment a known amount of jatropha oil is charged to a round bottom flask. A known amount of catalyst (NaOH) based on weight per cent of oil is mixed in excess mole per cent of methanol. The mixture of sodium hydroxide in methanol is added to the jatropha oil in the round bottom flask, while stirring the material of the flask. Required temperature is maintained by controlling the electrical heating till the reaction is completed. After complete addition of methanol-NaOH solution, samples are drawn at regular interval (5-10 min) to confirm the formation of methyl ester. The formation of methyl ester is checked by using thin layer chromatography (TLC) technique. After the completion of methyl ester formation, a known amount of sulfuric acid in methanol is added to the methyl ester to neutralize the sodium hydroxide present in the ester. The excess methanol present in the methyl ester is recovered by distillation with electrical heating and constant stirring. A sample of jatropha oil methyl ester is analyzed for acid value and then refined with NaOH solution to remove the free fatty acids. The transesterification reaction temperature was maintained at 65°C for two hours keeping the molar ratio of methanol to oil at 6:1 and sodium hydroxide concentration of 0.7 weight percentage of oil and percentage of excess methanol used is 200%. The refined sample was further cooled and centrifuged to remove residual soap. The *p*H level of the organic layers is measured and neutralized separately. The washed samples were further dried. Under optimal condition the yield of jatropha oil methyl ester from jatropha oil is about 97%.The reaction parameter such as methanol/oil molar ratio, % of excess alcohol, reaction time and temperature, concentration of catalyst were optimized for the production of jatropha oil methyl ester. Various fuel properties of jatropha oils and jatropha oil methyl esters were determined experimentally to ascertain their suitability as diesel fuel.

Characterization

Physical and chemical properties were determined by using standard test methods. These standard values were calculated and compared with USA (ASTM D6751), Germany (DIN 51606), India (BIS) and European Organization (EN 14214). Flash point, fire point, viscosity, cloud points, pour point (PP), cetane number, carbon residue, acid value, iodine value, saponification number (SN), etc. had been determined[19-23]. Theoretical and experimental value of important chemical properties like acid value, saponification value and iodine value of jatropha oil were calculated by following equation:

Experimental

Acid value = (No. of ml of N/10 KOH used * 5.6) /mass of oil in gram

Saponification value=(No. of ml of N/2 KOH taken–No. of ml of N/2 acid used in back titration)* 28/mass of oil in gram.

Iodine value = IV= (Difference of ml of the titration value of blank and the sample*1.27)/mass of oil taken in gram

Theoretical

Saponification value SN= Σ (560 × Ai) / MWi, Iodine value IV = Σ (254 × D × Ai)/MWi,

where Ai=percentage composition, D=No. of double bond, MWi=Molecular mass of each component.

Results and Discussion

In the present work a comparison is made between theoretical and experimental value of important chemical properties like acid value, saponification value and iodine value for different non-edible oils have been compared and presented in Table 1[(Ref 24)]. The theoretical values are in well agreement with their experimental values indicating that if the composition of vegetable oils is known, we can find out their properties by theoretical equations within agreeable error. The fuel properties of jatropha oil, jatropha oil methyl ester and diesel were compared and given in Table 2. From the various properties, it is found that the calorific values of these methyl esters are 37.2mj/kg, which are low, compared to diesel fuels (42.0mj/kg). The methyl ester, however, has higher cloud and pour points than conventional diesel fuel. This is important for engine operation in cold (or) cooler environments. Kinematic viscosity and cetane values are slightly higher than diesel, which is favourable for combustion. Higher flash point is advantageous for fuel transportation. The various properties of jatropha oil methyl ester found to be comparable with that of diesel fuel.

Conclusion

Thus this study suggests that the jatropha oils can be used as a source of triglycerides in manufacture of biodiesel by esterification and/or transesterification. The biodiesel from refined vegetable oils meets the Indian requirements of high speed diesel oil. But the production of biodiesel from edible oils is currently much more expensive than diesel fuels due to relatively high cost of edible oils. There is a need to explore non-edible oils as alternative feed stock for the production of biodiesel. Non-edible oil like jatropha (***J. curcas***) is easily available in many parts of the world including India and it is cheaper compared to edible oils.

Table 1: Comparison of experimental and theoretical values of different properties of vegetable oils[24]

Vegetable oil	Experimental saponification value	Theoretical saponification value	Experimental iodine value	Theoretical iodine value	Experimental acid value	Theoretical acid value
Palm oil	105-110	106.45	97	95	190-210	218
Rapeseed oil	315.2	298.45	94.2	98	180-210	215
Linseed oil	189-195	188.12	165-205	170	197-204	181
Jatropha oil	196-200	199.24	96-105	101	5.31	8
Karanja oil	186-196	190	80-90	96	20	24
Mahua oil	190-195	191	60-65	63	18.38	27

Table 2 : Comparison of fuel properties of jatropha oil, jatropha oil methyl ester and diesel

Property	Unit	Jatropha oil	Jatropha oil methyl ester	Diesel	ASTM D 6751-02	DIN EN 14214
Density at 15°C	kg/m^3	918	880	850	875–900	860–900
Viscosity at 40°C	mm^2/s	35.4	4.84	2.60	1.9–6.0	3.5–5.0
Flash point	°C	186	162	70	>130	>120
Pour point	°C	-6	-6	-20	—	—
Water content	%	5	Nil	0.02	<0.03	<0.05
Ash content	%	0.7	Nil	0.01	<0.02	<0.02
Carbon residue	%	0.3	0.025	0.17	–	<0.3
Sulphur content	%	0.02	Nil	—	0.05	—
Acid value	mg KOH/g	11.0	0.24	0.35	<0.8	<0.50
Iodine value	—	101	104	–	–	–
Saponification value	—	194	190	–	—	—
Calorific value	MJ/kg	33	37.2	42	—	—
Cetane number	—	23	51.6	46	—	—

ASTM - American Society for Testing and Materials
DIN - Deutsches Institut für Normung (German Institute for Standardization).

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