Journal of Aquatic Biology and Fisheries Vol. 2/2014/ pp. 632 to 640

BIODIESEL PREPARATION AND CHARACTERIZATION FROM TRANSESTERIFICATION OF *SAMADERA INDICA* OIL HAVING HIGH FATTY ACIDS

Shereena, K.M.
M E S Asmabi College, Vemballur, Kodungalur, Trissur, Kerala
Email: Sheri.moidu@gmail.com.

Received on: 10 October 2013, accepted on: 12 December 2013

Abstract: Biodiesel, a promising substitute as an alternative fuel has gained significant attention due to the predicted shortness of conventional fuels and environmental concern. Biodiesel can result in significant reductions in a number of air pollutants such as particulate matter dropped, global warming impact from CO_2 dropped by almost 80 percent, Hydrocarbons were reduced by nearly 70 percent and carbon monoxide decreased 48 percent. The utilization of liquid fuels such as biodiesel produced from *samadera indica* oil by transesterification process represents one of the most promising options for the use of conventional fossil fuels. Currently, most of the biodiesel is produced from the refined edible type oils using methanol and an alkaline catalyst. However, large amount of non-edible type oils and fats are available. The difficulty with alkaline-esterification of these oils is that they often contain large amounts of free fatty acids (FFA). These free fatty acids quickly react with the alkaline catalyst to produce soaps that inhibit the separation of the ester and glycerin. A two-step transesterification process is developed to convert the high FFA oils to its mono-esters. The first step, acid catalyzed esterification reduces the FFA content of the oil to less than 2%. The second step, alkaline catalyzed transesterification process converts the products of the first step to its mono-esters and glycerol. The major factors affect the conversion efficiency of the process such as molar ratio and amount of catalyst are analyzed. The two-step esterification procedure converts *Samadera indica* seed oil (SISO) to 87% of its methyl esters. The important physic chemical properties of biodiesel such as Kinematics Viscosity, Density, flash point, Cetane index and Heat of combustion are found out, the values were 4.1 mm^2/s, 114.5 °C , 100-130°C 49 and 2717.38 kg cal/mol respectively and the result were compared with that of biodiesel standards ASTM Standards D 6751 and European EN 14214. The smoke content of exhaust emission was tested. Smoke content is comparatively lesser than commercial diesel fuel. This study supports the production of biodiesel from unrefined *Samadera indica* seed oil (SISO) as a viable alternative to the diesel fuel can be used in existing diesel engine without any modification.

Key words: Fatty acid methyl ester, Free fatty acids (FFA), Acid catalyzed esterification, Renewable fuel, Feedstock, Cetane index, Heat of combustion, Alkaline-esterification

INTRODUCTION

World energy demand continues to rise. In these circumstances, alternative sources of energy gain importance. Biodiesel and alcohol are being considered to be supplementary fuels to the petroleum fuels in India (Subramanian *et al.,* 2005). Biodiesel, which is made from renewable sources, consists of the simple alkyl esters of fatty acids (Hanny and Shizuko, 2008). In 1996 the American Society for Testing and Materials (ASTM) standard defined biodiesel as "the mono alkyl esters of long chain fatty acids derived from renewable lipid feedstock, such as vegetable oils or animal fats, for use in compression ignition (diesel) engines" (Guo and Yan, 2005). It is renewable since it is produced from renewable sources (vegetable oils or animal fats), therefore can be produced domestically, which can reduce a country's dependency on imported fuel and solve agricultural overproduction problems in some countries. Biodiesel is biologically degradable (Zhang *et al*., 1998 and Korbitz, 1999) and does not contribute to a net rise in CO level in the atmosphere, and consequently to the greenhouse effect. The life cycle analysis of biodiesel showed that overall CO emissions were reduced by 78% compared with petroleum-based diesel fuel (Garpen, 2005). It is non-toxic which does not contain sulphur and any aromatic compounds, but contains 10% to 11% oxygen. These characteristics of biodiesel contribute a better quality and environmentally friendly exhaust gas emissions due to reducing of carbon monoxide, unburned hydrocarbon, particulate matter and air toxics in the exhaust gas, compared to petroleum–diesel fuel (Mohamad *et al*., 2002 and Carraretto *et al*., 2004). Biodiesel has higher flash point (about 150°C) than diesel fuel (about 50°C), hence it is less volatile, and is safer to store and transport the fuel. It has good lubricant properties with respect to petroleum diesel (Guo and Yan, 2005).

At present, the high cost of biodiesel is the major obstacle to its commercialization. Exploring ways to reduce the high cost of biodiesel is of much interest in recent biodiesel research. Approximately 70–95% of biodiesel cost is attributed to raw feedstock cost (Zhang *et al*., 2003). So the use of cheap and non-edible vegetable oils, animal fats and waste oils as raw feedstocks for biodiesel production is an effective way to reduce the cost of biodiesel. *Samadera indica* seed oil (SISO) is a potential cheap feedstock for biodiesel production compared with refined and edible- grade vegetable oils, such as soybean oil, rapeseed oil and sunflower oil. Fatty acid composition of *Samadera indica* oil compared with other non-edible oil is given in the Table 1.

Samadera indica is a tree belonging to the family of *Simarubacecae*, found in evergreen forest in west coast along back waters and sandy places in Kerala. All parts of this plant are bitter to taste and the nuts yield golden yellow bitter oil. Seed kernel contains 33% oil and used in ayurvedic medicine. SISO contains about 13.5% free fatty acids (FFA). During alkaline-catalyzed transesterification, high content FFA will react with alkali catalysts to produce soaps which will inhibit the transesterification for biodiesel production. Furthermore, the large amount of soap can gel and also prevent the separation of the glycerol from the ester (Demirbas, 2003). Acid-catalyzed transesterification, despite its insensitivity to FFA in the feedstock, has been largely ignored mainly because of its relatively slower reaction rate (Zhang *et al*., 2003a). Therefore a process combining pretreatment with alkaline-catalyzed transesterification for feedstocks having high FFA content was investigated by many authors (Canakci and Van Gerpen, 2001; Ramadhas *et al*., 2005; Veljkovic *et al*., 2006; Berchmans and Hirata, 2008).

Generally, when the FFA level is less than 2 mg KOH/g corresponding to a free fatty acid content of 1%, the FFA can be ignored. Alkaline refining, acid-catalyzed esterification, distillation, solvent extraction and membrane separation can be used for the reduction of FFA of vegetable oils (He, 2005). Also acid-catalyzed esterification of high FFA content vegetable oils is a typical method of biodiesel production due to high reaction speed and high yield (Canakci and Van Gerpen, 1999). Some raw feedstocks with high FFA such as yellow and brown grease (Canakci and Van Gerpen,2001), rubber seed oil(Ramadhas *et al*., 2005), mahua oil (Ghadge and Raheman, 2005,2006), tobacco seed oil (Veljkovic *et al*., 2006), waste cooking oil (Wang

Table 1. Fatty acid composition of SISO in comparison with the other oils (Ramadhas et al., 2005; Sahoo et al., 2007)

Fatty acid composition (%)	Formula	Structure	*Samadera indica* seed oil	Rubber (*Hevea brasiliensis*)	Karanja (*Pongamia pinnata*)	Jatropha (*Jatropha curcas*)
Palmitic acid	$C_{16}H_{32}O_2$	16:0	9.0	10.2	11.7	16.0
Stearic acid	$C_{18}H_{36}O_2$	18:0	7.4	8.7	7.5	6.5
Oleic acid	$C_{18}H_{34}O_2$	18:1	36.2	24.6	51.6	43.5
Linoleic acid	$C_{18}H_{32}O_2$	18:2	48.6	39.6	16.5	34.4
Linolenic acid	$C_{18}H_{30}O_2$	18:3	1.7	16.3	2.7	0.8

et al., 2007) and jatropha oil(Tiwari *et al.*, 2007) have been used to produce biodiesel with acid-catalyzed esterification followed by transesterification using alkaline catalyst.

The present work was undertaken to investigate the pretreatment process for reducing the FFA content of SISO to less than 1% for SISO biodiesel production. This paper focuses on the reaction parameters that affect the conversion of FFA in crude SISO by means of acid-catalyzed esterification with methanol. The main goal was to develop an approach that would enable us to understand the relationships between the variables and the acid value after pretreatment, and discuss the potential of SISO as a raw feedstock for biodiesel production.

EXPERIMENTAL

a. Materials

Samadera indica (gaertn.) Noofebom seed oil was purchased from Indian oil merchants located in the Wayanadu district, Kerala, India. *Samadera indica* (gaertn Nootebom) is abundantly available in this area. Methanol, sulphuric acid, sodium hydroxide, and other chemicals were of analytical reagent grade.

The unrefined *Samadera indica* seed oil used in this experiment was golden yellow in color with an initial acid value of 26.93 mg KOH/g. The fatty acid composition of *Samadera indica* seed oil in comparison with other oils is given in Table 1. *Samadera indica* seed oil consists of 16.4% saturation comprising of palmitic and stearic acids and 86.5% unsaturation comprising mainly of oleic, linoleic and linolenic acids. Saturation fatty acid methyl esters increase the cloud point, cetane number and improve stability whereas more polyun-saturates reduce the cloud point, cetane number and stability (Ramadhas *et al*.,2005).

b. Acid-catalyzed esterification of *Samadera indica* seed oil

200 ml of *Samadera indica* seed oil sample was taken into a round bottomed flask equipped with a reflux condenser and heated to 50°C temperature. 1% (v/v) H_2SO_4 in methanol (0.8% v/v) was added to the flask. The mixture was stirred and heated to 60-65°C. After the reaction, the mixture was taken in a separating funnel and allowed to settle for a period of 8 hrs. The top methanol-water layer was removed. The main objective of acid catalysed esterification was to reduce the acid value of the oils. The variables affecting the acid-catalyzed esterification such as methanol-to-oil molar ratio (3:1 - 11:1), catalyst amount (0.3 - 1.3 wt/v. % of oil) were studied (Junhua and Lifeng ,2008).

c. Alkali-catalyzed transesterification of Samadera indica seed oil

The pretreated Samadera indica seed oil was poured into a round bottomed flask equipped with a reflux condenser and heated to 60°C. 0.35% (w/v) of sodium hydroxide in 1.6% (v/v) methanol added to the reaction flask. The methanol to oil molar ratio was 9:1. Excess amount of sodium hydroxide was added to neutralize the residual FFA in the oil mixture. The mixture was allowed to react for 90 min at 60°C with the stirring speed of 600 rpm. After the completion of the reaction, the product was allowed to settle overnight in a separating funnel for separation of biodiesel. The lower glycerol layer was drawn off. The excess of methanol in the upper biodiesel layer was recovered by condensation. The reaction time depended on the type of feedstock used. After that, the biodiesel layer was washed and dried. This process was repeated for the complete conversion of 1000 ml/SISO.

d. Physico-chemical properties of SISO biodiesel

The physical and chemical properties are important criteria to assess the suitability of biodiesel under preparation for further use. The physicochemical properties of biodiesel namely, acid value, iodine value, saponification value, kinematic viscosity, density, flash point, cloud point, cetane number and heat of combustion of SISO biodiesel were determined under laboratory conditions. The cetane number (CN) and heat of combustion (HG) were calculated (Krishnangkura, 1986 and Krishnangkura, 1991) from the following equation by using the estimated saponification value (SV) and iodine value (IV).

Cetane number, $CN = 46.27 + 5458.3 / SV - 0.225\ IV$

Heat of combustion, HG of FAME = 618,000 / SV – 0.08 IV – 430

and compered the result with the standard limits of ASTM and European standards (ASTM, 2003 and EN 14214, 2003).

The fatty acid composition of biodiesel was determined by GC MS. The identification of gas chromatography (GC) peaks corresponding to the components of the methylester is based on the direct comparison of the retention time and mass spectral data with those for standard compounds.

GC MS analysis was performed using a Hewlett –Packard HP6890 N/5973 Gas chromatography/ mass spectrometer (HP, Minnesota, USA) equipped with a HP 5 silica capillary column (30m x 0.32mm, film thickness of 0.2µm). The carrier gas was helium; the inlet temperature was set at 280° C, while the column temperature was initially at 40° C (held for 3 minutes). The temperature was increased to 200°C at 20° C per minute (held for 10 minutes) and then to 210°C at 10° C per minute. The mass spectrometer was operated in the positive electron impact mode with ionization energy of 70 ev. The ion source temperature was 230°C. Mass units were monitored from 35 to 425/mz. The methyl ester component was identified by comparing their retention time and mass spectra with NIST mass spectral library.

RESULTS AND DISCUSSION

Effect of methanol-to-oil molar ratio and H_2SO_4 on reduction the acid value of SISO in acid esterification

Samadera indica seed oil had an initial acid value 26.93mg KOH/gm corresponding to FFA level of 13.54%, which was far away from 2% limit for satisfactory transesterification using alkali catalyst. Therefore, FFA content was first converted into esters by pretreatment process using an acid catalyst H_2SO_4 (1%v/v) to reduce the acid value of the *Samadera indica* seed oil was 1.79 mg KOH/gm. The acid value of after the pretreatment steps and methanol-to-oil molar ratio are shown in Table 2.

Table 2. Effect of methanol-to-oil molar ratio and H_2SO_4 on reduction the acid value of SISO in acid esterification

Molar ratio	Yield of Biodiesel (%)	Acid value (mgKOH/g)
3:1	60	4.21
5:1	71	3.51
7:1	83	2.86
9:1	95	1.79
11:1	97	1.71

The molar ratio of alcohol to vegetable oil is one of the important factors that affect the conversion efficiency as well as the production cost of biodiesel. The conversion efficiency is defined as the product of the process represented in terms of percentage. The optimal molar ratio of alcohol to oil for maximum conversion efficiency was determined for *Samadera indica* seed oil chosen in the present study. Methanol to oil molar ratio was found to vary from 3:1 to 11:1. The maximum ester conversions were obtained at the methanol to oil molar ratio of 9:1, the acid value was reduced to less than 2 mg KOH/g, which satisfies transesterification using an alkaline catalyst. With further increase in methanol to oil molar ratio, there was only a little improvement in the product yield. Therefore, the methanol to oil molar ratio was fixed at 9:1 for the transesterification process.

Moreover, it was observed that for high alcohol amount added the set up required longer time for the subsequent separation stage since separation of the ester layer from the water layer becomes more difficult with the addition of a large amount of methanol. This is due to the fact that methanol, with one polar hydroxyl group, can work as an emulsifier that enhances emulsion. Therefore, increasing the alcohol amount to oil is another important parameter affecting the biodiesel yield and biodiesel purity, apart from catalyst concentration and reaction time. This result is in line with the report of many investigations based on neat vegetable oils (Leung and Gue, 2006;Zhang *et al.*, 2003b; Freedman *et al.*, 1984)

Effect of catalyst amount on reduction of acid value of SISO in transesterification

The effect of catalyst amount varied in the range of 0.3–1.3% for six different values was investigated to find out the optimal concentration. The effect of catalyst on conversion efficiency is shown in Table 3. The optimal NaOH concentration required for the transesterification process to obtain maximum yield (87%) of biodiesel was 0.7% for the *Samadera indica* seed oil. Large amount of soap was observed in excess amount of sodium hydroxide added experiments. This is because addition of excess alkaline catalyst caused more triglycerides participation in the saponification reaction with sodium hydroxide, resulting in the production of more amount of soap and reduction of the ester yield (Leung and Gue, 2006). During the experiments, it was observed that complete transesterification was not possible with an insufficient amount of an alkali catalyst loading. After transesterification reaction acid was reduced to 0.45mg KOH/gm from 1.79 mg KOH/gm.

Table 3. Effect of catalyst amount on reduction of acid value of siso in transesterification

Catalyst concentration (%, w/v)	Yield of Biodiesel (%)	Acid value (mg KOH/g)
0.3	70	0.78
0.5	79	0.62
0.7	87	0.45
0.9	83	0.52
1.1	78	0.59
1.3	69	0.81

The high acid number can cause damage to injector and also result in deposits in fuel system and affect the life of pumps and filters. The maximum limit of acid value biodiesel is 0.50mgKOH/gm as prescribed in ASTM biodiesel standard ASTM D 6751 and European biodiesel standard EN 14214 (Moser,2009). The acid values of the biodiesel prepared from *Samadera indica* seed oil tested was within the biodiesel standard limit of ASTM D 6751 and EN 14214 in Table 4.

Properties of biodiesel

Fuel properties like, Kinematics Viscosity, Density, Flash point, acid value (AV), iodine value (IV) and saponification value (SV) were estimated. The cetane number (CN) and higher heating values (HHVs) of methyl ester were calculated based on the estimated SV and IV (Tables 4). The estimated SV and IV were 120.3 and 195.79 respectively. The CN value of the of methyl ester was 49 and the HG was 2717.38 (kg cal/mol). CN is the ability of fuel to ignite quickly after being injected. Better ignition quality of the fuel is always associated with higher CN value. This is one of the important parameter, which is considered during the selection of methyl esters for use as biodiesel. For this different countries/organization have specified different minimum values. Biodiesel standards of USA (ASTM D 6751), Germany (DIN V51606) and European Organization (EN 14214) have set this value as 47, 49, and 45- 50, respectively (biodiesel standard DIN, 1994; EN, 2003; ASTM, 1999). In our experiment SISO methyl ester has CN value within the limits all biodiesel standards.

Heat of combustion is the thermal energy that is liberated upon combustion, so it is commonly referred to as energy content. Higher calorific value and higher heat released during combustion leads to higher thermal efficiency. Lowering the calorific value due to the addition of the methyl esters leads to injection of higher quantity of the fuel to achieve the same power output as compared to diesel (Srivastava and Verma, 2008). Factors that influence the energy content of biodiesel include the oxygen content and carbon to hydrogen ratio. Generally, as the oxygen content of FAME is increased, a corresponding reduction in energy content is observed (De oliveira *et al*., 2009). Since the power developed by the engine is directly proportional to the heat energy liberated as a result of combustion and thus the heating value of a fuel has become a promising property (Saravanan *et al*.,2008).

Another important criterion for selection of methyl esters is its degree of unsaturation, which is measured as IV. To an extent, the presence of unsaturated fatty acid component in methyl esters is required as it restricts the methyl esters from solidification. However, with higher degree of unsaturation, methyl esters are not suitable for biodiesel as the unsaturated molecules react with atmospheric oxygen and are converted to peroxide, cross-linking at the unsaturation site can occur and the material may get polymerized into a plastic like body. At high temperature, commonly found in an

Table 4. physicochemical properties of siso after transesterification reaction

Parameters	Values				
	Initial	After acid esterification	After alkaline transesterification	ASTM Standards D 6751	European (EN 14214)
Acid value	26.93±1.10	1.79±0.32	0.45±0.25	0.50 mg KOH/g	0.50mgKOH/g
Iodine value	120.64±0.90	--	120.3±1.06	--	120I_2 /100g
Saponification value	223.0±2.22	209.84±1.05	195.79 ± 0.91	--	--
Kinematics Viscosity at 40°C	26.27	12.57	4.1	1.92 – 6.0(mm^2/s)	3.5-5.0 (mm^2/s)
Density	120.63	--	114.5	--	860-900 °C
Flash point	--	--	115	100-130°C min	--
Cetane index	--	--	47.12 ± 0.50	47 min	45-50
Heat of combustion (kg cal/mol)	--	--	2717.38±47.02	--	--

internal combustion engine, the process can get accelerated and the engine can quickly become gummed up with the polymerized methyl esters. To avoid this kind of situation, biodiesel standards have set a minimum limit of IV in their specifications. (EN 14214) (biodiesel standard EN, 2003).

The flash point is the lowest temperature at which fuel emits enough vapours to ignite. Flash points can indicate the possible presence of highly volatile or non flammable and combustible materials (Awang and May, 2007). The flash point does not affect combustion directly, but it makes biodiesel safer with regard to storage, fuel handling and transportation(Owen and Coley, 1995). The ASTM D 6751 standard specified a maximum flashpoint of 130° C though the intent is to get a minimum value of 100ºC. Flash points of SISO methylester was 115° C within the limits of ASTM standard.

Viscosity is defined as the resistance to flow of a fluid. Kinematic viscosity has been observed at 40ºC in SISO biodiesel was found 4.1mm^2/s which met ASTM D6751 and EN 14214 specifications (limits are 1.9– 6.0 mm^2/s in ASTM D6751 and 3.5–5.0 mm^2/s in EN 14214). High viscosity causes poor fuel atomization during the spray, increases the engine deposits, needs more energy to pump the fuel and wears fuel pump elements and injectors (Kinast, 2003). High viscosity also causes more problems in cold weather, because viscosity increases with decreasing temperature (Tat and Gerpen, 1999; Joshi and Pegg, 2007).

Generally, methyl esters with higher CN are favored for use as biodiesel. However, with increase of CN, IV decreases which means degree of unsaturation decreases. This situation will lead to the solidification of methyl esters at higher temperature. To avoid this situation, the upper limit of CN has been specified in US biodiesel standards (ASTM D 6751-99 & ASTM PS 121-99). In the present study, SISO biodiesel showed all the physicochemical parameters estimated were met the limits of biodiesel standards ASTM D6751 and EN 14214 specifications. So SISO methylesters is suitable to use as a source for large scale production of biodiesel.

GC MS of *samadera indica* oil methylester are presented in Fig. 1. It was found that oleic acid was predominant fatty acid in SISO methylester. Oleic and linoleic acids comprised more than 80% of the fatty acid composition. Total unsaturated fatty acid was calculated to be 73.07%, which was higher than the total saturated fatty acid content.

The smoke density of blends (B5, B20 and B50) of *S.indica* FAME was found to be 37.9%, 39.7% and 47.6% (minimum smoke density), 43.0%, 43.5% and 52.8% (maximum smoke density) respectively. The smoke density of B50 blend of *S.indica* FAME was slightly higher than diesel fuel tested (Fig.2)

CONCLUSIONS

The study on the biodiesel production process in *Samadera indica* seed oil which contained high FFA level showed that the quantity of catalyst and

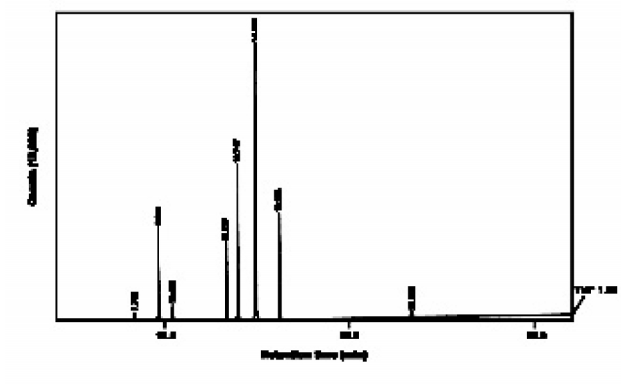

Fig. 1. GCMS of *samadesr indica* biodiesel

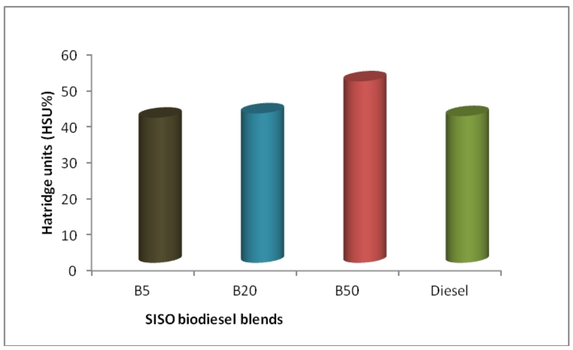

Fig. 2. Smoke density of SISO biodiesel blends (B5,B20,B50) and diesel

amount of methanol are the main factors affecting the production of methyl esters. The optimal values of these parameters for achieving maximum conversion of oil to esters. *Samadera indica* seed oil had an initial acid value 26.93mg KOH/gm corresponding to FFA level of 13.54%, which was first converted into esters by pretreatment process using an acid catalyst H_2SO_4 (1%v/v) to reduce the acid value to 1.79 mg KOH/gm which less than 2% limit for satisfactory transesterification using alkali catalyst. After transesterification reaction acid value reduced in to 0.45 mg KOH/gm. Addition of excess catalyst causes more triglycerides' participation in the saponification reaction leading to a marked reduction in the ester yield. Biodiesel production process is incomplete when the methanol amount is less than the optimal value. Operating beyond the optimal value, the ester yield would not be increased but will result in additional cost for methanol recovery. The optimal reaction conditions for production of methyl esters from *Samadera indica* seed oil are established as 72 ml of methanol for 200 ml of oil and 0.7 wt. % of NaOH catalyst for obtaining maximum yield of biodiesel. 92% of the biodiesel were obtained from 1000 ml of biodies. Based on the physico chemical parameters estimated, the *Samadera indica* seed oil methyl ester is suitable to use as a biodiesel. Thus, biodiesel derived from the sample used in the present study is an acceptable substitute for petrodiesel. Therefore, *Samadera indica* seed oil can be used as a raw feedstock for producing biodiesel in commercial scale in India

REFERENCES

ASTM. American Standards for Testing of Materials. 2003. D 189–01, D 240–02, D 4052–96, D 445–03, D482–74, D 5555–95, D 6751–02, D 93–02a, D 95–990, D97–02.

Awang, R. and May, Y.C. 2007. Effect of hydroxylated compounds on properties and emissions of palm biodiesel. *Amer. J. Appl. Sc*., 4: 99-101.

Berchmans, H.J. and Hirata, S. 2008. Biodiesel production from crude *Jatropha curcas* L. seed oil with a high content of free fatty acids. *Bioresource Technology*, 99: 1716–1721.

Biodiesel standard, DIN V51606, Germany 1994. (b) Biodiesel standard, EN 14214, European Standards Organization 2003. (c) Biodiesel standard, ASTM D 6751, USA 1999. (d) Biodiesel standard, ASTM PS 121, USA 1999.

Canakci, M. and Van Gerpen, J. 1999. Biodiesel production via acid catalysis. *Transactions of the ASAE,* 42(5): 1203–1210.

Canakci, M. and Van Gerpen, J. 2001. Biodiesel production from oils and fats with high fatty acids. *Transactions of the ASAE,* 44 (6): 1429–1436.

Carraratto C., Macor A., Mirandola, A. Stoppato, A. and Tonon, S. 2004. Biodiesel as alternative fuel: Experimental analysis and energetic evaluations. *Energy*, 29: 2195–2211.

De Oliveira, S.J., Polyanna M. Leite, Lincoln B. de Souza, Vinicius M. Mello, Eid C. Silva, Joel C. Rubim, Simoni M.P. Meneghetti and Paulo A.Z. Suarez. 2009. Characteristics and composition of *Jatropha gossypiifolia* and *Jatropha curcas* L. oils and application for biodiesel production. *Biom. Bioen.*, 33: 449-453.

Demirbas, A. 2003. Biodiesel fuels from vegetable oils via catalytic and noncatalytic supercritical alcohol transesterifications and other methods: a survey. *Energy Conversion and Management*, 44: 2093–2109.

EN 14214. European standard for biodiesel. 2003. http://www.din.de.

Freedman, B., Pryde, E.H. and Mounts, T.L. 1984. Variables affecting the yield of fatty esters from transesterified vegetable oils. *Journal of the American Oil Chemists' Society,* 61: 1638–43.

Gerpen J.V. 2005. Biodiesel processing and production. *Fuel Processing Technology*, 86(10): 1097-1107.

Ghadge, S.V. and Raheman, H. 2005. Biodiesel production from mahua (*Madhuca indica*) oil having high free fatty acids. *Biomass and Bioenergy*, 28: 601–605.

Ghadge, S.V. and Raheman, H. 2006. Process optimization for biodiesel production from mahua (*Madhuca indica*) oil using response surface methodology. *Bioresource Technology,* 97: 379–38

Guo and Yan. 2005. Alkaline-Catalyzed Production of Biodiesel Fuel from Virgin Canola Oil and Recycled Waste Oils. Ph.D. Thesis, 1-205.

Hanny Johanes Berchmans and Shizuko Hirata. 2008. Biodiesel production from crude *Jatropha curcas* L. seed oil with a high content of free fatty acids. *Bioresource Technology,* 99: 1716–1721.

He, D.P. 2005. Technology of Oils and Fats Refining. Chemical Industry Press, Beijing.

Joshi, R.M. and Pegg, M.J. 2007. Flow properties of biodiesel fuel blends at low temperatures. *Fuel.,* 86:(12): 143-51.

Junhua Zhang and Lifeng Jiang. 2008. Acid-catalyzed esterification of Zanthoxylum bungeanum seed oil with high free fatty acids for biodiesel production, *Bioresource Technology*, 99: 8995–8998..

Kinast, J.A. 2003. Production of biodiesels from multiple feedstocks and properties of biodiesels and biodiesel-diesel blends. National renewable energy laboratory final report, Golden, Colorado, Bettle, Beehted. NREL/SR-510-31466:1-47.

Korbitz, W. 1999. Biodiesel Production in Europe and North America, An Encouraging Prospect. *Renewable Energy*, 16: 1078 – 1083.

Krisnangkura, K.A. 1986. A simple method for estimation of cetane index of vegetable oil methyl esters. *J. Am. oil Chem. Soc.*, 63: 552-553.

Krisnangkura, K.A. 1991. Estimation of Heat of Combustion of Triglycerides and Fatty acid Methyl esters. *J. Am. oil Chem. Soc.*, 68(1): 56-58.

Leung, D.Y.C. and Gue, Y. 2006. Transesterification of neat and used frying oil: optimization for biodiesel production. *Fuel Processing Technology,* 87:883–90.

Mohamad I.A.W., Ghassan T. and Mohd A.Q. 2002. Utilization of ethyl ester of waste vegetable oils as fuel in diesel engines. *Fuel Processing Technology*, 76: 91-103.

Owen, K. and Coley, T. 1995. Automotive fuels Reference Book, 2nd ed., society of Automotive Engineers, Warrendale, PA, USA.

Ramadhas, A.S., Jayaraj, S. and Muraleedharan, C. 2005. Biodiesel production from high FFA rubber seed oil. *Fuel,* 84: 335–340.

Sahoo, P.K., Das, L.M., Babu, M.K.G. and Naik, S.N. 2007. Biodiesel development from high acid value polanga seed oil and performance evaluation in a CI engine. *Fuel,* 86: 448–454.

Saravanan, S., Nagrajan, G. and Lakshmi Narayana Rao, G. 2008. Effect of FFA of crude Rice Bran oil on the properties of diesel blends. *J. Am. oil Chem. Soc.*, 85: 663-666.

Srivastava, P.K. and Verma, M. 2008. Methyl Ester of Karanja oil as an Alternative Renewable Source of Energy. *Fuel,* 87: 1673-1677.

Subramanian, K.A., Singal, S.K., Saxena, M and Sighal, S. 2005. Utilization of liquid biofuels in automotive diesel engines: An Indian perspective. *J. Biom. Bioen.*, 29: 65–72.

Tat, M.E. and Gerpen, J.V. 1999. The kinematic viscosity of biodiesel and its blends with diesel fuels. *JAOCS.*, 76(12: 1511–3.

Tiwari, A.K., Kumar, A. and Rahemen, H. 2007. Biodiesel production from jatropha oil (*Jatropha curcas*) with high free fatty acids: an optimized process. *Biomass and Bioenergy,* 31: 569–575.

Veljkovic, V.B., Lakicevic, S.H., Stamenkovic, O.S., Todorovic, Z.B. and Lazic, M.L. 2006. Biodiesel production from tobacco (*Nicotiana tabacum* L.) seed oil with a high content of free fatty acids. *Fuel,* 85: 2671–2675.

Wang, Y., Ou, S., Liu, P. and Zhang, Z. 2007. Preparation of biodiesel from waste cooking oil via two-step catalyzed process. *Energy Conversion and Management,* 48(1): 184–188.

Zhang X., Peterson C., Reece D., Haws R. and Mller G. 1998. Biodegreadability of biodiesel in the aquatic environment. *Transactions of the ASAE*, 41(5): 1423-1430.

Zhang, Y., Dube, M.A., McLean, D.D. and Kates, M. 2003a. Biodiesel production from waste cooking oil: 1. Process design and technological assessment. *Bioresource Technology,* 89: 1–16.

Zhang, Y., Dubé, M.A., McLean, D.D. and Kates, M. 2003b. Biodiesel production from waste cooking oil: 2. Economic assessment and sensitivity analysis. *Bioresource Technology,* 90: 229–240.