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Full Length Research Paper

Optimization of base catalyzed transesterification of peanut oil biodiesel

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This paper is confined to the production and physico-chemical characterization of peanut oil biodiesel (POB). An optimum conversion of POB from triglycerides (TD) was achieved by using 1:6 molar ratio (methanol : oil) at 60°C. Fuel properties of POB were determined and compared with ASTM (American Standard Testing Material). The kinemetic viscosity at 40°C (eta) of POB (100%) was 5.908, specific gravity 0.918, density at 40°C (Rho) 0.0992, flash point (FP) 192, pour point (PP) 3°C, cloud point (CP) 6°C, and sulfur contents 0.0087. The engine performance by using POB in terms of consumption, efficiency and power output was quite comparable with petro-diesel (PD). It is concluded that most important factors affecting the fatty acid methyl esters (FAME) yield during transesterification are molar ratio of methanol to oil and reaction temperature.

Key words: Fatty acid methyl esters (FAME), transesterification, *Arachis hypogea* oil.

INTRODUCTION

There is a renewed interest in evaluating crop species as alternative sources of non- conventional energy since fossil fuels are quickly being depleted. Utilization of vegetables oils as an alternative source of energy is gaining greater importance throughout the world (Goering et al., 1982; Schwab et al., 1987). There are several reports of plant species evaluated for their potential as an alternate source of energy and hydrocarbon (Wang and Hufman, 1981). The vegetable oils like soybean oil in USA, rapeseed oil in Europe and palm oil in countries with tropical climate such as Malaysia are being used for the production of biodiesel (Knothe, 2002).

Among these oil yielding crops, *Arachis hypogea* is an oil seed bearing crop with 36% oil. The peanut, or groundnut (*A. hypogaea*) is a species in the legume family Fabaceae native to South America, Mexico and Central America (Dillehay, 2007). It is an annual herbaceous plant growing 30 to 50 cm tall. The leaves are opposite, pinnate with four leaflets, each leaflet 1 to 7cm long and 1 to 3 cm broad. The flowers are a typical 3 to 7 cm long containing 1 to 4 seeds. The direct use of vegetable oils in fuel engines is problematic. Due to their peaflower in shape, 2 to 4 cm across, yellow with reddish veining. After pollination, the fruit develops into a legume high viscosity and low volatility, they do not burn completely and form deposits in the fuel injector of diesel engines (Demirbas, 2003). Different ways have been considered to reduce the high viscosity of vegetables oils. Transesterification (Figure 1) with methanol or ethanol is considered to be basic process for conversion of crude vegetable oil to biodiesel (BD). BD is the name for a variety of ester based oxygenated fuel from renewable biological resources. It can be used in compression ignition engines with little or no modifications (Demirbas, 2002). BD is a renewable, domestic resource with an environmentally friendly emission profile, readily available and biodegradable (Zhang et al., 2003). BD has become more attractive recently because of its environmental benefits (Ramadhas et al., 2004). The aim of this study was to investigate optimum production, physico.chemical characterization and performance of environment friendly Peanut oil biodiesel (POB).

MATERIALS AND METHODS

Materials

Peanut seeds were supplied by oil seeds program National Agriculture Research Center (NARC), Islamabad. Catalyst NaOH, analytical reagent grade.

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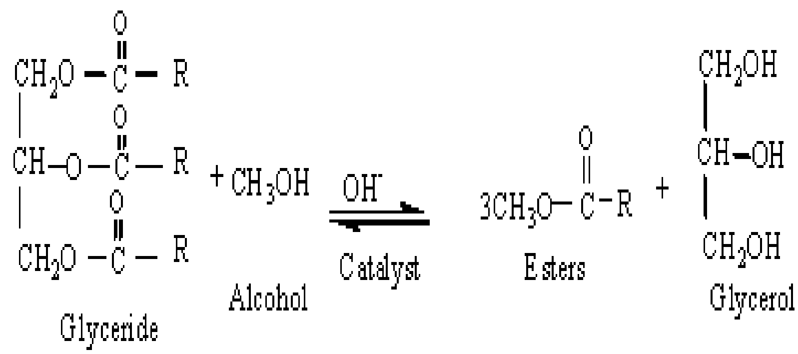

Figure 1. Transesterification reaction.

Oil extraction

Peanut oil was extracted from seeds by using electric oil expeller (KEK P0015-10127 Germany). The oil after extraction was subjected to filtration for purification by using filtration apparatus (W.S Automa).

Transesterification

Refined oil was converted to fatty acid methyl esters (FAME) according to standard procedure (catalytic low-temperature using NaOH as catalyst) described elsewhere (Freedman et al., 1986; Darnako and Cheryan, 2000). 2 liters of refined peanut oil was heated up to 120°C on hot plate (VWR, VELP- Scientifica Germany). Sodium methoxide was prepared by adding 12.5 gm NaOH in 400 ml of methanol. Sodium methoxide was added to oil when its temperature falls down up to 60°C. 0.6 ml of vinegar was added to remove unreacted base, glycerol and trace amount of soap. To obtain pure biodiesel, methods of washing with hot distilled water, dissolving in petroleum ether and then washing with hot distilled water, and neutralization with H_2SO4 (1:1) were performed in the refining process (Karaosmanoglu et al., 1996). The biodiesel after separation was washed using same amount of hot water (60°C) for three times to remove catalyst, NaOH and glycerol. The moisture in biodiesel was removed by using anhydrous sodium sulphate.

Fuel properties

Biodiesel was tested for fuel properties according to ASTM Standards. Fuel characteristics of biodiesel and petro-diesel (PD) include dynamic viscosity at 40°C (eta), kinematic viscosity at 40°C (ny), density at 40°C (Rho), color comparison, flash point (°C), cloud point (°C), pour point (°C), specific gravity at 60°F (Kg/1), sulfur contents (%), cetane index and distillation.

Fuel performance

The conventional diesel engine can be operated with biodiesel without modification in the engine (Clark et al., 1984). Engine performance of POB and PD in terms of fuel consumption, efficiency and power outputs were calculated in road run test. Compared to hydrocarbon based diesel fuels, the higher cetane number of biodiesel resulted in shorter ignition delay and longer combustion duration and hence, low particulate emissions.

RESULTS AND DISCUSSION

Transesterificaton of crude oil to FAME

The chemical process used for the production of methyl ester (Biodiesel) from crude oil is known as transesterification (also called alcoholysis). There are numerous transesterification citations in the scientific and patent literature (Bradshaw and Meuly, 1944; Freedman et al., 1984; Freedman et al., 1986; Schwab et al., 1987; Allen et al., 1945; Trent, 1945; Tanaka et al., 1981; Wimmer, 1992b; Ma et al., 1998a; Ma et al., 1998b and Ma et al., 1999). Among the alcohol that can be used in transesterification process are methanol, ethanol, propanol, butanol and amyl alcohol. During the transesterification of peanut oil, methanol was used to dissolve NaOH crystals (catalyst). Methanol is used most frequently because of its low cost and its physical and chemical advantages. It can quickly react with triglycerides (TD) and NaOH is easily dissolved in it (Ma and Hanna, 1999).

A catalyst is used to improve the reaction rate and yield. Catalysts are classified as alkali, acid or enzyme. In the transesterification process NaOH was used as a catalyst, as it exhibited the best behavior. The best results of NaOH catalyst were obtained in the range of 3.4% (weight of NaOH/weight of oil). Alkali-catalyzed transesterification is much faster than acid-catalyzed (Freedman et al., 1984). However if a glyceride has higher free fatty acid (FFA) contents and more water then acid-catalyzed transesterification is suitable (Sprules and Price, 1950; Freedman et al., 1984). Because reaction between the oil and alcohol is reversible, excess alcohol is used to shift equilibrium to the products side (Ma and Hanna, 1999).

Higher molar ratio results in a greater ester conversion in a shorter time. The molar ratio of oil to methanol during the transesterification process was fixed at 6:1. In the ethanolysis of peanut oil, a 6:1 molar ratio liberated significantly more glycerine than did a 3:1 molar ratio (Feuge and Grose, 1949). Freedman et al. (1984) studied the effect of molar ratio (from 1:1 to 6:1) on ester conversion with vegetable oils. Soybean, sunflower, peanut and cottonseed oils behaved similarly and achieved highest conversions (93-98%) at a 6:1 molar ratio. Tanaka et al. (1981) in his novel two-step transesterification of oils and fats such as tallow, coconut oil and palm oil, used 6:1-30:1 molar ratios with alkali catalysis to achieve a conversion of 99.5%.

The most important finding of this experiment was that a direct use of peanut crude oil can be realized as a raw material for catalyzed (NaOH) transesterification. Therefore, in addition to a simpler purification process, a high yield of FAME can be obtained through transesterification of peanut oil. This catalyzed transesterification method is more effective and efficient, therefore offers a potentially low cost with simpler technology for producing an alternative fuel for diesel engines. The considerable yield of FAME by the environment friendly method renders this technique ideally suitable for industrial application. The conversion rate increases with reaction time. Freedman et al. (1984) transesterified peanut, cottonseed, sunflower and soy-bean oils under the condition of methanol to oil ratio of 6:1, 0.5% sodium methoxide catalyst at 60℃. Rudolf Diesel, the inventor of compression-ignition engines, used first time peanut oil in 1900, while the fuel properties tests are almost always positive (Mazel et al., 1985 and Samson et al., 1985). The physico-chemical characteristics of peanut oil biodiesel (POB) closely resemble those of diesel fuel. This has been documented by many workers (Clark et al., 1984; Mittetbach and Tritthart, 1988).

It was found that peanut plant is suitable for biodiesel production for its high oil recovery and quality of oil. During the transesterification process conversion of crude oil into biodiesel was 88%. Conversion of crude oil to fatty acid methyl esters (FAME) was optimum at 60°C (Figure 2). Free fatty acid (FFA) contents in peanut oil were less than 2%. Anggraini and Wiederwertung (1999) found that FFA contents make the conversion of crude oils into biodiesel possible, conversion efficiency decreases considerably if FFA contents of > 3%. If oils with FFA contents of >3% were used, the transesterification would not occur (Dorado et al., 2002). Bradshaw and Meuly (1944) and Feuge and Grose (1949) also stressed the importance of oils being dry and free (<0.5%) of free fatty acid. Freedman et al. (1984) stated that ester yields were significantly reduced if the reactants did not meet these requirements.

Quality specification of POB

Physico-chemical characteristics of POF remain almost similar to high-speed diesel (HSD). The results of fuel properties are shown in Table 1 and quite comparable to those reported by Lotero et al. (2005), Peterson et al. (1992) and Encinar et al. (2005). Dynamic viscosity (eta), kinematic viscosity (ny) and density (Rho) at 40°C were measured by ASTM D975. The viscosity of transesterified oil, i.e., biodiesel, is about an order of magnitude lower than that of the parent oil (Dunn et al., 2001). The acceptable and prescribed range of viscosity at 40°C for biodiesel by ASTM Standard D675 is 1.9-6.0 mm^2/s. In this work the kinematic viscosity at 40°C of POB was 5.908. Kinematic viscosity has been included in biodiesel standards (1.9–6.0 mm2/s in ASTM D6751 and 3.5–5.0 mm2/s in EN 14214). It can be determined by standards such as ASTM D445 or ISO 3104 (Lee et al., 1995). Values for kinematic viscosity of numerous fatty acid methyl esters have been reported (Gouw et al., 1996). The difference in viscosity between the parent oil and the alkyl ester derivatives can be used to monitor biodiesel production (Fillipis et al., 1995). The effect on viscosity of blending biodiesel and conventional petroleum-derived diesel fuel was also investigated (Tat and Gerpen, 1999).

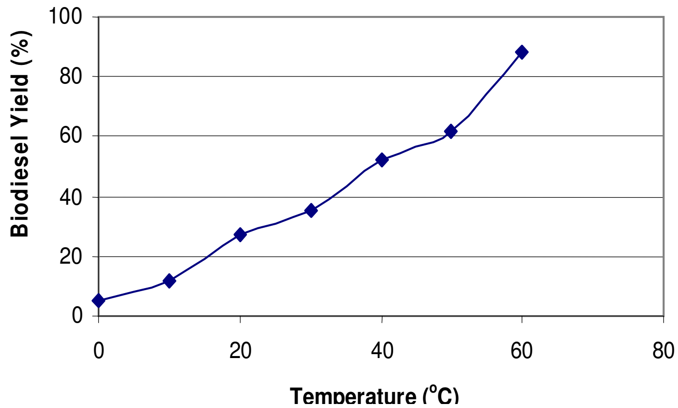

Figure 2. Effect of temperature on conversion of peanut oil to biodiesel at 1:6 molar ratio.

Viscosity refers to the thickness of the oil, and is determined by measuring the amount of time taken for a given measure of oil to pass through an orifice of the specific size. Viscosity affects injector lubrication and fuel automization. Fuels with low viscosity may not provide sufficient lubrication for the precision fit of fuel injection pumps, resulting in leakage or increased wear. Fuel automization is also affected by fuel viscosity. Diesel fuels with high viscosity tend to form larger droplets on injection, which can cause poor combustion, increased exhaust smoke and emissions (Encinar et al., 2002). The maximum specified ASTM value of viscosity is 4.0 cSt at 40℃ (Ma and Hanna, 1999). Wang et al. (2006) reported that high viscosity may lead to poor atomization of the fuel, incomplete combustion, choking of the injectors, ring carbonization and accumulation of the fuel in the lubricating oils. A way to avoid those problems and to improve the performance is to reduce the viscosity of vegetable oil. There are some methods to reduce the viscosity of vegetable oil such as fuel blending.

The specific gravity of peanut was 0.918, which matched with specific gravity of mineral diesel i.e. 0.847. Depending on the feedstock used, biodiesel specific gravity varies between 0.85-0.89. These results are nearly equal to those of Tat and Gerpen (1999). Flash point (FP) of POB was 192, which is higher than the

Table 1. Fuel Characteristics of POB and its blends.

Fuel properties	B 100 %	B 5 %	B 10%	B 20%	HSD ASTM D975
Dynamic Viscosity at 40°C (eta)	5.971	3.063	3.124	3.4246	3.2642
Kinematic Viscosity at 40°C (ny)	5.908	3.675	3.754	5.0450	1.3-4.1
Density at 40°C (Rho)	0.0992	0.8336	0.8323	0.84417	0.8295
Color Comparison	2.0	1.0	1.0	1.5	1.0
Flash point, °C	192	70	72	76	74
Pour point, °C	3	3	0	0	0
Cloud point, °C	6	3	3	3	6
Specific gravity Kg/1at 60°F	0.918	0.815	0.852	0.861	0.847
Sulfur contents, %	0.0087	0.5696	0.5016	0.4694	0.5862
Distillation IBP, °C	-	172.4	174.5	196.2	180.4
5%	-	198.2	199.3	210.3	201.4
10%	-	218.3	212.5	227.9	214.7
20%	-	236.5	245.9	234.8	235.7
30%	-	264.7	2068.0	256.6	261.0
40%	-	282.0	287.6	284.3	279.1
50%	-	300.9	302.8	309.1	295.1
60%	-	316.8	318.5	317.2	308.8
70%	-	330.9	335.0	332.7	322.5
80%	-	345.2	347.6	345.8	337.6
90%	-	366.5	370.0	366.9	356.9
FBP	-	402.9	419.2	428.0	374.1
%	-	97.5	97.2	97.3	97.7
%r	-	1.7	1.5	2.1	1.9

*ASTM=American Standard Testing Materials; HSD, High Speed Diesel; B100, Pure Biodiesel; B5, 5% POB + 95%HSD; B10,10% POB + 90%HSD; B20, 20% POB + 80%HSD; POB, Peanut oil Biodiesel.

mineral diesel. Flash point is the temperature at which the vapors above the fuel become flammable. Petroleum based diesel fuels have flash points of 50 to 80°C. Biodiesel has a flash point that is considerably higher than petroleum based diesel fuel. This means that the fire hazard associated with transportation, storage and utilization of biodiesel is much less than petroleum based diesel fuels. The flash point is a parameter that determines the safety of biodiesel during its handling and storage. The cloud point (CP) of POB was 6°C and pour point was 3°C which are in accordance with ASTM standards. There are various measures applied to describe the pour point (ASTM D-97), cloud point (ASTM D-2500) (Clements, 1996).

The other fuel properties like distillation (IBP) and color comparison are considered as important parameters in the characterization and specification of biodiesel. These all parameters showed similar behavior and their values meet the international biodiesel standard. The sulphur contents of POB were in traces as compared to HSD. Sulphur contents of POB were 0.0087, so that one could say that biodiesel is environmentally friendly. Unlike hydrocarbon-based fuels, the sulphur content of vegetable oils is close to zero and hence, the environmental damage caused by sulphuric acid is reduced. Moreover, vegetable oils take away more carbon-dioxide from the environment during their produc-tion than is added to it by their later combustion (Srivastava and Prasad, 2000).

Engine efficiency of POB

Engine efficiency of POB with reference to power consumption is shown in Table 2. Barsin et al. (1981) reported that when diesel engine was run with vegetable oil as fuel, produced equivalent power to that of the diesel fuel because fuel mass flow energy delivery increased due to higher density and viscosity of vegetable oil. It also increased fuel flow by reducing internal pump leakage. The lower mass-based heating values of vegetable oils required larger mass fuel flow to maintain constant energy input to the engine. Engine performance was nearly the same in terms of engine torque and horsepower with that of mineral diesel, but in case of biodiesel the emission profile was very low, which practically proves that biodiesel is environmentally friendly. Many researchers like Barnwal and Sharma (2005), Vellguth (1983) and Shankar et al. (2005) repor-ted that the CO, CO_2 and other emissions are reduced in biodiesel and its blends.

Table 2. Fuel performance of POB.

S/N	Fuel	Consumption rate	Efficiency
01	Diesel (HSD)	09.3 Lit/h	15.5 %
02	B100%	09.4 Lit/h	15.6 %
03	B20%	09.6 Lit/h	16.0 %
04	B10%	09.7 Lit/h	16.1 %
05	B5%	09.8 Lit/h	16.3 %

CONCLUSION

It is concluded from this study that peanut oil has low contents of saturated free fatty acid (FFA) and is suitable source for biodiesel production. In order to achieve maximum yield of biodiesel, transesterification of crude oil of this species was carried out at 60°C at 1:6 molar ratio. The fuel properties of POB were tested according to ASTM. Engine performance in terms of fuel consumption, efficiency and power out puts were comparable with petroleum-based diesel. The emission profile of POB was very low that proves that biodiesel is environmental friendly. Keeping in view all these properties it is concluded that in order to overcome the energy crises in future, mega cultivation of this crop may be carried out for biodiesel production at larger scale.

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