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Full Length Research Paper

Base catalyzed transesterification of sunflower oil biodiesel

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In this study, sunflower oil was investigated for biodiesel production. Sunflower is one of the leading oil seed crop, cultivated for the production of oil in the world. It has also been considered as an important crop for biodiesel production. Seeds for biodiesel production were procured from local farmers of Attock and Rawalpidni divisions. Electric oil expeller was used for the extraction of crude oil. Base catalyzed transesterifiction process is applied for optimum yield (80%) of biodiesel. Fuel properties of sunflower oil biodiesel were compared with American Society for Testing and Materials (ASTM). Engine efficiency of biodiesel with reference to power, efficiency and consumption of biodiesel blends (B100, B20 and B5) were determined. It was concluded that sunflower oil is one of the option for biodiesel production at a large scale depending on its mass cultivation.

Key words: Sunflower oil, transesterification, biodiesel, energy.

INTRODUCTION

Renewable energy is a commodity just like any other form of energy. It has a major role to play in meeting the needs of global energy demand and in combating the danger of global warming. The interest in many vegetable oils as diesel fuel substitutes is increasing and various oil containing crops are grown for this purpose. Vegetable oils, after been processed, can be used directly, blended in mixtures with diesel fuel, or inter-esterified and used in existing compression ignition engines. The commercial success of such fuels depends on their physical and chemical characteristics, their economic competitiveness compared with petroleum based fuels and on the achievement of a positive energy balance which in part depends on the energy input required to produce the oilseeds. Vegetable oils from crops such as soyabean, peanut, sunflower, rape, coconut, karanja, neem, cotton, mustard, Jatropha, linseed and castor have been evaluated in many parts of the world in comparison with other non-edible oils (Murugesan et al., 2008).

Spain, as most European countries, do not have enough reserves of fossil resources, which implies a dependency on petroleum imports in order to provide for the demand of petrol and diesel fuel in the transport sector. The supply of part of the demand with biodiesel would contribute to decreasing this dependency. On the other hand, energy crops have been considered as one of the best alternatives in the agricultural sector, its production for food purposes has been limited by the Production Association for Crops (PAC), thus allowing the development of new industries such as the agro-energy industry with employment creation and regional development. The production and yield forecast of this energy crop, as well as the possibilities of substituting diesel fuel by biodiesel, have

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Abbreviations: FAME, Fatty acid methyl ester; **HSD,** high speed diesel; **FFA,** free fatty acid; **IBP,** initial boiling point.

been studied, and it is established that it is possible to substitute approximately 4% of the diesel fuel consumed in the region by biodiesel obtained from sunflower oil (Coteron et al., 1997).

Sunflower is one of the leading oilseed crops cultivated for the production of oil in the world. It has also been considered as an important crop for biodiesel production, particularly in southern European countries. In Greece, sunflower is mainly grown in Evros in the northern part of the country, where more than 70% of the sunflower cultivated area is located. It is usually cultivated on non-irrigated clay loamsoils in a rotation with winter cereals (Schumacher et al., 1996; Ali et al., 1995).

About 80% of Europe's total biofuel is comprised of biodiesel produced from rapeseed and sunflower seeds. In 2005, EU (European Union) accounted for nearly 89% of all biodiesel production worldwide. 1.9 billion liters or more than half the world total biodiesel is produced by Germany (Anonymous, 2006).

Helianthus annuus L. (Sunflower) is a plant in the family Asteraceae. The oil contents of the sunflower varieties can vary from 38 to 50%. The plant is erect, often unbranched, fast growing, annual herb; stems 0.7 to 3.5 m tall; leaves alternate, ovate; flowering head terminal on main stem, 10 to 40 cm in diameter, achenes obovoid, compressed, slightly 4-angled; seeds are 0.5 to 1.5 cm in length and 0.3 - 0.9 cm in diameter. As with safflower, sunflower has a deep root system that can extract water and nutrients from the soil profile deeper than small grains. It responds to irrigation with yields increasing at about 150 pounds of seed per inch of water after the first seven inches.

Detailed systematic work has not been reported with reference to biodiesel of sunflower in Indo-Pak subcontinent. Therefore, keeping in view the energy crisis throughout the world, the present research work was based on evaluating the sunflower oil as source of renewable energy. The present study analyzed the fatty acid methyl ester (FAME) production, fuel properties analysis, determination of efficiency performance and fuel consumption in ordinary diesel engine.

MATERIALS AND METHODS

Seeds for biodiesel production and characterization were collected from resource based areas of the country during field trips. The seeds were also purchased from seed markets of Attock and Rawalpindi.

Biodiesel production

Oil extraction

Electric oil expeller (KEK P0015, 10127 Germany) was used for the extraction of crude oil from seeds. When extraction was completed, oil cakes were obtained as a by-product.

Transesterification

Transesterification consists of a number of consecutive, reversible reactions (Schwab et al., 1987 and Freedman et al., 1984). Whole process carried out in the biodiesel laboratory was summarized as:

Oil filtration: In the first step of transesterification, the crude vegetable oil was filtered with the help of electric filter (W. S Automa 2). Filtration was carried out in order to remove the impurities from the crude oil.

Thermal decomposition of triglycerides: Filtered oil was heated on hot plate (VWR, VELP- Scientifica Germany) for up to 120°C. Heating was carried out in order to break triglycerides into di and monoglycerides and to remove free fatty acid from the crude filtered oil.

Mixing of sodium methoxide: Sodium methoxide was prepared by dissolving NaOH (catalyst) in methanol in a fixed ratio (1:31). It was mixed with oil at 60°C, which is considered as optimal temperature for the conversion of triglycerides into FAME. Temperature clearly influenced the reaction rate and yield of esters. The molar ratio of methanol to oil was fixed at 1:6, which is optimal ratio for the transesterification of vegetable oils (Ahmad et al., 2008). Then oil was allowed to settle at room temperature for about 8 - 10 h. Glycerin and soap (by-products) were separated from the crude methyl ester after settling.

Biodiesel washing

Crude methyl ester was purified by washing gently with warm water. Washing was carried out at pH 4.5 in order to neutralize the residual catalyst and soap. Excess amount of water may be present in the washed methyl esters. According to the ASTM standard of biodiesel, this amount of water must be lowered to a maximum of 0.05% (v/v) (Anonymous, 2002). Anhydrous sodium sulfate (Na_2SO_4) was used to remove excess amount of water.

Fuel properties analysis

Fuel properties analysis was carried out according to ASTM Biodiesel Standards. Fuel characteristics of biodiesel and high speed diesel (HSD) which were tested 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.

Engine testing

The conventional diesel engine can be operated with biodiesel without modification in the engine (Clark et al., 1984). Engine performance of biodiesel and mineral diesel 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

Rising income and growing populations have increased energy demand. Energy is required in almost all aspect of every day life including agriculture, drinking water, lighting health care, telecommunication and industrial activities. Presently, the demand of energy is met by fossil fuels (coal, petroleum and natural gas). However, at the current rate of production, the world production of liquid fossil fuel (petroleum and natural gas) will decline by the year 2012. As energy consumption grows, so does emissions of greenhouse gases, with significant impact on global climate change. Scientific assessment based on the available instrumental observational records from the industrial era to the present day showed that global mean temperature has increased to between 0.3 and 0.6°C since the 19th century, while the mean sea level has risen between 10 and 25 cm over the same period. Renewable energy technologies are environment friendly and contribute effectively towards sustainable development. Recognizing the importance of the energy availability and stability to stimulate economic growth, the Malaysian government introduced the four-fuel strategy namely: Petroleum, natural gas, hydropower and coal to reduce the over dependence upon petroleum and to ensure reliability and security of supply. The success of the diversification policy is reflected in the reduced dependence on petroleum. Petroleum dependence for the power generation sector has been cut down from 98% in 1980 to 8% in 1999. Recently, the government has included renewable energy as the fifth fuel and thereby, increased the role of renewable energy as an alternative to the other sources of energy.

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 effect of catalyst NaOH 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 content and more water, then acid-catalyzed trans-esterification 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).

In this study, sunflower species is selected for its biodiesel production, fuel properties analysis and implementation in ordinary engine. Sunflower seed is a good source of biomass and biodiesel production. The color of sunflower oil is reddish brown; it contains palmatic acid (4%), stearic acid (4%), oleic acid (78%) and linoleic acid (14%) (Karemee and Chadha, 2005). During the transesterification process of sunflower, conversion of crude oil into biodiesel was 80%. Conversion of crude oil to FAME was optimum at 70°C.

Free fatty acid (FFA) contents in sunflower biodiesel 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 content is >3%. If oils with FFA contents of >3% were used, the transesterification would not occur (Dorado et al., 2002). Bradshaw and Meuly (1994) 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 specifications of biodiesel

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, that is, biodiesel, is about an order of magnitude lower than that of the parent oil (Dunn and Knothe, 2001). The acceptable and prescribed range of viscosity at 40°C for biodiesel by ASTM Standard D675 is 1.9 to 6.0 mm^2/s. In the present work, the kinematic viscosity at 40°C of sunflower was 4.719. Kinematic viscosity has been included in biodiesel standards (1.9 – 6.0 mm^2/s in ASTM D6751 and 3.5 – 5.0 mm^2/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).

The specific gravity of sunflower biodiesel was 0.892, which matched with specific gravity of mineral diesel (0.847). Depending on the feedstock used, biodiesel specific gravity varies between 0.85 and 0.89. These results are nearly equal to those of Tat and Gerpen (1999). 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°C (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 these problems and improve

Table 1. Fuel characteristics of biodiesel blends of sunflower with mineral diesel.

Fuel property	B 100 (%)	B 5 (%)	B 10 (%)	B 20 (%)	HSD ASTM D975
Dynamic viscosity at 40°C (eta)	5.321	5.031	4.169	3.781	3.2642
Kinematic viscosity at 40°C (ny)	4.719	4.762	4.223	4.321	1.3-4.1
Density at 40°C (Rho)	0.860	0.849	0.842	0.878	0.8343
Color comparison	2.0	1	2.0	1.5	2.0
Flash point (°C)	183	79	76	85	60-80
Pour point (°C)	-5	-1	-2	0	-35 to -15
Cloud point (°C)	4	3	5	6	-15 to 5
Specific gravity Kg/1at 60°F	0.892	0.874	0.882	0.916	0.851
Sulfur contents (%)	0.0029	0.5262	0.5183	0.4259	.05 %
Distillation IBP (°C)	-	170.9	172.6	194.7	180.4
5%	-	172.4	172.6	194.8	201.4
10%	-	199.2	200.9	211.5	214.7
20%	-	213.0	215.0	229.1	235.7
30%	-	237.3	248.2	235.7	261.0
40%	-	274.6	268.5	264.3	279.1
50%	-	286.9	283.4	288.0	295.1
60%	-	301.7	304.5	314.2	308.8
70%	-	311.9	320.5	336.0	322.5
80%	-	333.0	353.2	376.5	337.6
90%	-	394.6	382.3	408.1	356.9
FBP	-	402.4	416.8	430.2	374.1
%	-	99.6	99.2	99.7	97.7
%r	-	2.5	1.7	2.3	1.9

*ASTM = American Standard Testing Materials; HSD = high speed diesel; B100 = pure biodiesel; B5 = 5% biodiesel + 95%HSD; B10 = 10% biodiesel + 90% HSD; B20 = 20% biodiesel + 80%HSD.

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.

Flash point of sunflower was 183, which is higher than the 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 lesser 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 of sunflower was 4 and pour point was -5 which is in accordance with ASTM standards. There are various measures that are applied to describe the pour point (ASTM D-97) and cloud point (ASTM D-2500) (Clements, 1996).

The other fuel properties such as distillation initial boiling point (IBP) and color comparision, which are considered as important parameters in the characterization and specification of biodiesel, were also compared with the ASTM standards. All these parameters showed similar behavior and their values meet the International Biodiesel Standard. The sulphur contents in the biodiesel of sunflower were in traces, so that they were negligible as compared to mineral diesel. Sulphur contents of sunflower biodiesel were 0.0029, respectively, 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 production than that which is added to it by their later combustion (Srivastava and Prasad, 2000).

Engine efficiency of biodiesel

Engine efficiency of biodiesel with reference to power consumption is shown in Table 2. According to experiments, the engine efficiency varies well by using biodiesel blends B100 %, B20 % and B5 %. The engine efficiency and power consumption were tested by using both biodiesel and mineral diesel. Twenty five parts of

Table 2. Comparative analysis of *Helianthus annuus* L. biodiesel performance with HSD.

S/N	Fuel	Consumption rate (L/h)	Efficiency (%)
01	Diesel (HSD)	10.7	17.8
02	B100%	10.5	17.5
03	B20%	10.3	17.1
04	B10%	10.1	16.8
05	B5%	09.9	16.5

sunflower oil and seventy five parts of diesel were blended as diesel fuel (Ziejewski et al., 1986). Schlick et al. (1988) evaluated the performance of a direct injection 2.59 L, 3 cylinder 2600 series Ford diesel engine operating on mechanically expelled-unrefined soybean oil and sunflower oil blended with number 2 diesel fuel on a 25:75 v/v basis. The power remained constant throughout 200 h of operation. Excessive carbon deposits on all combustion chamber parts precludes the use of these fuel blends, at least in this engine and under the specified Education Maintenance Allowances (EMA) operating conditions.

Barsin et al. (1981) reported that when diesel engine was run with vegetable oil as fuel, it 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) reported that the CO, CO_2 and other emissions are reduced in biodiesel and its blends, because biodiesel is oxygen in structure and it burns clearly all the fuels (Murugesan et al., 2008).

Conclusion

From the present study, it is concluded that sunflower is one potential source for biodiesel production. Detailed taxonomic and biodiesel production is very high in sunflower. The oil of this species has low content of saturated fatty acid and is a 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℃ and at 1:6 molar ratio. The fuel properties of biodiesel, that is, kinametic viscosity, specific gravity, flash point, pour point, cloud point, distillation and sulfur contents of biodiesel 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 selected species is very low and it proves that biodiesel is environmentally friendly. Keeping in view all these properties, it is concluded that in order to overcome the energy crises in future, mega cultivation of this species may be carried out for biodiesel production at larger scale.

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