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Base Catalyzed Transesterification of *Brassica alba* Oil and its Association with Mineralogy to Environment Friendly Biodiesel

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In present research, *Brassica alba* is studied for biodiesel potential. Crude oil recovery from seeds of *B. alba* is 36 %. Conversion of crude vegetable oil to biodiesel was 82, 83 and 85 % at molar ratio 1:6, 1:7 and 1:8, respectively. Fuel properties *i.e.* specific gravity of biodiesel (100 %) 0.992 and kinematic viscosity 6.71 were close to ASTM biodiesel standards. The other fuel properties like flash point, sulfur contents, distillation IBP and colour comparison showed similar behaviour and met the ASTM standards. Engine performance in terms of fuel consumption, efficiency and power outputs by using biodiesel (100 %) and biodiesel blends (B20, B10, B5) were similar to mineral diesel, which shows the practical and environment friendly performance in terms of these parameters. From the results of present study, it is concluded that this species is potential source for biodiesel. It is recommended that this species must be cultivated in soils with calcite and quartz minerals on large scale for biodiesel production and implementation to overcome the energy crisis.

Key Words: Base, Catalyzed transesterification, *Brassica alba*, Mineralogy, Environment.

INTRODUCTION

Increased concern for the security of oil supply and the negative impact of fossil fuels on the environment, particularly greenhouse gas emissions, has put pressure on society to find renewable alternatives[1]. Bioenergy from renewable sources is already a viable alternative to fossil fuels today; however, to meet the increasing need for bioenergy, several raw materials have to be considered. Seed oils are the organic material on earth and, therefore, are a promising raw material for bioenergy production[2].

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As energy demands increase and fossil fuels are limited, research is directed to search alternative renewable fuels. Biomass has been found to produce low-molecular-weight organic liquids, which can be used or proposed for vehicles. A potential diesel oil substitute is biodiesel, consisting of methyl esters of fatty acids produced by the transesterification of triglycerides of vegetable oils with methanol in the presence of a catalyst[3]. Due to the great molecular similarities of biodiesel to parafinic diesel fuel compounds, this alternative fuel has a chance of fulfilling the demands that diesel engine makes from its fuel. Essentially, no engine modifications are required to substitute biodiesel for diesel fuel that can maintain the engine performance. In addition, biodiesel is better than diesel fuel in terms of sulfur content, ash point, aromatic content and biodegradability[4]. There have been various studies in Europe, US & Japan and most of the conventional methods for biodiesel production use a basic or acidic catalyst[5].

With agricultural commodity prices approaching record lows and petroleum prices approaching record highs, it is clear that more can be done to utilize domestic surpluses of vegetable oils while enhancing energy security. Because biodiesel can be manufactured using existing industrial production capacity and with conventional equipment, it provides substantial opportunity for immediately addressing energy security issues[6].

Various studies have been made in US, Brazil, Canada, Europe and Japan to search plants based biodiesel resources but no reference of such studies is available in Pakistan. In current scenario biodiesel is an emerging technology in Indo-Pak subcontinent. A few studies have been undertaken to systematically investigate the indigenous potential of oil yielding species in Pakistan[7,8].

Rapeseeds oil: In India *Jatropha* plant is one of the important source of raw material for biodiesel production. Under the name of rapeseed and mustard, seven important annual oil seed/crops belonging to the Brassicaceae (Cruciferae) are grown in India. They are Indian mustard (*Brassica juncea*. (L) Czern. & Coss), commonly known as Rai, the three ecotypes of Indian rape, *B. campestris* L. sp. oleifera *viz.*, toria, brown mustard and yellow mustard. Swede rape (*B. napus* L.), Ethiopian mustard (*B. carinata*) and rocket seed (*Eruca sativa*). These species are regarded as of Asiatic origin besides *Eruca sativa* believed to be a native of southern Europe and North Africa[9].

Brassica alba is native to the Mediterranean region and the Crimea, but introduced into northwestern Europe, Russia, Japan, North and South America, Australia, New Zealand, India, North Africa, Pakistan and China. It has become naturalized in many areas and is a weed of cultivated lands, especially flax-fields; a quick-growing long-day annual which prefers temperate climates with some humidity; can withstand high temperatures, but hot days during flowering and ripening may reduce seed setting and lower the quality of seed; requires high nutrient soils with high level of nitrogen, but may be grown on a wide range of soils from light to heavy, growing best on relatively heavy sandy loamy soils including oolitic limestone; not suited to very wet soils. Ranging from boreal moist to wet through tropical dry forest life zones, white mustard occurs[10] where annual precipitation varies from 3.5 to 17.9 dm (mean of 43 cases = 7.7), annual temperature from 5.6 to 24.9 °C (mean of 43 cases = 10.5) and pH of 4.5 to 8.2 (mean of 36 cases = 6.6). The renewed interest in environmentally compatible fuels has led to the choice of rapeseed oil as the main alternative to diesel fuel in Europe[11].

In present project, *Brassica alba* (chitti sarson) is targeted with reference to alternative energy (biodiesel). Biodiesel and its blends (B5, B10, B20) from this species have been investigated for their fuel properties and tested in ordinary diesel engine.

EXPERIMENTAL

Brassica alba seeds were obtained from oil seeds programme, National Agricultural Research Center. The oil was extracted by using electric oil expeller (KEK P0015-10127, Germany). Methanol, sodium hydroxide, sodium sulphate and acetic acid of analytical grade were obtained from Merck (Germany).

Transesterification: The method used for synthesis of methyl esters (Biodiesel) from crude oil was transesterification. Initially 2 L *Brassica alba* oil was heated on hot plate (VWR, VELP-Scientifica Germany) up to 120 ºC. A known amount of sodium hydroxide (12.6 g) was dissolved in 400 mL methanol to prepare sodium methoxide (catalyst), which was chosen as the catalyst for this work because it is employed by a substantial proportion of industrial biodiesel facilities[12]. This catalyst was added to oil at 60 ºC at which the conversion of triglycerides into fatty acid methyl esters (FAME) was assumed to be maximum.

The molar ratio of oil/methanol was fixed at 1:6, 1:7 and 1:8 since the literature suggests that this is the optimal ratio for vegetable oil transesterification[13-15]. Glycerol as byproduct was separated from the oil as the reaction completed. The crude methyl esters was washed with water at pH 4.5 to neutralize the catalyst and convert any soaps to free fatty acids (FFA), reducing their emulsifying tendencies. Centrifugation is then employed to separate the biodiesel from the aqueous phase. The crude, washed methyl esters product, may contain several per cent of water. This must be lowered to a maximum of 0.05 % (v/v) to meet ASTM biodiesel specifications[16]. Esters were finally dried over anhydrous sodium sulfate and the final product obtained as a clear, light yellow liquid.

Fuel properties: Fuel properties of biodiesel (B100 %) and its blends (B5, B10 and B20 %) were tested according to ASTM biodiesel standards. Specific gravity at ASTM D-1298, flash point at ASTM D-93, pour point (ºF) at ASTM D-97, kinametic viscosity at 40 ºC, sulfur contents (D-4294) and distillation at ASTM D-86 were determined[17,18].

Diesel engine testing: Engine performance by using biodiesel and high speed diesel (HSD) in terms of fuel consumption, efficiency and power outputs were calculated during road run test on Toyota (2D). The engine set up was run for 2 h and the volume of the fuel used was recorded. This was repeated four times. When the engine was started, reading from ammeter and voltmeter were taken every 30 s for the first 6 min and at 3 min intervals for the remaining times.

RESULTS AND DISCUSSION

In present project, *Brassica alba* L. is investigated for biodiesel potential. It was found that *B. alba* is a suitable species for biodiesel production for its high oil (36 %) recovery and quality of oil. The oil colour is golden yellow, having a burning taste and gives light pungent smell. Generally the *Brassica* seed oil having long chain monosaturaterd fatty acids (82 %), erucic acid (15 %), oleic acid (14 %) and eicosenoic acid (37 %). Free fatty acids (FFA)[19] are 1 %. *B. campestris* and *B. rapa* also contain almost similar types of fatty acids as *B. alba*. Data of transesterification experiments revealed that conversion of crude oil into biodiesel varies in *B. alba i.e.* 82, 83 and 85 %, respectively at 1:6, 1:7 and 1:8 molar ratio (Figs. 1-3). Conversion of crude oil to fatty acid methyl esters (FAME) was maximum during transesterification process at 60 ºC.

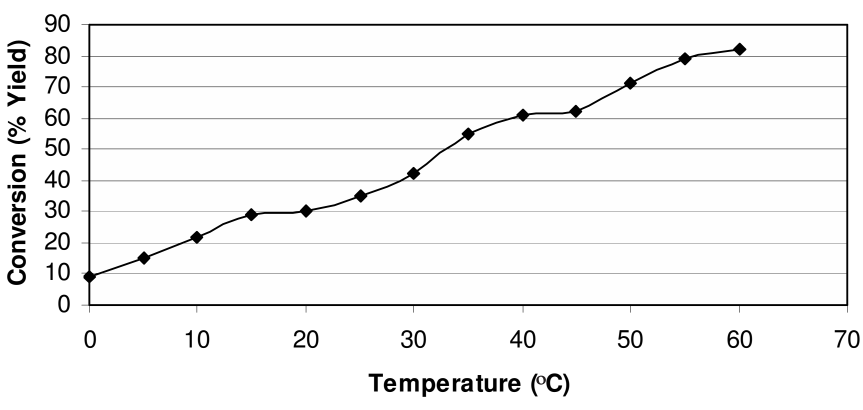

Fig. 1. Effect of temperature on conversion of *Brassica alba* crude oil to biodiesel at 1:6 molar ratio

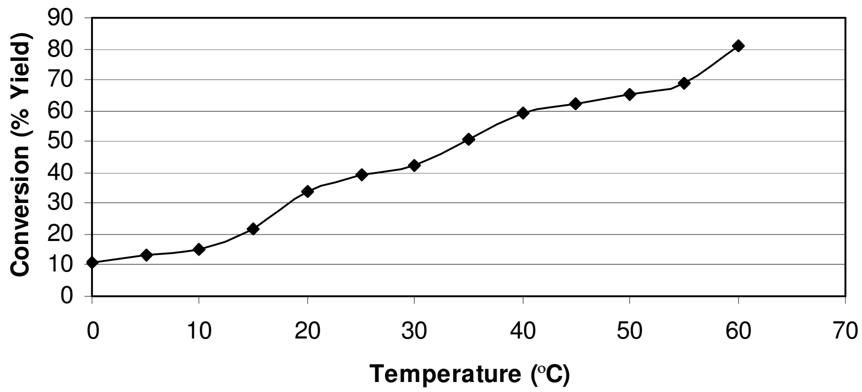

Fig. 2. Effect of temperature on conversion of *Brassica alba* crude oil to biodiesel at 1:7 molar ratio

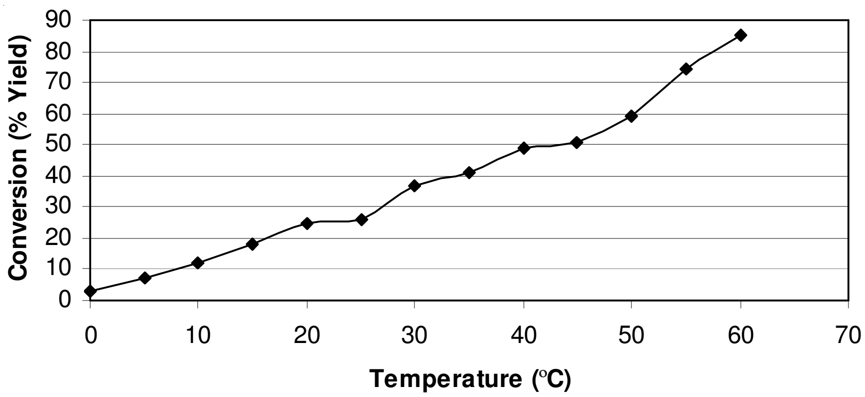

Fig. 3. Effect of temperature on conversion of *Brassica alba* crude oil to biodiesel at 1:8 ratio ratio

Effect of Molar ratio on transesterification: Conversion of crude vegetable oil to biodiesel increases with reactant ratio (moles of MeOH: moles of oil). It was found that conversion increases with the molar ratio[20]. The free fatty acid (FFA) contents in *Brassica* species are less than 2 %[21]. These FFA contents should make transesterification of the oils possible, FFA contents of > 3 % decrease the conversion efficiency considerably[22]. It is found that transesterification would not occur if oils with FFA contents of > 3 % were used[23]. In this work, it was found that there is optimal conversion at 1:8 molar ratio because FFA contents of rapeseed oil were > 2 %. To avoid corrosion problems in engine components, that are due to the presence of acid traces, basic catalyst instead of acid catalyst was selected[24]. In this work, basic catalyst NaOH was tested under the same conditions. The effect of NaOH concentration was studied in the range of 3.4 % (weight of NaOH/weight of oil). These results agree with those obtained by other authors.

During the process of transesterification by using frying oils with different alcohols also concluded that NaOH and KOH were the best catalysts[25,26].

Fuel properties of biodiesel: Table-1 shows the physio-chemical characteristics and quality of *Brassica alba* methyl esters (biodiesel). Density at 40 ºC (ρ) remains almost similar to high speed diesel. The values of the densities in the present analysis were quite comparable to those reported in the literature[27,28]. The specific gravity Kg/L at 60 ºF was also measured by ASTM D975. Mineral diesel exhibited a specific gravity of 0.847. Specific gravity of biodiesel in *Brassica alba* was 0.992. Biodiesel specific gravity is reported to vary between 0.85-0.89 depending on the feed stock used[29].

TABLE-1
FUEL PROPERTIES OF BIODIESEL BLENDS OF *Brassica alba* WITH HSD

Fuel properties	B100%	B5%	B10%	B20%	HSD ASTM D975
Dynamic viscosity at 40 ºC	6.192	4.312	4.426	3.611	1.3-4.1
Kinematic viscosity at 40 ºC	5.719	4.821	4.112	5.321	1.9-6
Density at 40 ºC	0.899	0.852	0.843	0.861	0.8343
Colour comparison	2.0	1.5	1.8	2.4	2.0
Flash point (ºC)	140	110	100	85	60-80
Pour point (ºC)	-6	0	0	0	-35to-15
Cloud point (ºC)	2	-7	-8	-12	-15 to 5
Specific gravity Kg/1at 60 ºF	0.992	0.863	0.892	0.926	0.851
Sulfur contents (%)	0.0130	0.4262	0.5628	0.4226	0.05 %
Distillation IBP (ºC)	-	172.3	174.5	196.7	180.4
5 %	-	174.3	174.5	196.7	201.4
10 %	-	199.5	200.6	213.6	214.7
20 %	-	217.0	219.0	226.0	235.7
30 %	-	240.5	243.5	230.4	261.0
40 %	-	268.4	271.4	258.6	279.1
50 %	-	285.4	286.3	282.0	295.1
60 %	-	302.6	305.0	311.4	308.8
70 %	-	316.0	323.0	343.3	322.5
80 %	-	332.6	342.3	387.9	337.6
90 %	-	386.4	379.4	433.5	356.9
FBP	-	405.6	428.0	440.4	374.1
%	-	98.4	98.3	98.3	97.7
%r	-	2.1	2.2	2.2	1.9

HSD = High speed diesel.

The ASTM standard D 6751 prescribed and acceptable viscosity at 40 ºC range for biodiesel to be 1.9-6.0 mm/s. In present work, the kinematics viscosity at 40 ºC of *B. alba* biodiesel 100 % (5.71) was close to the biodiesel standards. The other fuel properties like flash point, sulfur contents, distillation IBP and colour comparison studied showed similar behaviour and meet the international biodiesel standards.

The maximum values of cloud and pour points of biodiesel of this species in the present work is also in accordance with ASTM standards (Table-1). The flash point of biodiesel produced in this work was higher than that of mineral diesel. It is a parameter to consider in the handling, storage and safety of fuels and flammable materials. A higher value of flash point decreases the risk of fire. These parameters were also close to the biodiesel properties of rapeseed as studied by other workers[30]. The sulfur contents of biodiesel (100 %) was analyzed by ASTM D 975 and the values was 0.0130. Values of sulfur contents were almost negligible as compared to mineral diesel and so it may said that biodiesel is environment friendly.

Biodiesel testing: Results of experiments on engine testing with reference to power consumption and efficiency by using biodiesel was shown in Table-2. According to these findings it is clear that engine performance is very well by using biodiesel blends B100, B 20, B10 and B5 %. Consumption and efficiency of biodiesel was much close to mineral diesel which shows the practical and environment friendly performance in terms of these parameters.

TABLE-2
COMPARATIVE ANALYSIS OF *Brassica alba* BIODIESEL PERFORMANCE WITH HSD

Fuel	Consumption rate (L/h)	Efficiency (%)
Diesel (HSD)	9.0	17.75
B100 %	9.5	17.35
B20 %	9.1	17.60
B10 %	9.3	17.65
B5 %	9.4	17.68

Conclusion

From the results of present study, it is concluded that *Brassica alba* is viable source of biodiesel. Maximum yield of biodiesel was achieved through methanolysis of crude oil from this plant at 1:6, 1:7 and 1:8 molar ratios at 60 ºC. The fuel properties *i.e.* kinemetic viscosity, specific gravity, flash point, pour point, cloud point, distillation and sulfur contents of biodiesel produced was in accordance with the international biodiesel standards. Engine performance in terms of fuel consumption, efficiency and power outputs were comparable with mineral diesel. However, the environmental performance of biodiesel is much better than mineral diesel. It is concluded that this species may be cultivated on large scale for biodiesel production and implementation to overcome the crises of energy in future.

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