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Full Length Research Paper

Base catalyzed transesterification of wild apricot kernel oil for biodiesel production

Faizan Ullah*, Asia Nosheen, Ishtiaq Hussain and Asghari Bano

Department of Plant Sciences, Quaid-i-Azam University, Islamabad, Pakistan.

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Prunus armeniaca **L. grows wildly and is also cultivated at higher altitudes in temperate regions of Pakistan. Its kernel is a rich source of oil but its biodiesel production properties have not yet been exploited. During the present investigation, some quality parameters of kernel oil like acid value, free fatty acid content (as oleic acid), iodine value, specific gravity and saponification value pertaining to biodiesel production were studied. Biodiesel was produced through base (NaOH) catalyzed transesterification. An oil/methanol molar ratio of 1:6 and treatment of sodium methoxide with molecular sieves prior to mixing with kernel oil offered the higher (93%) biodiesel yield which is 4% higher than without the use of molecular sieves. Fuel properties, such as density, specific gravity, kinematic viscosity, color, flash, cloud and pour point were in accordance with American Society for Testing and Materials (ASTM) D 6751. However, the cloud, and pour points were slightly higher than the conventional diesel fuel. Results of the present investigation revealed that pre-treatment of methoxide with molecular sieves can improve the yield of biodiesel and the biodiesel produced through base catalyzed transesterification of wild apricot kernel oil has fuel properties quite comparable to those of mineral diesel and thus can be successfully utilized for applications in compression-ignition engines.**

Key words: Wild apricot, kernel oil, biodiesel.

INTRODUCTION

Energy is basic requirement for human existence on this habitable globe. The wide spread depletion of the world petroleum reserves and increased environmental concerns has stimulated recent interest in alternative resources for petroleum based fuels. In such a situation, biodiesel has arisen as a potential candidate to substitute petroleum based diesel (Mehar et al., 2006). It does not increase the level of carbon dioxide in the atmosphere and consequently, to the Green House Effect (Barnwal and Sharma, 2005).

Pakistan being a developing country needs more energy for rapid economic growth. The oil and gas sector is looking for indigenous resources to reduce its dependence on imported crude oil and there can be no better substitute than ethanol and Biodiesel. The utilization of edible vegetable oils for biodiesel production has recently been of great concern as they compete with food materials. Due to abundant utilization of vegetable oils for food, it is impossible to make use of these oils for fuel purposes. As a result, biodiesel production from them will be much expensive to be used as fuel as compared to diesel. One of the means to address the higher priced hurdle is to research and develop methods to reduce the cost of biodiesel. A reduced cost option is to produce biodiesel from waste fats and oils. Another option for cost reduction is to reduce the cost of processing through optimizing the process variables that affect the yield and purity of biodiesel (Reffat et al., 2008).

Prunus armeniaca L. belonging to family Rosaceae, grows wildly as well as cultivated at higher altitudes (1000-2700 m). It can grow over the five continents of the world and production level exceeds 2 million tons. Australia, France, Hungary, Iran, Italy, Morocco, Spain, Tunisia, Turkey are regarded as important apricot producer countries. While some of the countries such as Hungary, Morocco, Iran and Tunisia are important fresh apricot exporters, the others, such as Australia and Turkey, are the most important dried apricot producers and exporters (Jannatizadeh et al., 2008).

In Pakistan, it can be found in the inner valley of

*Corresponding author. E-mail: asgharibano@yahoo.com.

Table 1. Chemical and physical properties of wild apricot kernel oil.

Acid value (mg KOH/gm oil)	Free fatty acid content (% FFAs as oleic acid)	Iodine value (g I/100 g of oil)	Saponification number (mg of KOH/g of oil)	Specific gravity at 25ºC (g/cm^3)
1.683	0.84	103	173	91

Baluchistan, Kurrum agency, Hunza, Gilgit and Ladak (Fazlin et al., 2002; Baquar, 1989). Apricot kernels are generally used in the production of oils, cosmetics, active carbon and perfume industry (Guner et al., 1999). Its kernels are rich source of oil with oil content up to 48.70% (Ozcan, 2000).

The aim of the present investigation was to determine quality of wild apricot kernel oil pertaining to biodiesel production, to check quality of biodiesel produced and maximize the methyl ester yield.

MATERIALS AND METHODS

Collection of wild apricot kernels

Kernels were collected from Baltistan, Northern Areas Pakis-tan, allowed to air dry for two weeks and finely grinded with help of electric grinder.

Oil extraction

The oil was extracted with petroleum ether in a soxhlet extractor according to Association of Official Agricultural Chemistry (AOAC, 1960). The lipid extract was stored at 4˚C for further analysis.

Chemical properties of kernel oil

The acid value, free fatty acid content (as oleic acid), iodine value and saponification number of the oil were determined in accordance with American Oil Chemists' Standard methods (AOCS, 1997).

Biodiesel production

Biodiesel was produced through base (NaOH) catalyzed transesterification (Freedman et al.,1986), with some modification such that methoxide prepared by dissolving NaOH pellets into methanol was treated with molecular sieve (size A3) for 10 h to remove any of the chemical water produced during reaction of methanol with sodium hydroxide prior to transesterification. The ratio of oil to methanol was 1:6. A separate sample of biodiesel was also produced without using molecular sieve with same catalyst under similar operating conditions.

Washing of biodiesel

Biodiesel produced by transesterification was subsequently washed with warm water. The ester phase was placed in a glass column 3 cm in diameter and 50 cm long. Warm water was gently sprayed on the top of the column and incubated till 24 h for separation of two phases.

Drying of biodiesel

Biodiesel was dried by RFE at 200 rpm at 40℃ for 40 min.

Biodiesel physical properties

Biodiesel physical properties were determined according to American Society for Testing Materials (ASTM, 2003). The density was determined by a digital density analyzer using ASTM D 5002. The specific gravity (15℃) of the biodiesel was measured by ASTM D 287. The kinematic viscosity was determined at 40℃, using a viscometer according to ASTM D 445. The flash point was determined by a Pensky-Martens closed-cup tester using ASTM D 93. Cloud and pour point determinations were made using ASTM D 2500 and ASTM D 97. Colour was determined according to ASTM D1500.

RESULTS AND DISCUSSION

Properties of apricot kernel oil

The wild apricot kernel oil analyzed prior to transesterification reaction showed an iodine value of 103 (g of I/100 g of oil) and saponification values (mg of KOH/g of oil) of 185. Acid value of wild apricot kernel oil was 1.7 and free fatty acid content as 0.84% (as oleic acid). To complete alkali catalyzed reaction, a free fatty acid (FFA) value lower than 3% is needed (Dorado et al., 2002). The specific gravity for kernel oil investigated was 0.91 g/cm^3 (Table 1). These properties of wild apricot kernel oil showed that it can be successfully utilized for biodiesel production.

Yield of biodiesel

Maximum yield (93%, w/w) of biodiesel was obtained when sodium methoxide prepared by dissolving sodium hydroxide pellets into methanol was treated with molecular sieve before transesterification. The 89% conversion of oil to biodiesel occurred when methoxide was not treated with molecular sieve under same conditions (Figure 1). This indicated that the chemical water produced during preparation of methoxide by dissolving sodium hydroxide catalyst in methanol was absorbed by molecular sieve and therefore chances of soap formation were minimized leading to increased yield of methyl esters. Molecular sieve have been used to remove water from mixture produced during chemical reaction. Wang et al. (2006) reported that in lipase catalyzed biodiesel produc-

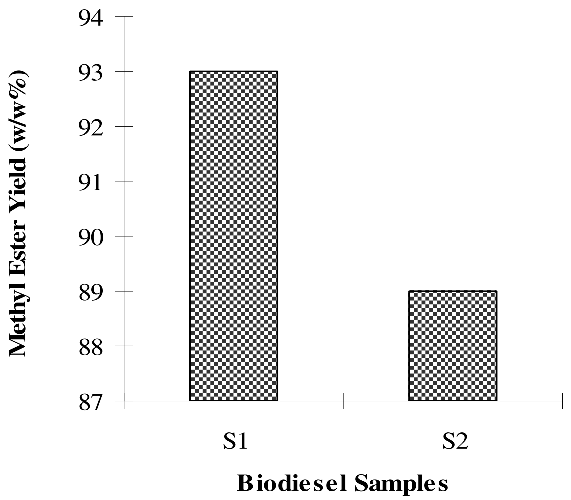

Figure 1. Comparison of methyl ester yield obtained from oil sample for which methoxide was treated with molecular sieve before transesterification with that not treated with molecular sieve. S1: Biodiesel obtained from kernel oil transesterification when methoxide was treated with molecular sieve. S2: Biodiesel obtained from kernel oil transesterification when methoxide was not treated with molecular sieve.

tion, molecular sieves can be used to remove moisture in the preparation of good quality biodiesel.

The basic catalysts are highly hygroscopic and they form chemical water when dissolved in the alcohol reactant (Van Gerpen et al., 2004).

$NaOH + CH_3OH \rightarrow Na\text{-}O\text{-}CH_3 + H_2O$

Komers et al. (2001) have earlier described that during the biodiesel production process, the material used in the transesterification should be water-free since the presence of water has negative effects on the reaction. Water can consume the catalyst and reduce catalyst efficiency. In base catalyzed methods of biodiesel production, the presence of water has negative effects on the yields of methyl esters and the presence of water significantly reduces the methyl ester yield and there occurs no oleic acid conversion to methyl oleate at any level of water in base catalyzed transesterification (Kusdiana and Saka, 2003). From the results it can be inferred that treatment of methoxide with molecular sieve (size A3) before mixing with oil can increase the yield of methyl esters.

Biodiesel properties

The important biodiesel properties of wild apricot kernel oil as measured according to accepted ASTM standard methods are presented in Table 2. These properties of wild apricot kernel oil methyl esters investigated in this study were in accordance with specified ASTM D 6751 standards.

Density and specific gravity

Density is of primitive importance in determination of biodiesel quality. The density of biodiesel produced from wild apricot kernel oil was 855 kg/m^3. The specific gravity, which is the ratio of the density of the liquid/density of water, of the biodiesel produced from wild apricot oil in the present study, was 0.877 (Table 2). Many quality parameters of biodiesel such as cetane number, heating values, fuel storage and transportation are closely related with specific gravity (Yuan et al., 2004). Correlation of fuel density with particulate emissions has been described earlier (Mulin, 1994). The ASTM standard for biodiesel specific gravity is in the range of 0.87.

Kinemetic viscosity

The kinematic viscosity of the biodiesel of the wild apricot kernel oil in the present study at 40℃ was 4.26 mm^2/s (Table 2). Proper operation of an engine depends on the proper viscosity of the liquid fuel. The viscosity of fuel is important for its flow through pipelines, injector nozzles and for atomization of fuel in cylinder (Roolia and Choo, 1999). The ASTM standard D 6751 for an acceptable kinemetic viscosity range at 40℃ for biodiesel varies between 1.9–6.0 mm^2/s. The kinematic viscosity (40℃) of wild apricot kernel oil biodiesel obtained in the present study meets the limits of ASTM standard D 6751 specifications.

Flash point

Flash point is a measure of the temperature to which a fuel must be heated such that a mixture of the vapors and air above the fuel can be ignited. The biodiesel produced from wild apricot oil had a flash point of 105℃ (Table 2). Biodiesel has a higher flash point when compared to diesel fuel (Ali et al., 1995). The flash point of neat biodiesel is higher than 93℃ (Bajpai and Tyagi, 2006). The flash point is of prime importance for storage and transportation of liquid fuels. It is therefore inferred that by making blend of wild apricot kernel oil methyl esters with HSD, the flash point of HSD can be improved which will make HSD safer in transportation and storage.

Cloud and pour points

Cloud point according to ASTM D-2500 is a measure of temperature at which the wax crystals first becomes visible and is related to warmest temperature at which these will form in fuel. Pour point is a measure of the fuel gelling temperature, at which point the fuel can no longer be pumped and is always lower than cloud point (Bajpai and Tyagi, 2006).

Table 2. Comparison of biodiesel quality from wild apricot kernel oil, ASTM standards for biodiesel and ASTM Specifications for High Speed Diesel.

Properties	Biodiesel from wild apricot kernel oil	ASTM Standards for Biodiesel	HSDASTM D975
Density at 15ºC (kg/m3)	855	847	0.8295
Specific gravity (g/cm^3) at 25ºC	0.87	0.89	0.847
Kinemetic viscosity at 40ºC (mm^2/s)	4.26	1.9-6	1.3-4.1
Flash Point (ºC)	105	130	74
Pour Point (ºC)	-15	--	0
Cloud Point (ºC)	-4	--	6
Colour	0.5	--	1-1.5

The values of Cloud point and Pour point for the biodiesel produced during present study were -4°C and -15°C respectively. According to ASTM standard D 6751, no limit is specified for Cloud point and Pour point. The reason is that the climate conditions in the world vary considerably, thus affecting the needs of biodiesel users in a specific region (Anwar and Rashid, 2008).

Colour of biodiesel

The colour of biodiesel obtained in the present study was in the range of 0.5. The standard for colour of HSD according to HSD ASTM D975 varies between 0.5-1. Thus the biodiesel produced through base catalyzed transesterification of wild apricot kernel oil agrees with the ASTM D6751 limits.

Conclusion

It can be inferred from the present findings that wild apricot kernel oil can be successfully processed into biodiesel and biodiesel yield can be improved by treating sodium methoxide with molecular sieve before mixing with oil for transesterification reaction. The biodiesel produced from wild apricot kernel can be successfully utilized in the compression ignition engines.

Economy of wild apricot kernel oil biodiesel

The benefit/cost ratio was evaluated for biodiesel produced from wild apricot kernel oil on Laboratory scale. The cost of biodiesel produced from wild apricot kernel oil was 1.2 U.S Dollar/L. This high cost is due to problems associated with collection of kernels from farmers and laborious pressing of kernels for oil extraction. The above estimated price for wild apricot kernel oil biodiesel appears high than existing price of high speed diesel (0.70 U.S Dollars/L) in Pakistan. However, the cost of production can be further reduced by utilizing byproducts of biodiesel such as glycerin for industrial uses (soap, cosmetics etc) and kernel cake as animal feed and preparation of inocula for biofertilizers. Moreover, there is favorable environment for large scale cultivation of this plant in the country which will further add not only in the reduction of biodiesel production cost but will also add to the food stock of the country.

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