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Assessment of Wild Safflower oil Methyl Ester as Potential Alternative Fuel

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ABSTRACT

Different vegetable oils with various compositions of fatty acids can be used for biodiesel production. Among them soybean, sunflower, rapeseed and palm are the most studied ones. Recently studies are being carried out for biodiesel production from less common or unconventional oilseeds. In this work wild safflower oil for first time was converted to fatty acid methyl ester (biodiesel) via alkali transestrification. The obtained results showed that, the produced biodiesel has high flash point (179 ºC) and better cold flow properties (CP -3 ºC and PP -9 ºC). Sulfur content and carbon residue of wild safflower methyl ester were found to be 0.01 (mass %) and 0.005 (mass %), respectively. Other determined fuel properties also were within the ASTM D6751 specification limits. Due to acceptable fuel properties and lower costs production, this oil can be a possible raw material for biodiesel production.

Keywords: Biofuel, Transestrification, Wild safflower, ASTM D6751.

INTRODUCTION

In the past few decades, fossil fuels mainly petroleum, natural gas and coal have been playing an important role as the major energy resources worldwide. However, these energy resources are none-renewable and are projected to be exhausted in the near future [1]. On the other hand, about 98% of carbon emissions result from fossil fuel combustion [2]. Therefore, there is an urgent need to find a new resource that is renewable, clean and reliable. Considerable attention was focused on the development of biofuel, with particular referring to the biodiesel [1,3].

Biodiesel is superior to conventional diesel in terms of its sulphur content, aromatic content and flash point. It is essentially sulphur free and non-aromatic while conventional diesel can contain up to 500 ppm SO_2 and 20-40 wt% aromatic compounds. These advantages could be a key solution to reduce the problem of urban pollution since transport sector is an important contributor of the gas emissions [4].

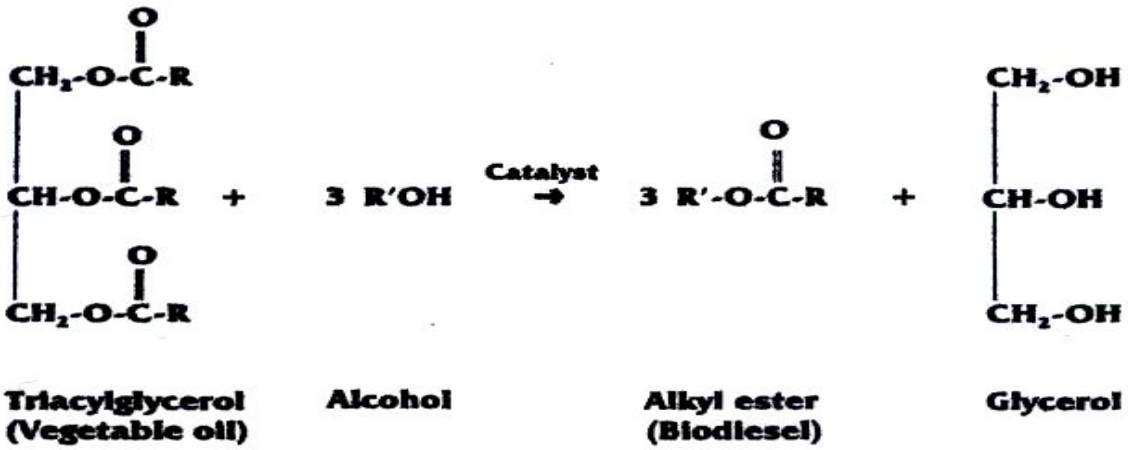

Fig.1. The transestrification reaction. R is a mixture of various fatty acid chains. The alcohol used for producing biodiesel is usually methanol (R′ = CH_3)

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Biodiesel is defined as the mono-alkyl esters of vegetable oils or animal fats, obtained by transestrifying oil or fat with an alcohol. The major reason for not using a neat vegetable oil as fuel is its high viscosity (usually in the range of 28-40 mm^2/s), which leads to operational problems in diesel engine including formation of deposits and injector coking due to poorer atomization upon injection into the combustion chamber. Transestrification (Fig. 1) of the oil reduces the viscosity of the oil to a range (usually 4-5 mm^2/s) closer to that of petrodiesel [5,6]. The successful introduction and commercialization of biodiesel in many countries around the world has been accompanied by the development of standards to ensure high product quality and user confidence. Some biodiesel standards are ASTM D6751 (ASTM = American Society for Testing and Materials) and the European standard EN 14214 [7,8] .

There are three types of oil as potential sources for biodiesel production, which are vegetable oil, animal fat and used cooking oil [9]. Currently, more than 95% of world biodiesel is produced from edible oils [10]. By converting edible oils into biodiesel, a lot of problems may arise; global imbalance to the food supply and demand market, deforestation and destruction of ecosystems [11]. A possible solution to overcome these problems is to use new biomass feedstocks that grow in marginal and waste lands, with lower cost production, higher oil yield and suitable oil composition.

Wild safflower (Carthamus oxyacantha) is an annual plant in Iran, Pakistan and India. It grows in any land and has no production costs prior to harvesting operation. According to Carpetian and Zarei [12], oil content of this plant is 22% and its oil composition consists of 4.78, 1.13, 15.7 and 78.39%, Palmitic (C16:0), Stearic (C18:0), Oleic (C18:1), Linoleic (C18:2) acids, respectively. No literature is available on the production of biodiesel from its oil. This study was carried out to assessment the suitability of wild safflower (c. oxyacantha) oil methyl ester, as alternative fuel.

MATERIALS AND METHODS

Wild safflower oil extraction:

The collected wild safflower seeds from sanandaj region (Kurdistan province) were dried at 40 ºC for 4 h using an oven, to moisture content of about 5%, and were then ground with a grinder. Oil from ground seeds was extracted with soxhlet method, using n-hexane solvent for 5 h, then the solvent removed by rotary evaporation under vacuum at 40 ºC [13].

Alkali transestrification of crude oil of wild safflower:

Prior to the transestrification, the raw oil (with FFA 18%) was kept in an oven at 105 ºC for 2-3 h to remove the water from it, and sodium hydroxide pellets were then dissolved in methanol by stirring to prepare sodium hydroxide-methanol mixture. The reaction was carried out as following conditions: methanol to oil molar ratio (6:1), catalyst concentration (1w/wt%), reaction temperature (60-65 ºC), ambient pressure, reaction time (1h) and stirring speed 400 rpm. The preheated crude oil was poured into 1 liter round bottom flask that was fitted with a thermometer and condenser. Then the NaOH- methanol mixture was added in the oil flask, and was continuously stirred to 400 rpm by means of magnetic stirrer for 1 hr. After 1 hr, the mixture was transferred into a separating funnel, and was allowed to settle under gravity for 20 hr. Two liquid phases were produced; the upper phase was methyl ester (biodiesel) and the lower was crude glycerin. The glycerin was drained out, and the methyl ester was then cleaned by washing with warm deionized water. Finally, the product was heated and dried [14-19].

Characterization of biodiesel:

Fuel properties of produced methyl ester (biodiesel) were measured by using ASTM standard methods, including density (ASTM D4052), kinematic viscosity (ASTM D445), flash point (ASTM D93), cloud point (CP) (ASTM D2500), pour point (PP) (ASTM D97), distillation limit (ASTM D1160), calorific value (ASTM D240), sulphur content (ASTM D2622), carbon residue (ASTM D189), and cetane index was calculated according to the ASTM D976 empirical equation;

$$\text{Cetane index} = 454.74 - 1641.416\, D + 774.74\, D^2 - 0.554\, T_{50} + 97.803\, [\log_{10}(T_{50})]^2$$

Where D = fuel density at 15°C in g/ml.

And T_{50} = the temperature corresponding to the 50% point on the distillation curve in degrees C.

RESULTS AND DISCUSSION

The fuel properties of produced methyl ester were determined by standard methods in triplicate and mean values were compared to ASTM D6751 biodiesel specification standard, soybean methyl ester, palm methyl ester and petroleum diesel. The Results obtained are presented in Table 1.

As shown in Table 1, some determined properties of wild safflower methyl ester namely, density, kinematic viscosity, calorific value were close to those of soybean and palm methyl esters, but it has higher flash point, lower CP

and PP than those of both methyl esters. Such a high flash point and better cold properties of wild safflower biodiesel may be attributed to the large proportion of unsaturated fatty acids [12] in its oil (more than 80%).

Table 1: Some properties of wild safflower methyl ester in comparison with ASTM D6751 (Biodiesel specification standard), soybean methyl ester, palm methyl ester and diesel fuel.

Property	ASTM D6751 [22]	Diesel [21,6]	Palm methyl Ester [21,1]	Soybean methyl ester [21,1]	Carthamus oxyacantha methyl ester [this study]
Density g/ml	-	0.82- 0.86	0.864	o.884	0.8816
Kinematic viscosity mm^2/s at 40 ºC	1.9- 6.0	2.0 – 4.5	4.42	4.08	4.13
Flash point ºC	130 min	55	135	131	179
Cloud point(CP) ºC	Report	-18	16	- 0.5	-3
Pour point (PP) ºC	-	-25	12	- 4	-9
Sulfur content (mass %)	0.05 max	0.1 max	-	-	0.01
Carbon residue (mass %)	0.05		-	-	0.005
Vacuum distillation end point ºC	360	-	-	-	352 (at 90% volume recycle)
Calorific value Mj/Kg	-	42	-	39.76	39.255
Calculated cetane index	47 min	46	57.30	45	48.99

The density of biodiesel from wild safflower (0.88 g/ml) was slightly higher than that of diesel (0.82-0.86 g/ml). The conversion of triglycerides into methyl or ethyl ester through the transestrification process reduces the viscosity by a factor of about eight and increases the volatility marginally [22]. The determined kinematic viscosity of wild safflower methyl ester as shown in table 1, was 4.13 mm^2/s at 40 ºC. The obtained value satisfied both ASTM D6751 standard (1.9-6.0 mm^2/s) and diesel (3.5-5.0 mm^2/s) requirements. For safe handling and storage, a proper flash point is required. Flash point of diesel fuel is 55 ºC, and according to the ASTM D6751 biodiesel must has minimum value of 130 ºC. The determined flash point of wild safflower methyl ester meets this requirement, and was 179 ºC [Table 1]. Cold flow properties are reflected by the values of cloud point (CP) and pour point (PP), and will be the deciding factor if the biodiesel produced can be used in cold climate countries. In addition, these properties are determined by types of fatty acids in the feedstock oil [1]. Biodiesel fuel derived from palm oil has poor cold flow properties (CP 16 ºC and PP 12º C), because it has high content of saturated fatty acids (more than 45 %). In this study CP and PP of produced fuel were -3 ºC and -9 ºC, respectively [Table 1]. As reported earlier [12] wild safflower oil has low content (7-8 %) of saturated fatty acids; therefore low values of CP and PP might be due to this low content of saturated fatty acids. Sulfur content and carbon residue of wild safflower methyl ester were found to be 0.01 (mass %) and 0.005 (mass %) [Table 1]. Both these characteristics meet the specification requirements of ASTM D6751. The maximum allowable vacuum distillation end point of biodiesel (at 90% volume recycle) according to the ASTM D6751 is 360 ºC. As seen in table 1, the produced methyl ester with 352 ºC distillation end point (at 90% volume recycle) was satisfactory according to this requirement. The determined calorific value (higher heating value) of wild safflower methyl ester was 39.255 (Mj/Kg). There is no specification requirement for calorific value in biodiesel standards, and it was slightly lower than diesel. As depicted in table1, the calculated cetane index of produced fuel (48.99) meet the minimum cetane number requirement (47) in ASTM D6751 and was higher than of diesel fuel.

Conclusion

For first time wild safflower methyl ester (biodiesel) from its crud oil via alkali transestrification was produced. It can be found from the obtained results, the produced biodiesel has high flash point (179 ºC) and better cold flow properties (CP -3 ºC and PP -9 ºC). Other determined fuel properties also were within the ASTM D6751 specification limits. Due to acceptable fuel properties and lower costs production, this oil can be a possible raw material for biodiesel production.

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