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Biodiesel Production from Ricinus Communis Oil and Its Blends with Soybean Biodiesel

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In this study, local vegetable oil named as Ricinus Communis (RC) is used as the raw material for the production of biodiesel. In order to obtain RC oil, Soxhalet Extraction apparatus was used. This paper deals with the transesterification of Ricinus Communis oil with methanol to produce biodiesel. Moreover, this study analysis the fuel properties of RC biodiesel and soybean biodiesel blends. Various properties of the RC biodiesel, Soybean biodiesel and their blends such as the cold filter plugging point (CFPP), cetane number, flash point, kinematic viscosity and density were determined. Test results were compared well with European biodiesel standards EN 14214. Analysis showed that the cetane number and the cold flow behavior of the RC biodiesel and soybean biodiesel blends were improved due to the high cetane number (80) and the low cold filter plugging point (-35 °C) of RC biodiesel.

Keywords: Ricinus Communis, biodiesel, transesterification, biodiesel properties, cetane number, CFPP

0 INTRODUCTION

Biodiesel is an alternative fuel for diesel engines that is produced by chemically reacting vegetable oil or animal fat with alcohol and the catalyst. Biodiesel is miscible in diesel fuel, and can be easily blended with diesel fuel with minor or no modifications to the engine and fuel system. According to EU guidelines the consumption of bio-fuels for road transportation should represent 20% of the total fuel consumption by 2020 and the use of bio-fuels will be stimulated by environmental aspects [1]. For these reasons, biodiesel has become a popular topic in energy sources.

The most common way to produce biodiesel is the transesterification method, which refers to a catalyzed chemical reaction involving vegetable oil and alcohol to yield fatty acid alkyl esters (i.e., biodiesel) and glycerol [2]. The reaction requires a catalyst, usually a strong base, such as sodium and potassium hydroxide or sodium methylate. A catalyst is usually used to improve the reaction rate and the yield. Since the reaction is reversible, excess alcohol is used to shift the equilibrium to the product side. Especially methanol is used as alcohol because of its low cost and its physical and chemical advantages. Methanol can quickly react with vegetable oil and NaOH can easily dissolve in it. To complete a transesterification reaction stoichiometrically, a 3:1 molar ratio of alcohol to triglycerides is necessary. In practice, the ratio needs to be higher to drive the equilibrium to a maximum ester yield [3].

The transesterification conditions and biodiesel properties of RC oil were studied [4]. It has been concluded that the blends of RC biodiesel and diesel fuel up to approximately 40% of RC biodiesel meet most of the specifications of EN590. An optimization of transesterification of RC oil using central composite rotational design (CCRD) and response surface modeling method (RSM) has been reported by authors [5]. On the other hand, technical process and production cost of biodiesel plants from castor bean oil through a transesterification reaction using ethanol was studied [6]. It has been concluded that the castor bean oil is more expensive than the conventional ones used to produce biodiesel.

RC is cultivated for the seeds which yield fast-drying, non-yellowing oil, used mainly in industry and medicine. RC oil is critical to many industrial applications because of its unique ability to withstand high and low temperatures [7]. It is used in coating fabrics and other protective coverings, in the manufacture of high-grade lubricants, transparent typewriter and printing inks, in textile dyeing (when converted into sulfonated Castor Oil or Turkey-Red Oil, for

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dyeing cotton fabrics with alizarine), in leather preservation. Hydrogenated oil is utilized in the manufacture of waxes, polishes, carbon paper, candles and crayons. 'Blown Oil' is used for grinding lacquer paste colors, while when it is hydrogenated and sulfonated it can be used for preparation of ointments. Castor Oil Pomace, the residue after crushing, is used as a high-nitrogen fertilizer.

Previous studies on castor oil suggest that its uniquely high level of the hydroxy fatty acid ricinoleic acid may impart increased lubricity to the oil and its derivatives as compared to other vegetable oils [8].

1 MATERIAL AND METHODS

1.1 Materials and Apparatus

Ricinus Communis (Castorbean) seeds used in this study were supplied from Turkish vegetable sources. RC oil was produced by using Soxhalet Extraction method. Nearly 35 to 37% oil content was extracted from RC seeds. The chemicals which were used during the experiments were purchased from Merck and methanol was purified prior to use. Table 1 shows the technical specifications of chemicals. Diesel fuel with respect to EN 590 standards was purchased and used during the experimental studies.

Table 1. *Specifications of chemicals*

Chemicals	Density [kg/m^3]	Purity [%]
Methanol	790	99.5
Sodium Hydroxide Pellet	-	>99
Acetic Acid	1049	>98

Instruments used for analyzing the product; Zeltex ZX 440 NIR petroleum analyzer with an accuracy of ±0.5 for determining cetane number; ISL CPP 97-2 with an accuracy of ±0.5 ^{o}C for pour point and cold filter plugging point; Koehler Saybolt viscosity test for determining the viscosity; Kyoto electronics DA-130 for density measurement and Tanaka flash point control unit FC-7 for flash point determination. Fatty acid methyl ester content in the esterified oil was determined by Gas Chromatograph (GC equipped with a FID detector, capillary SP TM 2380 column (60 m x 0.25 mm x 0.2 m) Shimadzu GC-14A) and GC/MS, Thermo-Finnigan TR5 MS gas chromatograph connected to a TR-5 capillary column (60 m x 0.25 mm ID x 0.25 UM film).

1.2 Production and Purification Methods

1.2.1 Oil Production from Ricinus Communis seeds

Oil was extracted from RC seeds using Soxhlet extraction apparatus (1000 ml) and hexane was used as solvent. The dried Ricunus Communis seeds (4 x 36 g) were placed into a cellulose paper cone and extracted with 600 ml hexane for 5 h. The solvent was removed via a rotary vacuum distillation at 40 ^{o}C. The residue was filtered. Finally, the RC oil was stored at 20 ^{o}C [10].

1.2.2 Reaction Conditions and Equipment

A glass pilot reactor with a 1000 ml volume was used for atransesterification reaction. It is equipped with mechanical stirrer, cascade heater system, contact thermometer and condenser with a guard tube to prevent moisture entering into the system. 400 g of neutral Ricinus Communis oil (crude grade) was added to the reactor and heated up to 60 ^{o}C with stirring. After sodium methoxide addition (80 ml methanol and 4 g NaOH), stirring condition (600 rpm) and the reaction were continued for two hours at constant temperature.

1.2.3 Purification of the Produced Biodiesel

All the products of the transesterification reaction in this study were allowed to settle overnight so as to enhance separation. Two distinct liquid phases were formed during separation in such a manner that the crude ester phase presented at the top and the glycerol phase at the bottom. The glycerol phase was removed and the methyl esters layer was then washed with warm diluted acetic acid at 60 ^{o}C repeatedly until the residual became clear. The excess methanol and water in the ester phase were then removed by heating the product to 110 ^{o}C [9] to [11].

The primary purpose of the biodiesel washing step is to remove any soaps formed during the transesterification reaction. In addition, the warm diluted water with acetic acid provides neutralization of the remaining catalyst and removes product salts.

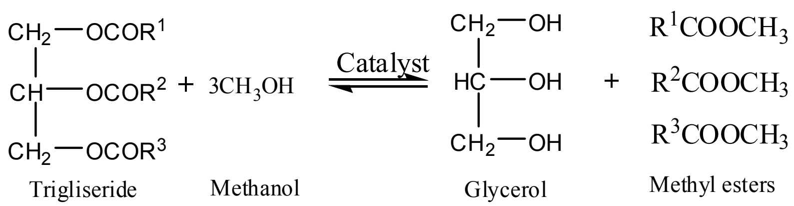

Fig. 1. *General equation for the transesterification of triglycerides*

The use of warm water prevents precipitation of saturated fatty acid esters and retards the formation of emulsions with the use of a gentle washing action. Slightly acidic water eliminates calcium and magnesium contamination and neutralizes remaining base catalysts. Gentle washing prevents the formation of emulsions and results in a rapid and complete phase separation [12].

2 RESULTS AND DISCUSSION

The fatty acid composition of RC oil determined by GC/MS is shown in Table 2. The methyl ester content of the reaction mixture was quantified using a sample (150 ml) which was taken from the reaction mixture at specified periods. The conversion ratio of triglyceride to methyl ester was analyzed by GC using an FID in both ASTM D 6751 and EN 14214 for soybean oil and RC oil. The result of transesterification reaction showed that all conversion values were in agreement with EN 14214. Table 3 shows the fatty acid methyl ester properties of the biodiesel produced from RC oil.

Biodiesel produced from RC oil was found to be much more viscous than other, more commonly tested, vegetable oil fuels (Table 4). Viscosity is one of the main drawbacks in the sense that its value is high, which means that it must be preheated in the fuel tank or blended with straight diesel during the cold winter periods [13]. According to the results, it has been determined that pure RC biodiesel usage can cause problems in the injection system because of its high viscosity. In order to solve the viscosity problem it can be suggested that RC biodiesel may use a mixture of others either diesel or biodiesels. Therefore, blending with Diesel fuel or other biodiesels may be the best solution for RC biodiesel usage in compression ignition engines.

Table 2. *Fatty acids contents of RC*

Fatty acids	Chemical formula	%
Palmitic acid	$CH_3(CH_2)_{14}COOH$	1.71
Linoleic acid	$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$	7.41
Oleic acid	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$	6.40
Stearic acid	$CH_3(CH_2)_{16}COOH$	2.04
Ricinoleic acid	$CH_3(CH_2)_5CH(OH)CH_2CH=CH(CH_2)_7COOH$	82.44

Table 3. *Analysis data of the RC biodiesel*

Properties	Units	RC biodiesel	EU biodiesel EN 14214 values	Test methods
% FAME	-	98	96.5	prEN 14103
Kinematic viscosity at 40 ^oC	mm^2/s	11.5	3.5 – 5.0	EN ISO 3104
Density at 15 ^oC	kg/m^3	920	860 – 900	EN ISO 12185
Flash point	^oC	>130	>120	EN ISO 3679
Cetane number	-	80	>51	EN ISO 5165
Cold filter plugging point	^oC	-35	Summer < 0, Winter < -15	EN 116
Pour point	^oC	-30	Summer < 4.0, Winter < -1.0	ISO 3016

Although the viscosity and the density of RC biodiesel were noted to be greater than that of diesel fuel, the cetane number was found in the range of EN 14214. Cetane number is known as a measurement of the combustion quality of diesel fuel. It has been observed that Ricinus Communis biodiesel has a higher cetane number, which causes shorter ignition delays, and thus, higher efficiency in engine.

In addition, the high flash point (more than 120 °C) makes the RC biodiesel in compliance with EN 14214.

Biodiesel derived from RC oil has a lower cold filter plugging point (CFPP) than other biodiesels.

The comparison of RC biodiesel with various vegetable oil esters is shown in Table 4 [14].

2.1. Low Temperature Property Study

The behavior of fuels under low temperature is an important quality measure. In order to assess biodiesel fuel performance in cold-temperature, various parameters have been suggested, including pour point (PP) and cold-filter plugging point (CFPP) [15].

The blends of RC and soybean biodiesel samples were therefore examined for their low temperature properties to study the effect of RC biodiesel on soybean biodiesel PP and CFPP. The results shown in Table 5 reveal that the higher RC biodiesel amount in blends gives the decreased PP and CFPP values of RC biodiesel-Soybean biodiesel blends.

2.2 Cetane Number Study

One of the major problems associated with the use of biodiesel, especially the one produced from soybean oil, is its low cetane number [16]. However, RC biodiesel has a higher cetane number, comparable to conventional biodiesels.

Cetane number and cold flow properties were determined in selected blends of RC biodiesel and soybean biodiesel. As shown in Table 5, the blending of 5% RC biodiesel to soybean biodiesel increased the cetane number of Soybean biodiesel from 45 to 48.

Table 4. *Comparison of RC biodiesel with various biodiesels*

Biodiesel produced from	Kinematic viscosity at 40 °C [mm²/s] EN ISO 3104	Cetane number EN ISO 5165	Pour point [°C] ISO 3016	Cold filter plugging point [°C] EN 116	Flash point [°C] EN ISO 3679	Density [kg/l] EN ISO 12185
Peanut oil	4.9	54	5	-	176	0.883
Soybean oil	4.5	45	1	-4	178	0.885
Babassu oil	3.6	63	4	-	127	0.875
Palm oil	5.7	62	13	11	164	0.880
Sunflower oil	4.6	49	1	-2	183	0.860
Ricinus Communis oil	11.5	80	-30	-35	>130	0.920
Diesel EN 590	3.06	50	-	-16	76	0.855

Table 5. *Comparison of properties of RC biodiesel, soybean biodiesel properties and their blends*

Biodiesel	Kinematic viscosity at 40 °C [mm²/s]	Cetane number	Cold filter plugging [°C]	Pour Point [°C]	Density [kg/m³]
Soybean	4.2	45	-4	1	884
Ricinus Communis (RC)	11.5	80	-35	-30	920
5% RC + 95% Soybean	4.5	48	-5	-2	887
10% RC + 90% Soybean	4.9	51	-7	-3	888
20% RC + 80% Soybean	5.6	56	-10	-6	891
50% RC + 50% Soybean	7.8	63	-20	-15	902

10% RC biodiesel and 90% soybean biodiesel, and 20% RC biodiesel and 80% soybean biodiesel blends were tested for cetane number and the results found were 51 and 56 respectively. Thus, the blending of RC biodiesel in soybean biodiesel increased the cetane numbers of the blends.

3 CONCLUSIONS

This study presents biodiesel production from RC oil and its determined biodiesel properties. It has been observed that while cetane number, flash point, cold filter plugging point and the pour point values of RC biodiesel were found in compliance with EN 14214, the viscosity and the density values were determined to be out of range. On the other hand, as soybean biodiesel has a low cetane number and high low temperature properties, the effect of RC biodiesel addition to soybean biodiesel was investigated. The conclusions of this study are summarized as follows:

1. RC oil can be used as a biodiesel raw material with its high oil content and its non-edible characteristics.
2. Cetane numbers of blends were increased with increased RC biodiesel contents. For this reason, RC biodiesel can be used as a cetane additive to improve cetane number of different biodiesel fuels.
3. The pour point and CFPP values were found to decrease with the increased RC biodiesel. From this point of view, RC biodiesel can be a very effective cold flow additive.
4. It can be said that pure RC biodiesel usage can cause problems in injection systems because of its high viscosity.

4 REFERENCES

[1] Hribernik, A., Kegl, B. (2007). The influence of biodiesel on the combustion and emission characteristics of a diesel engine. *Strojniški vestnik – Journal of Mechanical Engineering*, vol. 53, no. 10, p. 683-695.

[2] Zhang, Y., Dube, M.A., McLean, D.D., Kates, M. (2003). Biodiesel production from waste cooking oil: 1. Process design and technological assessment. *Bioresource Technology,* vol. 90, p. 1-16.

[3] Fangrui, M., Milford, A.H. (1999). Biodiesel Production: A review. *Bioresource Technology,* vol. 70, p. 1-15.

[4] Canoira, L., Galean, J.G., Alcantara, R., Lapuerta, M., Contreras, R.Y. (2010). Fatty acid methyl esters (FAMEs) from castor oil: Production process assessment and synergistic effects in its properties. *Renewable Energy*, vol. 35, p. 208-217.

[5] Cavalcante, K.S.B., Penha, M.N.C., Mendonça, K.K.M., Louzeiro, H.C., Vasconcelos, A.C.S., Maciel, A.P., Souza, A.G., Silva, F.C. (2010). Optimization of transesterification of castor oil with ethanol using a central composite rotatable design (CCRD). *Fuel*, vol. 89, p. 1172-1176.

[6] Santana, G.C.S., Martins, P.F., Silva, N.L., Batistella, C.B., Filho, R.M., Maciel, M.R.W. (2010). Simulation and cost estimate for biodiesel production using castor oil. *Chemical Engineering Research and Design,* vol. 88, p. 626-632.

[7] Comar, V., Tilley, D., Felix, E., Turdera, M., Neto, M.C. (2004). Comparative emergy evaluation of castorbean (Ricinus Communis) production systems in Brazil and the U.S. *Proceedings of IV Biennial International Workshop "Advances in Energy Studies,* p. 227-237.

[8] Goodrum, J.W., Geller, D.P. (2005). Influence of fatty acid methyl esters from hydroxylated vegetable oils on diesel fuel lubricity. *Bioresource Technology*, vol. 96, p. 851-855.

[9] Puhana, S., Vedaramana, N., Rama, B.V.B., Sankarnarayananb, G., Jeychandranb, K. (2005). Mahua oil (Madhuca Indica seed oil) methyl ester as biodiesel-preparation and emission characterstics. *Biomass and Bioenergy*, vol. 28, p. 87-93.

[10] Saloua, F., Saber, C., Hedi, Z. (2010). Methyl ester of [Maclura pomifera (Rafin.) Schneider] seed oil: Biodiesel production and characterization. *Bioresource Technology,* vol. 101, p. 3091-3096.

[11] Kafuku, G., Mbarawa, M. (2010). Biodiesel production from Croton megalocarpus oil and its process optimization. *Fuel*, vol. 89, p. 2556-2560.

[12] Van Gerpen, J., Shanks, B., Pruszko, R., Clements, D., Knothe, G. (2004). *Biodiesel Production Technology*. National Renewable Energy Laboratory, Colorado.

[13] McGuiness, P. (2008). Fuelling the car of the future. *Strojniški vestnik - Journal of Mechanical Engineering*, vol. 54, no. 5, p. 356-363.
[14] Barnwal, B.K., Sharma, M.P. (2005). Prospects of biodiesel production from vegetable oils in India. *Renewable and Sustainable Energy Reviews*, vol. 9, p. 363-378.
[15] Voća, N., Krička, T., Janušić, V., Jukić, Z., Matin, A., Kiš, D. (2008). Fuel properties of biodiesel produced from different raw materials in Croatia. *Strojniški vestnik - Journal of Mechanical Engineering*, vol. 54, no. 3, p. 232-244.
[16] Ramadhas, A.S., Jayaraj, S., Muraleedharan, C. (2004). Use of vegetable oils as I.C. engine fuels-A review. *Renewable Energy*, vol. 29, p. 727-742.