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Original Research Article

Investigation of biodiesel fuel from canola oil using various reaction parameters

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Abstract

The production of biodiesel fuel from canola oil was evaluated in this study. The process of alkali-catalyzed transesterification with methanol was carried out to examine the effects of reaction variables on the formation of methyl ester: variables which included alcohol: oil molar ratios of 3:1, 6:1, 8:1, 10:1, catalyst concentrations of 0.5, 1, 1.5, 2% w/w of oil, reaction temperatures of 30, 40, 50, 60^{o}C, and reaction times of 10, 20, 40, 60 min. The methyl ester yield from each reaction condition is calculated. The optimum conditions for transesterification of canola oil with methanol and KOH as catalyst were found to be 50^{o}C reaction temperature, 1 h reaction time, 8:1 molar ratio of canola oil to methanol and 1% catalyst (w/w). The resultant methyl ester content of 98%, plus all of the other measured properties of the canola biodiesel, compare the international standards EN 14214.

Keywords. Canola oil, methyl ester, transesterification.

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1. INTRODUCTION

The majority of energy demand is fulfilled by conventional energy sources like petroleum, coal, and natural gas. Petroleum-based fuels are limited reserves concentrate in certain regions of the world. The scarcity of known petroleum reserves will make renewable energy sources more attractive [1, 2]. Biodiesel, the monoalkyl esters of long chain fatty acids, is a chemically modified fuel derived from various kinds of vegetable oils and animal fats [3]. Meher et al. [4], which are composed primarily of high molecular weight triglycerides.

Vegetable oils from renewable oil seeds can be used when mixed with diesel fuels. Pure vegetable oil, however, cannot be used in direct-injection diesel engines, such as those regularly used in standard tractors, since engine cooking occurs after several hours of use.

Biolipids can be used to produce biodiesel. These are virgin vegetable oil feedstock; canola and soybean oils are most commonly used, though other crops such as mustard, palm oil, sunflower and even algae show promise, waste vegetable oil, animal fats; and non-edible oils such as jatropha, neem oil, castor oil, tall oil, *etc* [5, 6].

Vegetable oils are always triglycerides, generally with a number of branched chains of different lengths and different degrees of saturation. Vegetable oils have about 10% lower heating value than mineral Diesel due to the oxygen present in their molecules. The viscosity of vegetable oil is several times higher than that of mineral Diesel due to their large molecular mass and chemical structure [7]. With vegetable oil as a fuel, short term engine performance results are comparable to those with mineral Diesel, but long term results with vegetable oil or blends with mineral Diesel lead to severe engine deposits, piston ring sticking and injector coking [8, 9].

Several experimental researches have shown that the fuel properties of vegetable oils can be improved by transesterification. Transesterification is a chemical reaction in which alcohol reacts with the triglycerides of fatty acids in presence of a catalyst. The stoichiometric ratio for transesterification reaction requires three moles of alcohol and one mole of triglyceride to yield three moles of fatty acid ester and one mole of glycerol. Higher molar ratios result in greater ester production in a shorter time. The commonly accepted molar ratios of alcohol to vegetable oils are 3:1 to 6:1. The most commonly used catalyst materials for converting triglycerides into biodiesel are sodium hydroxide, potassium hydroxide, and sodium methoxide [4, 7, 10].

Biodiesel is a clean burning alternate fuel that is simple to use, biodegradable, nontoxic, and essentially free of sulfur. It is produced from domestic, renewable resources, which decreases dependency on foreign oil and contributes to the economy. The commercial use of biodiesel is strongly dependent on the price of the feedstocks so lower cost feedstocks are needed. The high cost of biodiesel, which is mainly due to the high costs of oil feedstock, is the main obstacle to its broader commercialization [11].

Canola is the genetically altered form of rapeseed, which consists of three species: Brassica napus, known as Argentine canola; Brassica rapa, known as Polish Canola; and Brassica juncea, known as quality canola brown mustard. All species belong to the *Brassicaceae* (Cruciferae) family, also known as the mustard family. Each canola species has distinct agronomic characteristics that should be considered when selecting a variety to grow. Spring and winter annual types are available in B. napus and B. rapa.

Canola was cultivated by ancient civilisations in Asia and the Mediterranean. Canola we know today was developed in the early 1970s using traditional plant breeding techniques; as a result of the efforts by Canadian plant breeders to remove the antinutritional components erucic acid and glucosinolates from rapeseed so that it would be absolutely safe for human and animal consumption. The plant also produced seeds with a very low level of saturated fat, 7% or below. This new oilseed was christened “canola” and there is a strict internationally regulated definition of canola that differentiates it from rapeseed, based upon canola oil having less than 2% erucic acid and the non-oil portion of the seed having less than 30 micromol/g glucosinolates in meal.

The objectives of this study were investigating the optimum reaction conditions for biodiesel production from canola oil, and study the effects of the variables on its alkali-catalyzed transesterification with methanol.

2. MATERIALS AND METHOD

2.1. Materials

The seeds of canola (*Brasicca napus Oleifera* sp.) were procured from the Black Sea Agricultural Research Institute, Samsun, Turkey. Dried methanol (max 0.005% H_2O, reagent grade) and diethyl ether (99.7%, analytical grade) were received from a local chemical store, Labkim, in Istanbul, Turkey. Analytical grade potassium hydroxide (KOH) was obtained from Merck, Germany. An electrical mill; BUCHI rotary evaporator (Rotavapor R-210) consisting of 1000 ml round flask and AND mark assay balance were used in laboratory studies.

2.2. Extraction of oil

Californium type canola seeds used in the study were dried at 120^{o}C for 1 hour. The dried seeds were transformed into very small particles by electrical mill. Canola oil obtained by solvent extraction method with diethyl ether solvent. Canola oil (CO) fatty acid composition and chemical properties of oil from Middle East Technical University, Petroleum Research Center (METU-PAL) was built.

2.3. Alkali-catalyzed transesterification

In this study, transesterification of canola oil with methanol via base (KOH) catalysis was carried out in a laboratory-scale setup. The equipment used for this study consisted of a 1000 ml reaction flask with rotary evaporator. In brief, the canola oil (100 g) was preheated to 30^{o}C before starting the reaction. The mixture in the reaction flask was heated and well-stirred at a constant stirring speed of 700 rpm for all test runs. The following rates were used to obtain the optimum reaction conditions in the experimental studies: 3:1, 6:1, 8:1 and 10:1 alcohol: oil molar ratios; 30, 40 50 and 60^{o}C reaction temperatures; 0.5%, 1%, 1.5% and 2% KOH catalyst concentrations; and 10, 20, 40 and 60 min reaction times.

The crude canola oil, methanol, and potassium hydroxide were used in amounts established for each experiment, with the oil preheated to the desired temperature in the reaction flask. In order to maintain its catalytic activity, the solution of potassium hydroxide in methanol was freshly prepared for each run. After the reaction, the mixture was allowed to settle by gravity for 12 h in the separatory funnel. Two layers were formed: the upper layer consisted of methyl ester, methanol traces, residual catalyst, and other impurities, whereas the lower layer consisted of glycerin, excess methanol, catalyst, and other impurities. The glycerin layer was then drawn off and the methyl ester layer was purified by washing with hot distilled water at 50^{o}C until the washing water had a pH value similar to that of distilled water. Finally, the produced quantity of methyl ester is calculated using the following formula:

Methyl esters yields (%) = grams of methyl esters produced / grams of oil used in reaction [×]100.

2.4. Fuel properties of COMEs

The canola oil methyl ester (COME) sample produced under optimal conditions was analysed at the Fuel Research Laboratory of the Marmara Research Centre of TUBITAK. The produced fuel properties of COME are determined following EN 14214 specifications. The determinations of ester content (EN 14103), density (EN ISO 3675), kinematic viscosity (EN ISO 3104), acid value (EN 14104), iodine value (EN14111), pour point (ENISO 3016), flash point (ASTM D 93), heating value (ASTM D 240), copper band corrosion (EN ISO 2160), cold filter plug point (EN 116), water content (ENISO12937), cetane number (EN ISO 5165), mono-/di-/ tri-glyceride content (EN14105), free and total glycerol (EN14105), sulphated ash content (EN ISO 3987), and sulphur content (EN ISO 20846) were carried out according to the cited standards.

3. RESULTS AND DISCUSSION

3.1. Characterization of the crude canola oil and canola biodiesel

Various chemical and physical properties of crude canola oil were given in Table 1. The predominant fatty acids in the oil and its various important properties are shown in Table 1. The fuel properties of canola oil methyl ester (COME) are determined and compared with EN 14214 biodiesel standards, as shown in Table 2.

Table 1. Properties of crude canola oil

Property	**Crude canola oil**
Fatty acid composition (%)	
Oleic acid (C18:1)	63.20
Linoleic acid (C18:2)	21.82
Linolenic acid (C18:3)	10.30
Stearic acid (C18:0)	1.90
Eicosenoic acid (C20:1)	1.82
Palmitic acid (C16:0)	0.30
Density at 20 ^{0}C (kg/m^3)	0.915
Kinematic viscosity at 20 ^{0}C (mm^2/s)	75.3
Acid value (mgKOH/g)	1.4
Iodine value (gI$_2$/100g)	114
Peroxide value (meq/kg)	0.8
Percentage oil content in seed (%)	40

Table 2. Properties of canola oil biodiesel in comparison with EN 14214

Analys	**Unit**	**Method**	**COME**	**EN 14214**
Ester content	%(m/m)	EN 14103	99.4	min 96.5
Density, 15 ^{o}C	g/cm^3	EN ISO 3675	0.883	0.86 - 0.90
Kinematic viscosity	mm^2/s	EN ISO 3104	4.60	3.5-5
Acid value	mgKOH/g	EN 14104	0.11	max 0.50
Iodine value	g iodine/100 g	EN14111	118	max 120
Pour point	^{o}C	ISO 3016	-12	max 0
Flash point	^{o}C	ASTM D93	105	min 101
Heating value	MJ/kg	ASTM D 240	39.96	min 35
Copper band corrosion (3 hours at 50 ^{o}C)	-	EN ISO 2160	1a	1a
Cold filter plug point	^{o}C	EN 116	-15	-15 - +5
Water content	mg/kg	ENISO12937	260	max 500
Monoglyceride content	%(m/m)	EN14105	0.06	max 0.80
Diglyceride content	%(m/m)	EN14105	0.19	max 0.20
Triglyceride content	%(m/m)	EN14105	0.08	max 0.20
Free glycerol	%(m/m)	EN14105	0.009	max 0.02
Total glycerol	%(m/m)	EN14105	0.06	max 0.25
Sulfated ash content	%(m/m)	EN ISO 3987	0.01	max 0.02
Sulphur content	mg/kg	EN ISO 20846	0	max 10

3.2. Effects of alcohol: oil molar ratio and reaction time

One important variable affecting the transesterification reaction was the alcohol: oil molar ratio. Theoretically, the stoichiometric ratio for transesterification reaction requires one mole of triglyceride and three moles of alcohol to yield three moles of fatty acid alkyl esters and one mole of glycerol. However, since this reaction is in fact reversible, a higher molar ratio is required in order to drive the equilibrium to the right for achieving a greater alkyl ester product [4, 6, 10, 12].

The alcohol: oil molar ratio (3:1, 6:1, 8:1 and 10:1) was varied to establish the effect of varying amount of methanol on COMEs production. In all sixteen experiments, 700 rpm rate of agitation, 60°C reaction temperature and 1% KOH were employed. The optimum yield (98%) of COMEs was gained at alcohol: oil molar ratio of 8:1 (Fig. 1).

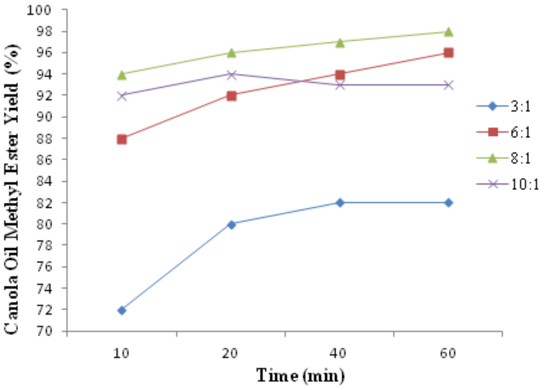

Fig. 1. Effect of alcohol:oil molar ratio on the yield of canola oil methyl esters

Higher quantities (beyond 8:1) of methanol had an adverse effect on COMEs production. At alcohol:oil molar ratios greater than 8:1, separation of esters from glycerol was difficult. The unreacted methanol, when present, can suppress the gravity decantation so that the apparent yield of COMEs decreases because traces of glycerol may remain in the biodiesel phase [2, 6, 13, 14].

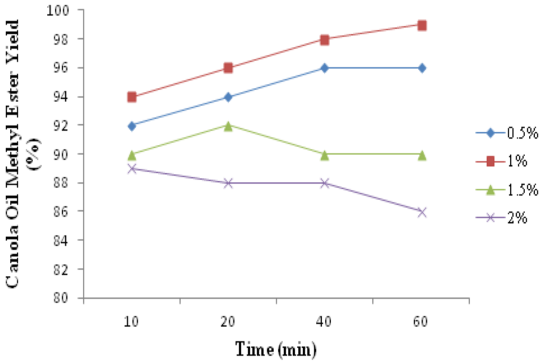

Fig. 2. Effect of KOH concentration on the yield of canola oil methyl esters

3.3. Effects of catalyst concentration and reaction time

Because the presence of a catalyst accelerates the transesterification reaction, another important variable that affects the conversion of a triglyceride to its ester is the catalyst concentration [4].

While appraising the effect of catalyst amount on COMEs production, a range of sixteen experiments were conducted with varying concentrations (0.5%, 1%, 1.5% and 2% w/w) of KOH. In all experiments, alcohol:oil molar ratio of 8:1, agitation intensity 700 rpm and reaction temperature 60°C were utilized. Fig. 2 depicts the optimum yield of COMEs at 1% catalyst.

The catalyst concentrations higher than 1% exhibited adverse effects on COMEs yield, which is in line with the work of Dorado et al. [15] and Rashid et al. [13], who reported that the soap formation in the presence of high catalyst amount increases the viscosity of reaction leading to lower methyl ester yields. At the lowest catalyst concentration, 0.5% w/w of oil, the reaction was the slowest, being insufficient to catalyze the reaction to completion.

3.4. Effects of reaction temperature and reaction time

In this study, the effects of reaction temperature and reaction time on the alkali-catalyzed transesterification of crude canola oil were investigated. Literature data shows that reaction temperature has an important role in alkali-catalyzed transesterification [4, 6, 9, 10]. For studying the effect of temperature on the transesterification reaction, the reaction temperature was varied as 30, 40, 50 and 60°C, while in all sixteen experiments, 700 rpm rate of agitation, molar ratio of alcohol to oil (8:1) and 1% KOH were employed. The effect of reaction temperature on the ester yield is shown in Fig. 3.

It is found that both the reaction time falls below 50°C and rises above 50°C, the amount of ester decreases. Several researchers found that the temperature increase influences the reaction in a positive manner [1, 5, 6, 9, 16]. Dorado et al. [15], report that the ester yield slightly decreases above 50°C reaction temperature. It may probably be due to a negative interaction between the temperature and catalyst concentration due to the side reaction of saponification. High reaction temperature tends to accelerate the saponification of the triglycerides by the alkaline catalyst before completion of the transesterification.

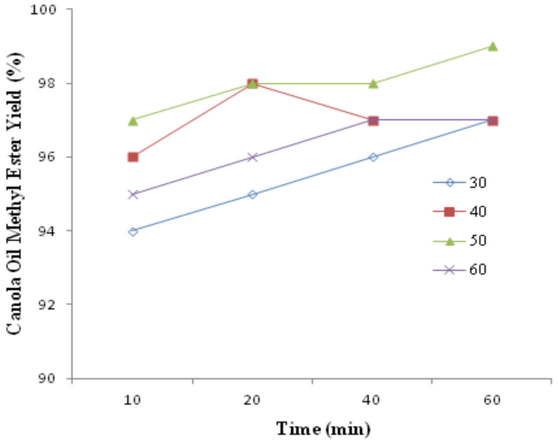

Fig. 3. Effect of reaction temperature on the yield of canola oil methyl esters

4. CONCLUSION

Base catalyzed transesterification was studied with KOH catalyst for biodiesel production from canola oil. The optimum conditions for production was a alcohol:oil molar ratio of 8:1, a catalyst concentration of 1% w/w of oil, and a reaction temperature and time of 50°C and 60 min, respectively. (However, at a catalyst concentration higher than 1% w/w of oil, the methyl ester content decreased due to soap formation, which was a hindrance for this reaction). This set of optimised conditions provided 98% COMEs yield. Fuel properties of COMEs were quite comparable with those of EN 14214.

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