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The present study investigated the transesterification process used in the production of canola oil methyl ester from canola oil and methanol over synthesized KF/Al_2O_3 catalysts. Different amounts of KF solution (15-65 wt. %) were impregnated into alumina. Loading 35 wt. % of KF into an alumina (35% KF/Al_2O_3) catalyst gave the maximum yield of 99.6% under the following reaction conditions: 60 $^\circ$C, 8-h reaction time, 15:1 molar ratio of methanol/canola oil, and 3 wt. % of catalyst. The fuel properties of canola oil methyl ester were tested, including ester content, density, viscosity, flash point, copper strip corrosion, total and free glycerol, acid value, distillation temperatures, pour point, freezing point, and calculated cetane index. The calculated cetane index was 62.8. The pour point (–10 $^\circ$C) and freezing point (–12.9 $^\circ$C) were lower than those of No. 2 diesel fuel. The results show that the produced canola oil methyl ester can safely be used as an alternative diesel fuel.

Key Words: Biodiesel, fuel properties, transesterification, heterogeneous basic catalyst

Introduction

Biodiesel is a biodegradable, non-toxic clean-burning alternative fuel produced by the transesterification of renewable sources, such as vegetable oil, animal fat, and used cooking oil. Its properties are similar to those of diesel fuels and, therefore, biodiesel is a strong candidate for replacing diesel fuels.[1] Biodiesel can be used in compression-ignition (diesel) engines with little or no modification. Transesterification of vegetable oil to

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biodiesel (fatty acid methyl ester, FAME) can be catalyzed by bases, acids, and enzymes. Commercially used homogeneous alkali catalysts are NaOH, KOH, and their alkoxides. Lately, solid base catalyzed transesterification has become a promising alternative to homogeneous base transesterification for biodiesel production. The minimization of soap formation, separation, corrosion, and environmental problems are the main advantages of solid base catalysts.[2-5]

The use of solid base catalysts relys on the treatment of various catalyst supports, i.e. porous powders of zirconia, titania, and alumina, with Na, NaOH, KCl, K_2CO_3, KNO_3, KI, KBr, and KF. Alumina-based catalysts were studied by several researchers. Na/NaOH/γ-Al_2O_3, a heterogeneous base catalyst, was the first to be adopted for transesterification of soybean oil to biodiesel.[5] Xie et al. investigated a solid catalyst prepared by impregnating potassium compounds (KI, KF, KOH, and KNO_3) into alumina for the transesterification of soybean oil.[3,6] KI (35 wt. %) on an alumina catalyst gave the highest conversion (90%) under the following conditions: reaction temperature of 65 °C, 8-h reaction time, 15:1 methanol/oil ratio, and 2.5 wt. %. of catalyst.[3] Maximum conversion of 87% was achieved over 35 wt. % of KNO_3 impregnated into an alumina catalyst under the following reaction conditions: a 15:1 molar ratio of methanol to soybean oil and a reaction time of 7 h. In these studies catalyst activities correlated well with their corresponding basic properties.

Lately, a significant amount of research has focused on transesterification of canola oil over solid base catalysts. A series of alkali metal (Li, Na, and K) promoted alkali earth oxides (CaO, BaO, and MgO), as well as K_2CO_3 supported on alumina (Al_2O_3) were prepared and used as catalysts for transesterification of canola oil with methanol. Four catalysts—K_2CO_3/Al_2O_3 and alkali metal (Li, Na, and K) promoted BaO—were effective for transesterification with > 85 wt. % of methyl esters.[7] Ilgen and Akin investigated the production of biodiesel from canola oil with different alcohols over Mg-Al hydrotalcite catalysts.[8] The highest triglyceride conversion rate (71.9%) was achieved after 9 h of reaction at 60 °C, with a 6:1 molar ratio of methanol to canola oil and a 3 wt. % catalyst with 125-150-μm particles. MgO-supported KOH catalysts were investigated for transesterification of canola oil and 20 wt. % KOH loaded on MgO gave the highest conversion of canola oil (99.36%) and the highest FAME yield (95.05%).[9] In our previous publication, the synthesized KF/Al_2O_3 solid base catalyst showed the highest activity in the transesterification of canola oil with methanol, gave very stable methyl ester content during the reaction, and had the highest yield (99.6%) at the end of the 8-h reaction at 60 °C, with a 15:1 methanol/oil ratio and 3 wt. % of catalyst.[10]

Biodiesel has been characterized according to its density, viscosity, high heating value, cetane index, cloud and pour points, distillation characteristics, and flash and combustion points, with regards to ISO norms.[11] Monoglyceride, diglyceride, and triglyceride content, bonded, free, and total glycerol levels, acid value, and iodine number were selected for the quality control of biodiesel.[12] Most recently, transesterified sesame seed oil,[13] Terminalia catappa L,[14] rice brain oil biodiesel,[15] palm oil biodiesel,[16] and karanja oil biodiesel[17] were reported to be in the acceptable range for use as biodiesel in diesel engines. Alptekin and Canakci have reported the densitiy and viscosity of biodiesel-diesel fuel blends.[18] According to their results, the density and viscosity of the blends increased as the biodiesel concentration in the entire fuel blend increased.

In the present study we investigated the fuel properties of biodiesel produced by transesterification of canola oil with methanol over a synthesized solid KF/Al_2O_3 catalyst. Different amounts of KF solution (15-65 wt. %) impregnated into alumina were investigated. Surface area of the synthesized catalysts was determined by nitrogen adsorption, using a multipoint BET sorptometer. Basic strength of the synthesized catalysts was

evaluated following a Hammett indicator procedure. Transesterification reaction parameters—alcohol to oil ratio (15/1), temperature (60 °C), amount of catalyst (3 wt. %), and reaction time (8 h)—were set constant in this study. Some of the most important fuel properties, including ester content, density, viscosity, flash point, copper strip corrosion, total and free glycerol, acid value, distillation temperatures, pour point, and freezing point, were measured and compared to the standards. The cetane index was calculated based on specific gravity and the 10%, 50%, and 90% distillation temperature of the fuels.

Experimental

Materials

Alumina (γ-Al_2O_3) and potassium fluoride (KF) were obtained from Merck. Analytical-grade methanol (purity 99.8 vol. %) was obtained from Riedel-de Haën. Commercial canola oil was purchased from a local food market. Free fatty acid content of the canola oil was determined to be 0.085%, based on the AOCS Cd 3a-64 method.

Catalyst preparation and characterization

The incipient-wetness impregnation method was used to prepare the solid base catalysts used in this study. Incipient-wetness impregnation utilizes a quantity of water less than or equal to that required to fill the pores of the support material. Details of the method were reported in our previous publication.[10] The water absorbance of Al_2O_3 was experimentally determined. A mixture containing 0.059 g of alumina Al_2O_3 and 1 mL of distilled water was placed in a centrifuge tube and centrifuged at 1000 rpm for 2 min, while another centrifuge tube with some water was placed at the opposite side. Excess water on top of the alumina was removed and weighed. The water absorbance of alumina was then calculated from the difference between the weight of wet and dry alumina. Different concentrations of KF aqueous solution (15, 25, 35, 45, 55, and 65 wt. %) were prepared based on the water absorbance of alumina. During the impregnation step, 3.25 g of alumina in a 250-mL flask was placed in an ultrasonic water bath. A vacuum was applied to the alumina for some time in order to open the pores. The prepared KF solution was added drop-wise on the alumina using a peristaltic pump. Then the prepared impregnate was dried at 393 K for 16 h. The finish catalyst for the transesterification reaction was obtained by calcination at 773 K for 3 h. Calcination temperature and time were taken from the study by Xie and Li.[6] The basic strength of these catalysts was evaluated following a Hammett indicator procedure[6,19] The nitrogen absorbance method, using a multipoint BET sorptometer, was used for the determination of the BET surface area values of the synthesized catalysts. Prior to each surface area measurement, all samples were kept in an oven overnight under vacuum at 110 °C.

Biodiesel production

The conversion of the vegetable oil to biodiesel, i.e. the transesterification reaction of the triglycerides to fatty acid methyl esters was performed in a jacketed 1000-mL batch reactor equipped with a reflux condenser and a magnetic stirrer. Initially, heterogeneous solid catalyst and methanol were mixed in the reaction vessel, and canola oil was added to the reaction mixture. The system was heated to the desired temperature and the mixing rate was kept constant at 600 rpm during the reaction. During the experiments the alcohol to oil ratio

of 15:1, temperature of 60 °C, 3 wt. % of catalyst, and reaction time of 8 h were set constant, according to our previously published results.[10] After 8 h of the transesterification reaction, the reaction mixture was separated from the catalyst via filtration under vacuum and then poured into a separator funnel in which it was kept constant overnight. The biodiesel and glycerol layers had different densities and thus were easily separated. The upper layer was biodiesel and the bottom layer was, essentially, glycerol. Chemical analysis of the methyl ester content of the biodiesel phase was performed using an Agilent 6890 gas chromatograph equipped with a flame ionization detector (FID) and with a Carbowax 20 M capillary column, according to European Standard EN 14103 (2003).[20]

Kinematic viscosity

Biodiesel is much less viscous than the oil from which it is made. In diesel engines viscosity affects injector lubrication and fuel atomization.[15] In the present study kinematic viscosity was determined using a COMECTA Cannon-Fenske viscometer, according to the ASTM D445 standard test method.

Density

Density is an important parameter for diesel fuel injection systems. Many performance characteristics, such as cetane number and heating value, are related to density.[21] This property influences the efficiency of fuel atomization.[22] Density in the present study was measured using an Anton Paar DMA 35_N density meter at 15 °C, according to the ASTM D941 standard test method.

Flash point

The flash point temperature of diesel fuel is the minimum temperature at which the fuel will flash upon application of an ignition source. One of the most important advantages of biodiesel is that its flash point is greater than that of diesel fuel, which is reflected in the specifications in the standards. The flash point of biodiesel must be a minimum 120 °C and 130 °C, according to EN 14214 and ASTM 6751, respectively. This parameter was determined in the present study according to the ASTM D93 standard test method.

Copper strip corrosion

Corrosion is a chemical action that destroys the surface of a metal by oxidation alone or in combination with a chemical process. It should be tested in fuels, especially for transportation and storage conditions. Free fatty acids and some sulphur compounds that exist in biodiesel may cause corrosion. In the present study corrosion level was measured according to the ASTM D130 standard test method.

Ester content

Biodiesel is the name of the ester generally defined as the mono alkyl ester made from renewable sources, such as vegetable oil and animal fat, through the transesterification process. Use of biodiesel with low conversion is a significant issue as the unconverted triglycerides could polymerize and eventually build up in fuel lines, causing

partial clogging of these lines, which could cause significant power loss. High ester content is a measurement of the completeness of the transesterification reaction. In the present study, the conversion of canola oil to fatty acid methyl esters was measured using an Agilent 6890 gas chromatograph equipped with a flame ionization detector (FID), and with a Carbowax 20 M capillary column, according to European Standard EN-14103 (2003).[20]

Total and free glycerol

Glycerine is a by-product of the transesterification reaction. The stoichiometry of the transesterification reaction requires a 3:1 molar ratio to yield 3 mol of ester and 1 mol of glycerol. Total and free glycerol is used to determine the level of glycerine in the fuel and includes the free glycerine portion of any unreacted or partially reacted oil or fat. High levels of free glycerine can cause injector deposits as well as clogged fuelling systems, and can result in the build up of free glycerine at the bottom of storage and fuelling systems.[23] In the present study this parameter was tested according to the A.O.C.S. Ca 14-56 method.

Acid value

The acid value measures the amount of unreacted acids remaining in the finished fuel, and is also an indicator of oxidized fuel. The acid value defines the number of milligrams of potassium hydroxide necessary to neutralize the free acids in 1 g of sample. A high acid value will damage fuel pumps and fuel filters.[24] In the present study the free fatty acid of canola oil and biodiesel were determined according to the A.O.C.S. Cd 3a-64 method. The acid value was calculated according to Eq. (1).

Acid value, mg KOH/g of sample = [(**A** - **B**) x **N** x **56.1**]/**W** (1)

where **A** = mL of standard alkali used in titrating to the middle of inflection in the titration curve of sample, **B** = mL of standard alkali used in titrating to the same pH meter reading as for the blank, **N** = normality of the standard alkali, and **W** = g of sample.

Distillation temperatures

Distillation is an indicator of the purity of finished fuel. Distillation includes determination of the range of boiling points for the fuel and is used to characterize the fuel in terms of the boiling temperatures of its components.[25] In the present study distillation temperatures were determined according to the ASTM D86 standard test method.

Cetane index

The cetane index is a measure of the ignition quality of a fuel and influences white smoke and combustion roughness. The cetane index is based on specific gravity and the 10%, 50%, and 90% distillation temperatures of the fuel. This parameter was calculated according to the ASTM D4737 standard test method in the present study.

Pour point and freezing point

Liquids have a characteristic temperature at which they turn into solids, known as their freezing point. On the other hand, pour points define the lowest temperature at which the fuel can still be moved, before it has gelled.[26] The pour point and freezing point are used to characterize the cold flow operability of fuel, because the pour point and the freezing point of fuel affect the utility of a fuel, especially in cold climate conditions. The pour point and the freezing point were determined in the present study according to the ASTM D97 and ASTM D2386 standard test methods.

Results and discussion

The surface area, basic strength, basicity, and the corresponding conversion to biodiesel values of the synthesized catalysts are reported in Table 1. The BET surface area of alumina was about 140 m^2/g; however, the BET surface area of the synthesized catalysts was between 32.2 and 4.1 m^2/g. This was an expected outcome, as the surface and the pores of the alumina were covered by potassium fluoride during the impregnation process. A significant reduction in pore volume was also observed after impregnation and calcination. As can be seen in Table 1, a strong relationship between the basicity of the catalysts and the activity of the catalysts was observed. In the literature this relationship is explained as follows: high basicity together with high activity of the catalyst might be partially due to K_2O phase formation on the surface of this type of catalyst and Al-O-K groups in the composite due to decomposition products of the loaded K compounds.[3,6,10]

Table 1. Physical properties and catalytic activities of the synthesized catalysts.

Catalyst	BET area (m^2/g)	Pore Volume (cm^3/g)	Pore Diameter (nm)	Basic Strength (H_)	Basicity (mmol/g)	Yield of ME (%)
Al$_2$O$_3$	140.2	0.261	7.4	< 7.2	-	-
KF (15%)-Al$_2$O$_3$	32.2	0.086	10.4	15.0-18.4	0.445	93.6
KF (25%)-Al$_2$O$_3$	28.3	0.082	11.9	15.0-18.4	0.486	95.3
KF (35%)-Al$_2$O$_3$[a]	25.1	0.077	12.3	15.0-18.4	0.521	99.6
KF (45%)-Al$_2$O$_3$	11.4	0.064	16.2	15.0-18.4	0.501	98.4
KF (55%)-Al$_2$O$_3$	4.3	0.056	17.9	15.0-18.4	0.506	96.1
KF (65%)-Al$_2$O$_3$	4.1	0.055	18.1	15.0-18.4	0.508	96.2

Reaction conditions: Methanol/oil: 15:1; temperature: 60 °C; reaction time: 8 h; catalyst amount: 3 wt. %.
[a] Boz and Kara[10].

Recovery of catalyst from the reaction mixture is an important operational parameter. Reuse of 35 wt.% KF into the Al_2O_3 catalyst was tested in the transesterification of canola oil with methanol in our previous publication.[10] Three successive runs were carried out under the same operating conditions (methanol/canola oil: 15:1; catalyst amount: 3 wt.%; reaction time: 2 h; stirring rate: 600 rpm; T: 60 °C). Conversion of triglyceride was reported as 95% (1st use), 63% (2nd use), and 62% (3rd use).

Transesterification reactions of canola oil with methanol over synthesized catalysts were carried out at 60 °C, with a methanol/canola oil ratio of 15:1, catalyst amount of 3 wt. %, and 8 h of reaction. The highest yield

of methyl ester was obtained over 35 wt. % KF/Al_2O_3 of catalyst; therefore, biodiesel production was performed over this catalyst and the most important fuel properties of biodiesel (canola oil methyl ester) were determined and compared with the standard tests (Table 2). In this study the European Standard EN-14214:2002 and the US Standard ASTM D 6751 were used as international standards. The values of the fuel properties obtained for the sample, and the reference values for biodiesel according to EN-14214 and ASTM D-6751 are summarized in Table 2. According to EN-14103, the minimum acceptable purity for biodiesel is 96.5% in methyl esters. The purity of biodiesel in the present study, in terms of methyl esters conversion, was 99.6%.

Table 2. Fuel specifications of canola oil methyl ester and diesel fuels.

Property	Diesel Fuels [a]		Present research Canola methyl ester	EN 14214	ASTM D-6751
	N.D	S.E			
Density (g/cm^3)	0.8424	0.8368	0.881	0.86-0.90	-
Viscosity (mm^2/s)	3.4301	2.7109	4.44	3.50-5.00	1.90-6.00
Pour Point (°C)	− 6	< −21	−10.0	-	-
Freezing Point (°C)	-	-	−12.9	-	-
Ester Content (%)	-	-	99.6	96.5	-
Flash Point (°C)	58	55	135.7	min. 120	min. 130
Acid Value (mg KOH/g)	-	-	0.72	max. 0.50	max. 0.80
Copper Strip Corrosion (3 h 50 °C)	-	-	No 1A	max. No. 1	max. No. 3
Total Glycerol (%)	-	-	0.24	max. 0.25	max. 0.24
Free Glycerol (%)	-	-	0.02	max. 0.02	max. 0.02
Calculated Cetane Index	57.8	55.8	62.8	-	-
Distillation (%)					
IBP	-	-	315		
10%	239	228	351		
50%	305	283	353		
90%	372	350	359	-	90% max. 360
EBP	405	372	374		
Recovery	-	-	98.8		
Residue	-	-	0.7		
Loss	-	-	0.5		

IBP: Initial boiling point; EBP: end boiling point; N.D.: normal diesel (Petrol Office); S.E.: (Shell extra diesel)
[a] Alptekin and Canakci [18].

Free fatty acid content of canola oil was 0.085%, according to the AOCS Cd 3a-64 method. The acid value of canola oil was calculated as 2.08 mg of $KOHg^{-1}$. The acid value of canola oil was reduced from 2.08 to 0.72 kg KOH/g after the transesterification reaction. This value was an acceptable value according to the ASTM D-6751 standard. Total and free glycerol of the product were also within the acceptable range of EN-14214 and ASTM D-6751 standards.

The main purpose of the transesterification of oils is to reduce high viscosity values. The viscosity of canola oil at 40 °C was substantially reduced from 36.88 to 4.44 mm^2/s after the transesterification reaction. The calculated cetane index of canola methyl ester was higher than that of diesel fuels, which suggests that the

biodiesel has better combustion properties. On the other hand, the pour point and the freezing point of canola methyl ester were –10.0 °C and –12.9 °C, respectively. The pour point and the freezing point are fuel properties important to the usability of produced biodiesel in cold climate conditions. The flash point is considered in the handling, storage, and safety of fuels. The high flash point of canola methyl ester shows that it is a safer fuel to handle. The 90% distillation temperature was in the range recommended by the ASTM D-6751 standard.

A comparison of the fuel properties of the canola oil methyl ester obtained in this study with the biodiesel produced by other researchers[15,17,18,27] is shown in Table 3. Biodiesels were produced from different feed stocks by the other researchers given in Table 3 using homogeneous catalysts different than that used in the present study. Transesterification of canola oil in a heterogeneous system produced better fuel properties, as compared to fuel produced with a homogeneous system. The properties of our canola oil methyl ester were similar to other biodiesels, except that the canola oil methyl ester produced in this study had a higher pour point and calculated cetane index. The flash point of the canola oil methyl ester produced in this study was higher than that of the canola oil methyl ester obtained in the study by Alptekin and Canakci.[18] In their study homogeneous transesterification of canola oil with methanol over 1% KOH of the oil's weight gave a 97.1% methyl ester yield. It can be concluded that a heterogeneous-catalyzed system for the production of canola oil methyl ester gave a higher methyl ester yield and better fuel properties, which are comparable to those of the standards.

Table 3. Comparison of the properties of canola oil methyl ester with the biodiesels produced by other researchers.[15,17,18,27]

Property	Present research COME	ROME[a]	PME[b]	KOME[c]	SOME[d]	SFOME[d]	COME[d]
Density (g/cm^3)	0.881	0.877	0.880	0.876	0.8845	0.8840	0.8828
Viscosity (mm^2/s)	4.44	5.29	5.7	9.6	3.9713	4.0303	4.3401
Pour Point (°C)	–10.0	– 2	-	7	0	– 1	–8
Ester Content (%)	99.6	-		-	-	97.1	99.2
Flash Point (°C)	135.7	183	164	187	139	157	107
Acid Value (mg KOH/g)	0.72	-	-	-	0.16	0.14	0.14
Total Glycerol (%)	0.24	-	-	-	0.11	0.09	0.12
Free Glycerol (%)	0.02	-	-	-	0.020	0.016	0.010
Calculated Cetane Index	62.8	-	-	-	60.1	60.9	61.5
Distillation (%)							
10%	351	-	-	-	348	350	350
50%	353	-	-	-	350	352	352
90%	359	-	-	-	357	358	359
EBP	374	-	-	-	380	384	382

EBP: End boiling point; COME: canola oil methyl ester; ROME: rice bran oil methyl ester; PME: palm oil methyl ester; KOME: karanja oil methyl ester; SOME: soybean oil methyl ester; SFOME: sunflower oil methyl ester.

[a] Sinha et al.[15].   [b] Srivastava and Verma[17].   [c] Rehaman and Phadatare[27].   [d] Alptekin and Canakci[18].

Conclusions

The effects of KF loading into alumina were investigated for the transesterification of canola oil with methanol. It was observed that 35 wt. % of KF into Al_2O_3 was the best catalyst and gave a methyl ester content of 99.6% under the following conditions: 60 °C, methanol/oil ratio of 15:1, 3 wt. % of catalyst, and 8 h of reaction. The canola oil methyl ester obtained was characterized to determine its suitability for use as a fuel in diesel engines. The viscosity of canola oil reduces substantially after transesterification and becomes comparable to that of diesel fuel. The flash point and calculated cetane index of our canola oil methyl ester were higher than those of diesel fuel. The higher flash point of the canola oil methyl ester makes it a safer fuel. The higher calculated cetane index suggests better combustion properties of the biodiesel. The produced biodiesel's fuel characteristics indicate that it can be used as a substitute diesel fuel.

Acknowledgements

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