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Transesterification of *Camelina Sativa* Oil using Supercritical and Subcritical Methanol with Cosolvents

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Transesterification of camelina oil using supercritical methanol with hexane as a cosolvent and subcritical methanol along with potassium hydroxide as a cosolvent/catalyst was investigated to study the methyl ester conversion process. It was found that cosolvents play a vital role in reducing the severity of critical operational parameters and maximize the biodiesel yield. The experimental results from the process parametric evaluation studies show that supercritical methanol with hexane as a cosolvent could produce maximum methyl esters using the following conditions: reaction temperature of 290 °C, methanol to oil ratio of 45, and reaction time of 40 min. For subcritical methanol condition with 0.3 wt % potassium hydroxide as a cosolvent, methyl ester yields of +90% are obtained using the following conditions: reaction temperature of 180 °C, methanol to oil molar ratio of 30, and a reaction time of 20 min. Process variables critical to the methyl ester conversion are determined to be cosolvent ratio, molar ratio of alcohol to oil, and reaction time. Fuel properties of the biodiesel produced are comparable to those of regular diesel and conform to the ASTM standards.

1. Introduction

Biodiesel is a nontoxic, biodegradable, renewable fuel that can be produced from a range of organic feedstock including fresh or waste vegetable oils, animal fats, and oilseed plants. Biodiesel has significantly lower emissions than petroleum-based diesel when it is burned, whether used in its pure form or blended with petroleum diesel. It does not contribute to a net rise in the level of carbon dioxide in the atmosphere and alleviates the intensity of the greenhouse effect.[1,2] In addition, biodiesel is better than diesel fuel in terms of sulfur content, flash point, aromatic content, and biodegradability.[3]

Vegetable oils are becoming a promising alternative to diesel fuel because they are renewable in nature, environmental-friendly and can be produced locally. *Camelina sativa* is an underexploited crop species of great economical potential. *Camelina sativa* oil is rich in omega-3 fatty acids and yields an average of 1200–1400 pounds per acre.[4] The production cost for *Camelina sativa* oil is substantially lower than many other oil crops such as rapeseed, corn, and soybean, which makes camelina an attractive potential crop for biodiesel and many other industrial applications.[5] *Camelina sativa* has positive energy balance for the production of biodiesel ester (net energy ratio = 1.47).[6]

Biodiesel production by transesterification reaction can be catalyzed with alkali, acid, or enzyme catalysts. Alkali and acid transesterification processes require shorter reaction time and lower costs as compared to the enzyme catalyst process.[7,8] The alkali process gives high purity and yield of biodiesel in a shorter reaction time.[2] However, this process is not suitable for feedstocks with high free fatty acid (FFA) content. As a result, a two-step transesterification process (acid esterifica-tion followed by alkali transesterification) was developed to reduce high free fatty acid content and improve the biodiesel yield.[9] Longer reaction time and lower recovery of catalyst were the drawbacks of the two-step process. To overcome these disadvantages of the two-step acid catalyzed process, a process using both homogeneous Lewis acid catalyst and heterogeneous metal oxide catalyst was implemented.[10,11] However, for this process, the reaction temperature was high and catalyst activity was weak, which resulted in low methyl ester yield. In order to solve these problems, Saka and Demirbas have proposed that biodiesel can be prepared from vegetable oil through a noncatalytic transesterification via supercritical alcohol method.[12–14] The basic premise of super-critical treatment is to exploit the effect of pressure and temperature upon thermophysical properties of the solvent, such as dielectric constant, viscosity, specific weight, and polarity.[15] Table 1 compares the physiochemical

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Table 1. Physicochemical Properties of Methanol at Ordinary and Supercritical Conditions

properties	ordinary condition (25 °C, 1 bar)	supercritical condition (250 °C, 20 MPa)
specific gravity, kg/l	0.7915	0.272
ionic product, log K_w	−0.77	not available
dielectric constant	32.6	7.2
viscosity, Pa-s	5.4×10^{-4}	0.58×10^{-4}
hydrogen bonding No.	1.93	< 0.7
solubility parameter $(MPa)^{1/2}$	7.1	4.1

properties of methanol at an ordinary condition and a supercritical condition.[16−18]

Supercritical methanol is believed to be able to solve the problems related to two-phase mixing of methanol/oil by forming a single phase due to the lower value of the dielectric constant of methanol in the supercritical state.[19] Compared to the conventional transesterification method, this novel method is noncatalytic, requires shorter reaction time for complete conversion of oil to ester, is environmentally benign, and can be applied to a variety of feedstock. However, the synthesis of biodiesel by supercritical methanol has some drawbacks, such as high cost of the equipment and high energy consumption due to high temperature and pressure conditions, which are not viable for large-scale industrial applications.[20] It has been reported that the value of the solubility parameter of methanol may decrease and become closer to that of vegetable oil if proper temperature and pressure conditions are employed.[21] It was also reported that as the reaction temperature is increased by 10 °C, the solubility of vegetable oils in methanol also increases at the rate of 2 ± 3% (w/w).[22] Therefore, for practical purposes, it is beneficial to investigate the use of a cosolvent, which can increase the mutual solubility of methanol and vegetable oil at low reaction temperatures. Cosolvents, such as carbon dioxide, hexane, and calcium oxide[23−25] added to the reaction mixture can decrease the severity of the reaction parameters. Moreover, since there is more than one possible critical point for a binary system, the addition of an appropriate cosolvent can decrease the critical point of methanol and allow the supercritical reactions to be carried out under milder conditions.[26] The transesterification of soybean oil with KOH as a cosolvent to increase the mass transfer between oil and methanol was investigated.[20] KOH as a cosolvent/catalyst could decrease the energy of the transition state, thereby increasing the rate of the reaction. The supercritical methanol with potassium hydroxide can largely decrease the reaction parameters, such as reaction pressure and temperature.

In this study, transesterification of camelina oil using supercritical methanol with hexane as a cosolvent and subcritical methanol with potassium hydroxide (KOH) as a cosolvent/catalyst are investigated. Effects of different reaction parameters on the biodiesel yield are presented.

2. Experimental Section

2.1. Materials and Methods. Cold-pressed *Camelina sativa* oil was obtained from Marx Foods Company, New Jersey, USA. Potassium hydroxide flakes (KOH) and hexane (95%, Optima) were procured from Fisher Scientific. To test the physicochemical properties of the oil, ethanol (95% v/v), hydrochloric acid, and diethyl ether were available from Fisher Scientific. Extra-pure 99% methanol was purchased from Acros Organics. For GC-MS analysis, ASTM D6584 individual stock and internal standard mix kit (44898U, Supelco) was procured from Sigma-Aldrich. The super/subcritical methanol process was carried out in the PARR 4593 Microreactor with a 4843-controller (Parr Instrument Company, Illinois, USA).

2.2. Characteristics of *Camelina Sativa* Oil. The quality of oil is expressed in terms of the physicochemical properties such as acid value and saponification value. The saponification value of camelina oil was reported as 193.3 (mg KOH/g). The acid value of camelina oil was found to be 3.2 mg KOH/g, corresponding to a free fatty acid (FFA) level of 1.58%. It has been reported that transesterification would not occur if FFA content in the oil was above 3 wt %.[27] The viscosity at 40 °C and the pour point of *Camelina sativa* oil were determined to be 14.0 mm²/s and −23.33 °C, respectively.

2.3. Experimental Procedure. A noncatalytic biodiesel production route with supercritical methanol has been developed. This method allows for a simple process and high yield of biodiesel due to simultaneous transesterification of triglycerides and methyl esterification of fatty acids.[28] The connection diagram and the actual experimental setup of PARR 4593 microreactor (temperature limit: 273−623 K, pressure range: 0−140 bar) are shown in Figure 1, panels a and b, respectively. In the supercritical methanol with a cosolvent (hexane) method, the experimental plan involved three levels of methanol to oil molar ratio varying from 25:1 to 55: 1; five levels of cosolvent to oil ratio: 0, 0.05, 0.1, 0.2, and 0.3 (v/v of oil); four levels of reaction time: 20, 30, 40, and 60 min; and reaction temperature varying from 240 to 320 °C. The conversion reaction for camelina oil with supercritical methanol with hexane as a cosolvent was carried out at 1650 psi (114 bar) pressure in the Parr microreactor.

For the subcritical methanol with a cosolvent/catalyst (KOH) method, the experimental plan involved 5 levels of methanol to oil molar ratio varying from 6:1 to 40: 1; five levels of cosolvent to oil ratio: 0, 0.1, 0.2, 0.3, and 0.4 (w/w % of oil); four levels of reaction time: 10, 20, 30, and 40 min; and reaction temperature varying from 100 to 220 °C. The conversion reaction for camelina oil using subcritical methanol with KOH as a cosolvent/catalyst was carried out at 1305 psi (90 bar).

2.4. Supercritical Transesterification Mechanism. The transesterification reaction mechanism at supercritical methanol conditions is given in Figure 2, and the reaction mechanism of transesterification of vegetable oil in the supercritical methanol and ethanol proposed by Saka and Kusdiana[21] is shown in Figure 3. This hypothesis was based on the mechanism developed by Krammer and Vogel[29] for the hydrolysis of esters in sub/supercritical water. In addition, Saka and Kusdiana[21] suggested that methanol and ethanol behave as acid catalysts in the supercritical synthesis. In a catalyst-free transesterification with supercritical methanol, it is assumed that the hydroxyl

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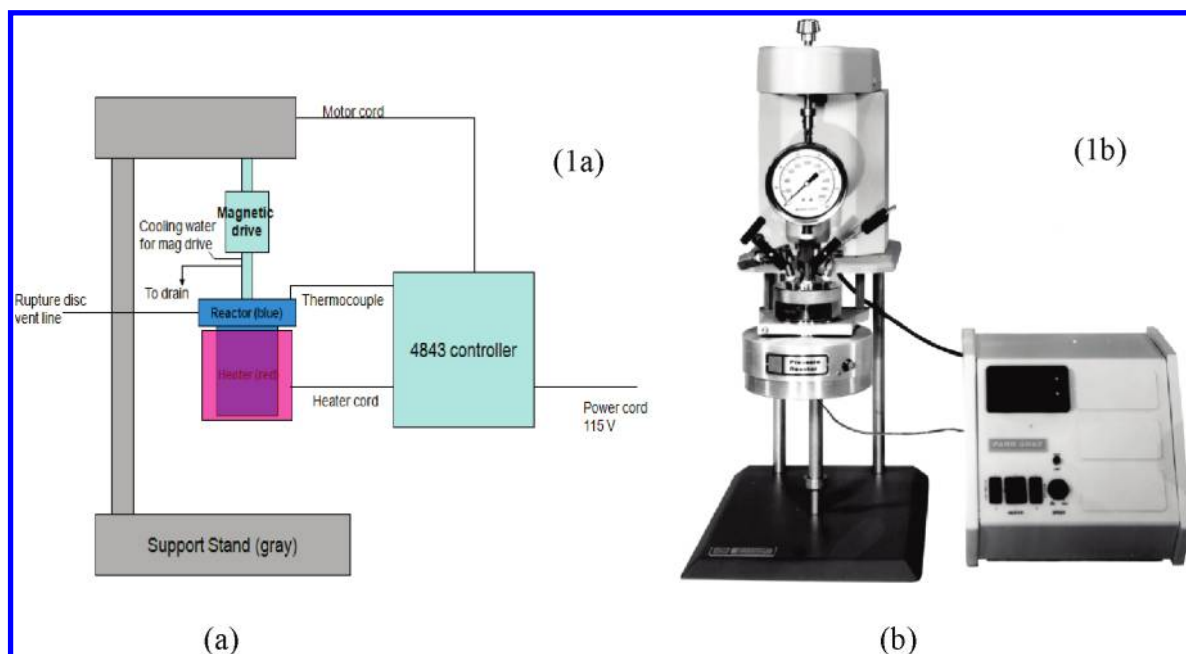(29) Krammer, P.; Vogel, H. *Supercritical Fluids* **2000**, *16*, 189–206.

Figure 1. Microreactor connection diagram (a), and a photo of the Parr 4593 Microreactor with the 4843 controller (b).
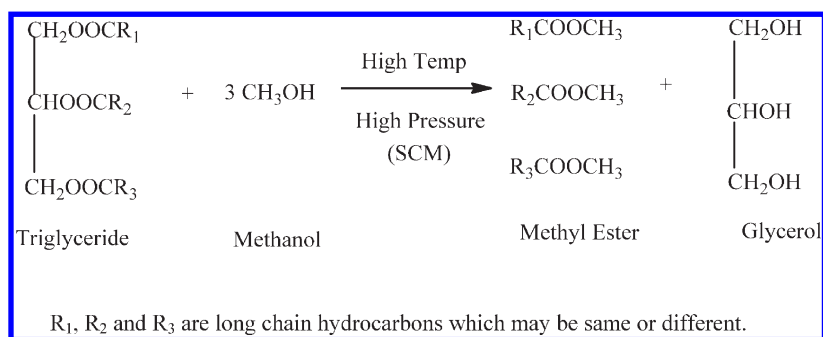

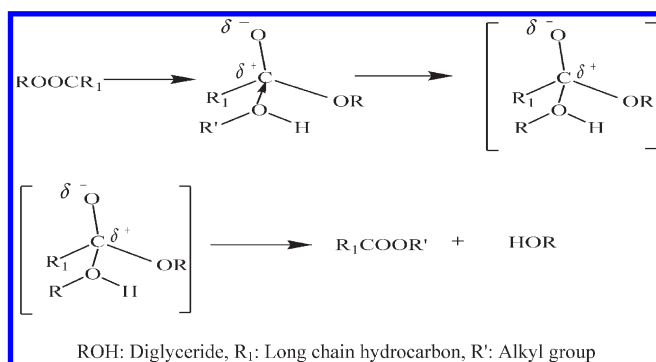**Figure 2.** Transesterification reaction at supercritical methanol condition.

Figure 3. A proposed reaction mechanism of transesterification of vegetable oil/triglycerides in supercritical methanol.

Figure 4. GC-MS chromatogram of camelina biodiesel.

group of the alcohol molecule directly attacks the carbonyl group of the triglyceride. Liquid methanol is a polar solvent that has hydrogen bonds between the OH oxygen and the OH hydrogen to form the methanol clusters. In the supercritical state, depending on pressure and temperature, the intermolecular hydrogen bonding would be significantly decreased, thus the polarity of methanol decreases in the supercritical state, which would allow methanol to act as a free monomer; therefore, supercritical methanol has a hydrophobic nature with a lower dielectric constant. As a result, nonpolar triglycerides can be well solvated with supercritical methanol to form a single
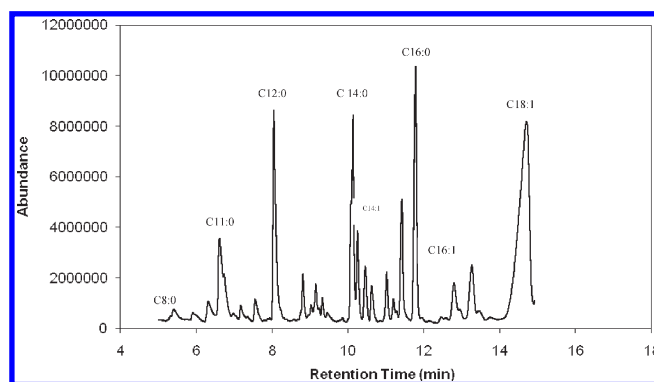
phase of vegetable oil/methanol mixture. Saka and Kusdiana[14] reported that this phenomenon promotes the transesterification of vegetable oils and is completed in supercritical methanol/ ethanol via a methoxide transfer, whereby the fatty acid methyl ester and diglyceride are formed. In a similar way, diglyceride is transesterified to form methyl ester and monoglyceride, which is converted further to methyl ester and glycerol in the last step.

2.5. Analysis of Biodiesel Conversion. For the quantification of reaction products, the samples were analyzed by a gas chromatography–mass spectrometry (GC-MS) system incorporated with an Agilent 5975 C mass-selective detector (MSD)
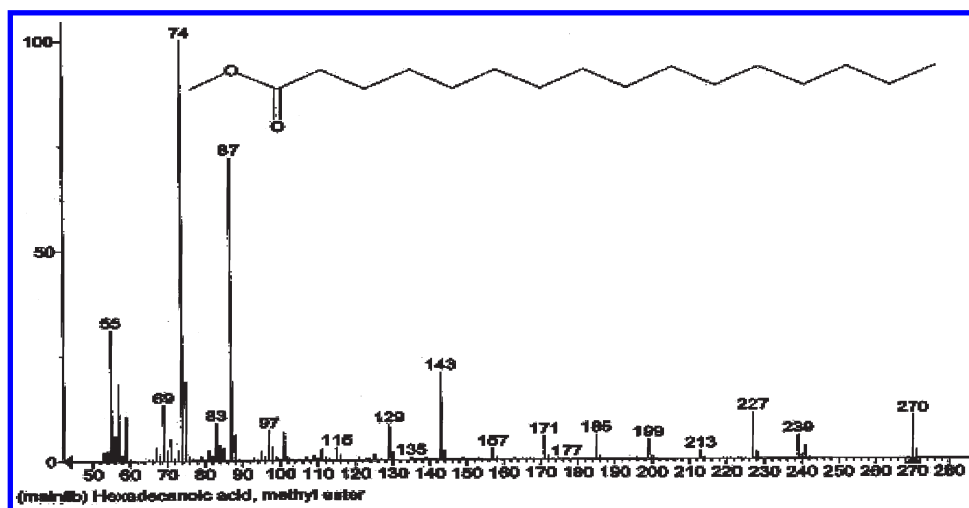
Figure 5. Mass spectrum (EI) of hexadecanoic acid, methyl ester (i.e., palmitic acid methyl ester) C16:0 in the NIST library.
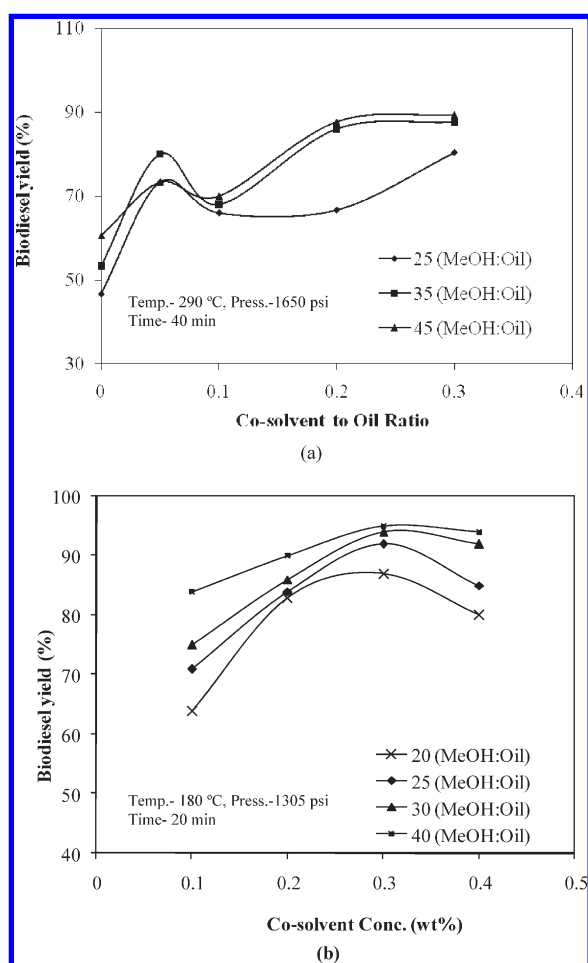

Figure 6. Effect of cosolvent (hexane) on supercritical methanol transesterification (a); effect of cosolvent (KOH) on subcritical methanol transesterification (b).

and an Agilent 7890 A gas chromatograph equipped with a capillary column (HP-5 MS, 5% phenyl methyl silox 30 m × 250 μm × 0.25 μm nominal). Supelco 37 Component FAME mix (catalog No. 47885-U) was used as reference standard mixture, containing 10 mg/mL of the fatty acid methyl ester (FAME) reference standard mix in methylene chloride. Helium was used as the carrier gas. The injection was performed in splitless mode. The parameters of the oven temperature program consist of:

start at 100 °C with 10 °C/min intervals up to 240 °C (1 min) and up to 300 °C with 20 °C/min intervals. From GC-MS analysis, it can be shown that *Camelina sativa* oil contains a major proportion of unsaturated fatty acids. Gas chromatogram for camelina biodiesel is shown in Figure 4. Mass spectrum (EI) of hexadecanoic acid, methyl ester (i.e., palmitic acid methyl ester) C16:0 in the NIST library obtained using the GC-MSD is shown in Figure 5.

3. Results and Discussion

In this section, results from process parametric evaluation studies are discussed. First, the effect of cosolvent with different methanol to oil ratios was studied and, based on the methyl ester yields obtained, the cosolvent to oil ratio was fixed to study the effect of other reaction parameters such as methanol to oil ratio, reaction temperature, and reaction time.

3.1. Camelina Biodiesel at Supercritical and Subcritical Methanol with Cosolvents. *3.1.1. Effect of Cosolvent on the Biodiesel Yield.* Introducing a cosolvent into the transesterification process can increase the mutual solubility of methanol and vegetable oil at low reaction temperatures.[30] Hexane was added into the reactant mixture to enhance the formation of a single phase between methanol and camelina oil and to accelerate the reaction rate at supercritical condition. Figure 6a shows the effect of cosolvent to oil ratio in relationship with different methanol to oil molar ratios (25:1 to 45:1). It indicated that a little hexane could improve the methyl ester yield. As shown in Figure 6a, the methyl ester yield was 46.6% without hexane, whereas the yield increased to 73.33% with 0.05 (v/v) cosolvent to oil ratio and at methanol to oil molar ratio of 25:1. The maximum yield was obtained at 0.3 (v/v) cosolvent to oil ratio. As shown in Figure 6b, for subcritical methanol with KOH as a cosolvent, the maximum methyl ester yield was obtained at 0.3 wt % of KOH concentration. The main reason for this effect is that the mutual solubility between methanol and camelina oil was enhanced with addition of cosolvents, so the reaction rate was increased. In comparison to conventional alkali transesterification method, the amount of KOH used in the subcritical methanol was only 10% of that used in the conventional method.[9] Therefore, by inducing cosolvent

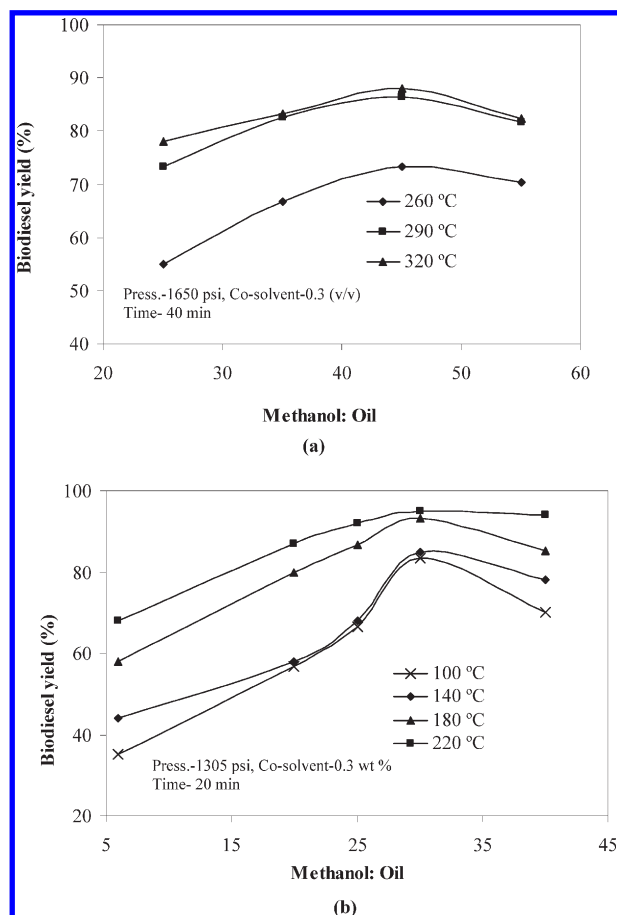(30) Scott, R. L.; Bunsenges, B. *J. Phys. Chem.* **1972**, *76*, 296.

Figure 7. Effect of methanol to oil ratio on supercritical methanol transesterification (a); effect of methanol to oil ratio on subcritical methanol transesterification (b).

in the subcritical methanol, the reaction parameters have become less severe as compared to the supercritical method. It was also observed during the subcritical conversion with KOH as a cosolvent/catalyst, the yield decreased at KOH concentration above 0.3%. This could be attributed to saponification or emulsification tendency of the catalyst.

3.1.2. Effect of Methanol to Oil Molar Ratio on Biodiesel Yield. The amount of methanol required for the transesterification was analyzed in terms of the methanol/oil molar ratio. The stoichiometric methanol/oil molar ratio required for a complete transesterification is 3:1. However, in practice, this is not sufficient to complete the transesterification reaction. A higher molar ratio is required to drive the reaction toward completion at a faster rate.[31] However, higher molar ratio of methanol to oil result in increased pressures, which impose stringent requirements on the reaction vessel.

For supercritical methanol experiments, the methanol/oil molar ratio was varied between 25:1 and 55:1 along with different temperature combinations between 260 and 320 °C as shown in Figure 7a. For subcritical methanol experiments, the methanol/oil molar ratios between 6:1 and 40:1 along with different temperature combinations between 100 and 220 °C were tested as shown in Figure 7b. For subcritical condition, the reaction pressure was maintained at 1305 psi. Comparing the supercritical methanol with subcritical, it
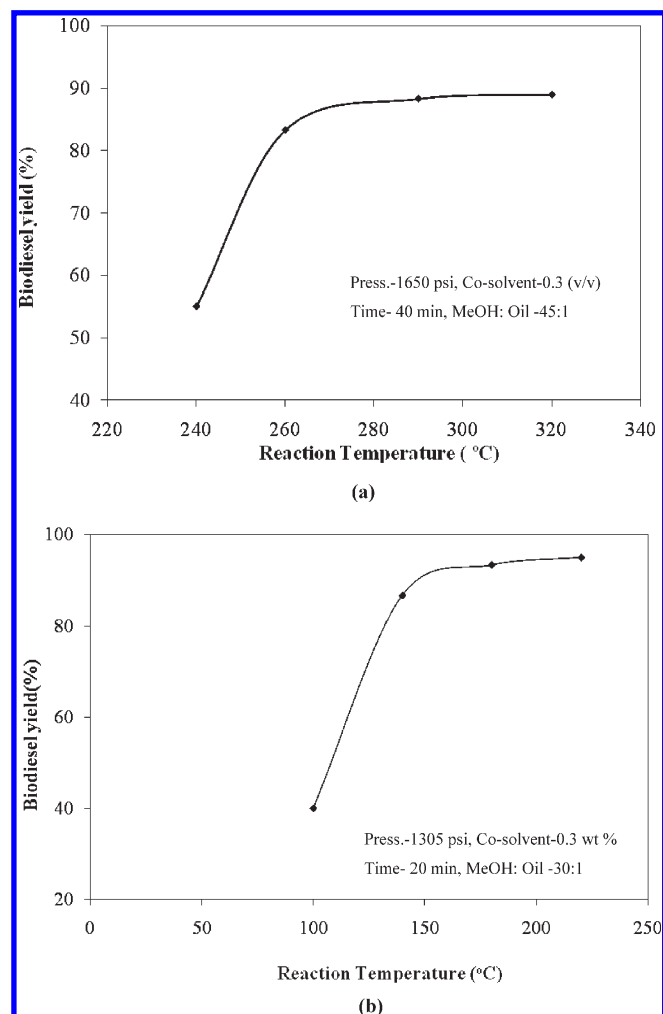
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Figure 8. Effect of reaction temperature on supercritical methanol transesterification (a); effect of reaction temperature on subcritical methanol transesterification (b).
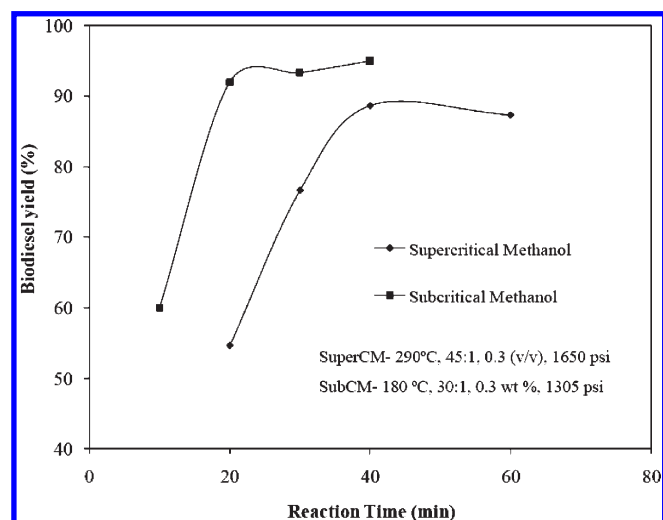

Figure 9. Effect of reaction time on supercritical and subcritical methanol transesterification.

was observed that the reaction temperature was decreased from 290 to 180 °C to achieve nearly same biodiesel yield.

The maximum biodiesel yield in super- and subcritical methods with cosolvents was obtained at methanol to oil

Table 2. Fuel Properties of Methyl Ester from *Camelina Sativa* Oil

properties	camelina biodiesel at supercritical methanol	camelina biodiesel at subcritical methanol	regular diesel	biodiesel standard ASTM D6751−02	testing methods
specific gravity	0.886−0.90	0.881−0.89	0.85	0.87−0.90	ASTM D4052
viscosity (mm^2/s) at 40 °C	3.69−3.75	3.19−3.25	2.6	1.9−6.0	ASTM D445
calorific value (MJ/kg)	44.97−45.124	45.01−45.18	42		ASTM D240
cetane No.	48.32−49.45	49.14−50.15	46	47 min.	ASTM D613
pour point (°C)	−12 to −9	−9 to −4	−20	−15 to 10	ASTM D97

molar ratios of 45:1 and 30:1, respectively. However, when the amount of the methanol/oil molar ratio was over 45:1 in supercritical and 30:1 in subcritical conversions, an excess methanol started to interfere with the glycerin separation due to increased solubility, which resulted in lower biodiesel yields.[32]

3.1.3. Effect of Reaction Temperature on Biodiesel Yield. Figures 8a and 8b show the influence of reaction temperature on biodiesel yield at super and subcritical methanol conditions. For supercritical methanol experiments, the reaction temperature was varied between 240 and 320 °C with methanol to oil ratio of 45: 1, cosolvent (hexane) to oil ratio of 0.3 (v/v), and the reaction pressure held at a constant value of 1650 psi. For subcritical methanol experiments, the reaction temperature was varied between 100 and 220 °C with methanol to oil ratio of 30:1 and 0.3% cosolvent KOH (wt/wt % of oil), and reaction pressure held at a constant value of 1305 psi. The maximum methyl ester yield was obtained at 290 and 180 °C, respectively, for the super- and subcritical methanol methods. The severity of the reaction temperature was significantly reduced in the supercritical as well as subcritical methanol conversions with cosolvents as compared to the supercritical methanol method without any cosolvent.[33] At low reaction temperature, the yield was low and increased rapidly as reaction temperature increased. It was observed that increasing the reaction temperature, especially at supercritical condition, has favored the biodiesel yield.[25]

3.1.4. Effect of Reaction Time on Biodiesel Yield. One of the advantages of supercritical or subcritical methanol reaction with cosolvents is that it reduces the reaction time along with the severity of the reaction parameters. Figure 9 shows the effect of reaction time on biodiesel yield. For super- and subcritical methanol, reaction times of 40 and 20 min, respectively, resulted in maximum methyl ester yields. As shown in Figure 9, for the subcritical conditions at 180 °C and 1305 psi, the methyl ester yield increases slightly for reaction time greater than 20 min.

Comparing to the conventional alkali method, the reaction time was reduced from 120 to 20 min in the subcritical methanol with KOH as a cosolvent method. The same influence was observed by Yin et al.[20] in the production of biodiesel from soybean oil using cosolvents. These results indicate that using the cosolvent method, biodiesel production

costs and production efficiencies can be improved, especially, in large scale industrial applications.

3.2. Fuel Properties of Methyl Ester from *Camelina Sativa* Oil. The fuel properties of biodiesel from *Camelina sativa* oil with corresponding testing methods are given in Table 2. The viscosity of biodiesel from *Camelina sativa* oil was comparable to the regular diesel viscosity, that is, 2.6 mm^2/s. Hence, no hardware modifications are required for handling this fuel (biodiesel) in the existing engines. The cetane number was estimated as 49.14−50.15 and was found to be higher than the ASTM[34] biodiesel standards. A higher cetane number indicates a good ignition quality of a fuel. The pour point of camelina biodiesel was found to be between −12 and −9 °C, indicating good compatibility of fuel in the cold season. Fuel consumption and vehicle operation with camelina ester are similar to those of rapeseed methyl ester.[35]

4. Conclusions

Synthesis of biodiesel from *Camelina sativa* oil via supercritical and subcritical methanol with cosolvent is feasible and superior to the conventional tranesterification method. The new process reduces the severity of critical process parameters, increases biodiesel yield, and requires less energy for biodiesel conversion.

Experimental results demonstrated that the cosolvents play an active role in increasing the mutual solubility of methanol and vegetable oil at low reaction temperatures at supercritical conditions. Under the supercritical methanol conditions with hexane as a cosolvent, the maximum camelina biodiesel yield was observed at reaction temperature of 290 °C with a methanol to oil ratio of 45 and reaction time of 40 min.

The subcritical methanol with potassium hydroxide can largely decrease the severity of the reaction parameters, such as reaction temperature and pressure. For the subcritical methanol method, +90% biodiesel yield was obtained at the following process conditions: reaction temperature of 180 °C, methanol to oil molar ratio of 30, reaction time of 20 min and 0.3 wt % potassium hydroxide (KOH) as a cosolvent/catalyst. The methyl esters produced by the cosolvent methods meet the ASTM biodiesel standards.

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