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Biodiesel Production Using Supercritical Methanol in Bench-Scale Reactor

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Abstract: Biodiesel is preferred as an alternative fuel due to its sustainability and easy availability of raw materials. Studies to improve biodiesel production time and costs are gaining importance in terms of being used in higher portions as a fuel. Traditional catalytic biodiesel production is time- energy-consuming due to feedstock preprocessing, product separation, and purification steps. Non-catalytic biodiesel production using supercritical alcohol may shorten and eliminate the pre- and post-production stages in terms of time and cost compared to traditional methods. In this study, canola oil was converted to biodiesel using supercritical methanol. Biodiesel production was carried out in the bench-size supercritical reactor that was fabricated as part of this study. The higher yield was obtained from biodiesel produced using canola oil and supercritical methanol compared to the traditional catalytic methods. 98.8 % yield was obtained at 240˚C and 8.3 MPa which were just above the critical temperature and pressure of methanol. Including reaction and separation, the complete process via supercritical transesterification took 180 minutes, while the whole traditional base-catalyzed transesterification process takes approximately one day.

Keywords: Biodiesel, Supercritical methanol, Transesterification

Introduction

Catalytic biodiesel (BD) production is a time and energy-consuming process that involves various preprocessing, separation, and purification steps. In contrast, non-catalytic BD production using supercritical alcohol offers the potential to simplify these stages (Saka & Kusdiana, 2001; Demirbas, 2006). Supercritical alcohol can create a homogeneous phase with triglycerides at high pressures and temperatures, allowing reactions to occur without needing a catalyst. The separation of BD from glycerol is also easier in the supercritical method than in conventional technologies requiring additional purification steps. While the supercritical method requires high temperatures and pressures, it presents advantages over traditional methods.

Supercritical methanol (SCM) refers to methanol in a state above its critical point as shown Figure 1, where the phase boundary between liquid and vapor disappears. At these conditions, methanol exhibits a liquid-like density and gas-like transport properties such as diffusivity and viscosity. The single-phase characteristics of SCM make it an excellent solvent for biodiesel production.

Although base catalyzed transesterification has been used for BD production for decades, the feedstock used has certain limitations, including their free fatty acid (FFA) and water content, the length of time required for the purification of reaction products, and the large amount of waste water that is generated (Meher et al., 2006; Sharma & Singh, 2007). As a solution to these problems, in 1998 Diasakou et al. developed the non-catalytic transesterification method using a subcritical temperature of methanol (240°C, 220°C, 235°C). Previous studies have investigated supercritical transesterification using methanol as a supercritical fluid. Researchers have explored various temperatures, pressures, reactor sizes, and oil types to achieve high conversion rates within

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short reaction times. For instance, Saka and Kusdiana (2001) successfully produced BD from rapeseed oil using SCM in a 5 mL Inconel 625 batch reactor, achieving over 95% conversion in 5 minutes. Table 1 summarizes some of the notable studies on SCM transesterification with different oils and reaction conditions.

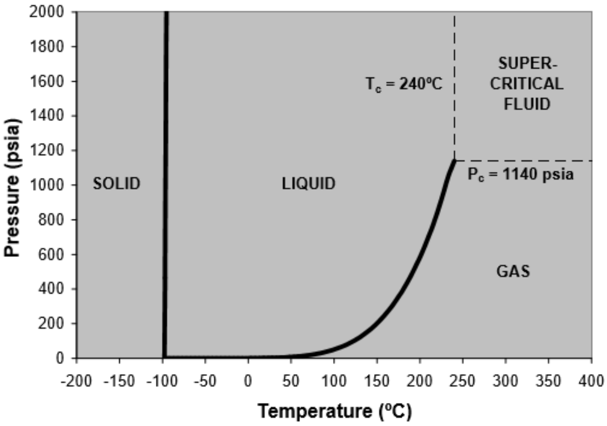


Figure 1. Phase diagram of methanol (Ebert, 2008)

Table 1. Some SCM transesterification of various vegetable oils (Silva & Oliveria, 2014).

Temperature Pressure	Oil type	Oil :Alcohol (molar ratio)	Reaction time	Reactor type	Conversion of methlyester	Reference
350°C, 450 bar	rapeseed	1:42	4 min	5 mL,BR Inconel	>95 %	Saka and Kushidiana, 2001
350°C, Not recorded	hazelnut	1:41	5 min	100 mL, BR, SS	95 %	Demirbaş, 2002
350°C, 200 bar	sunflower	1:40	40 min	8 mL, BR, SS	96 %	Madras et al., 2004
350°C, 180 bar	coconut	1:42	7 min	TR,SS	95 %	Bunyakiat et al., 2006
280°C, 250 bar	soybean	1:42	30 min	200 mL BR	90 %	He et al., 2007
300°C, 150 bar	soybean	1:40	20 min	BR	70 %	Wang et al., 2008
350°C, Not recorded	palm oil	1:40	20 min	BR	80 %	Tan et al., 2010
350°C, 350 bar	palm olein	1:40	~15min	TR	85 %	Choi et al., 2011
270°C, 100 bar	waste canola	1:1 (mass ratio)	45 min	BR	96.4 %	Lee et al., 2012

BR: batch reactor; TR: tubular reactor; SS: stainless steel

While maximum operating pressures, operating temperatures, and reactor sizes were reported in previous studies to be 450 bars (Saka & Kushidiana, 2001), 350°C and 200 mL (He et al., 2007), their minimum values were 100 bar, 270°C (Lee et al., 2012) and 5 mL (Saka & Kushidiana, 2001), respectively.

It was necessary to design and manufacture a bench-scale batch reactor in order to meet the extreme process conditions of high pressure and temperature required to manufacture BD using the supercritical fluid method (Al-Shanableh, 2017; Al-Shanableh & Savas, 2022). By using the designed supercritical reactor, canola oil was transformed into BD. This study focuses on the production of BD using supercritical methanol (SCM) in a bench-scale reactor.

Method

Materials

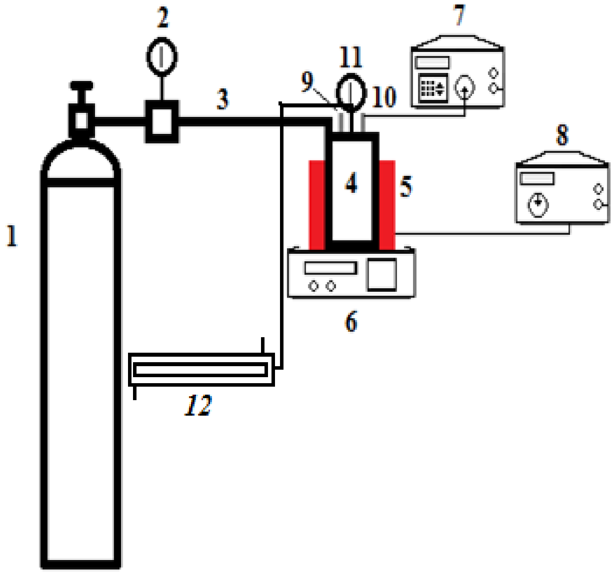
Refined canola oil (RCO) and anhydrous methanol (MeOH) were used as the feedstock for BD production. The canola oil was purchased from a local supermarket, while the methanol (99.8 % purity) was obtained from Merck. Fatty acid compositions of RCO was determined following the EN ISO 5508 in the TRNC- Ministry of Health-Directorate State Laboratory-Nicosia using Gas Chromatography (GC). Fatty acid content of RCO was found as 0.08 wt % of lauric acid (C12:0), 5.63 wt % of palmitic acid (C16:0), 1.57 wt % of stearic acid (C18:0), 62.97 wt % of oleic acid (C18:1), 21.34 wt % of linoleic acid (C18:2), 6.99 wt % of linolenic acid (C18:3), 0.46 wt % of arachidic acid (C20:0) and 1.04 wt % of gondeic acid (C20:1). Trace amounts of other FA constituents like 0.001 wt % of erucic acid (C22:1) in RCO were not taken into consideration.

Experimental Setup for Biodiesel Production by SCM

The experimental setup involved a bench-size, batch-type reactor designed to handle the extreme process conditions of high temperature and pressure as shown in Figure 2 (Al-Shanableh, 2017).

Figure 2. Photograph of designed and manufactured supercritical reactor.

The experimental setup for one-step supercritical methanol transesterification was designed to operate under high temperatures and pressures. Nitrogen gas was used as an inert medium to provide pressure, and a flexible high-pressure hose connected the supercritical reactor. The reactor was equipped with an external heater, insulating mantle, electromagnetic stirrer, safety valve, pressure gauge, and thermocouple for temperature measurement. A laboratory type double pipe heat exchanger served as the condenser. The experimental setup used is illustrated in Figure 3.



1: Nitrogen tube (200 bar)
2: Pressure regulator
3: Flexible high pressure nitrogen line
4: Supercritical reactor
5: Heater & insulating mantle
6: Magnetic stirrer
7: Electronic processes controller (display)
8: Power supply of heater
9: Release & Safety valves
10: J type thermocouple
11: Pressure gage
12: Condenser

Figure 3. Schematic diagram of supercritical BD production set-up

Experimental procedure for Biodiesel Production by SCM

The supercritical methanol transesterification of canola oil was carried out using the experimental setup described above and following the steps in the flowchart as shown in Figure 4.

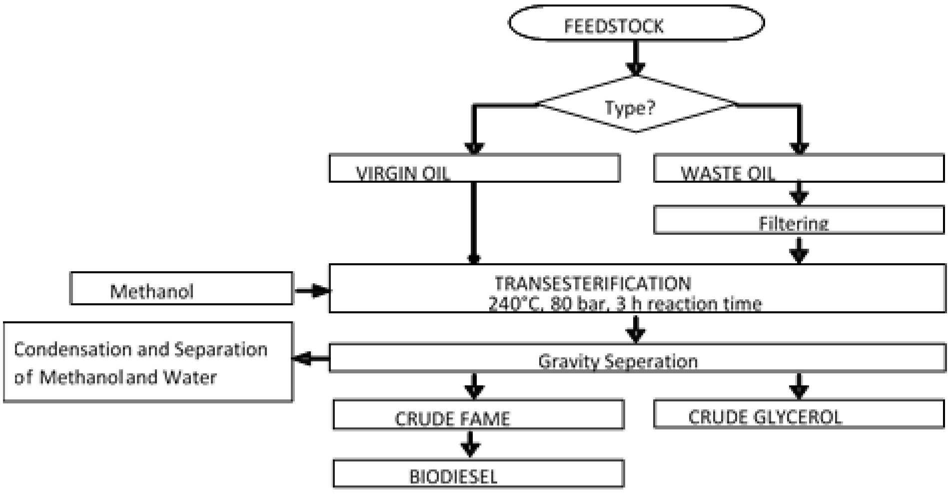


Figure 4. Flowchart for the experimental procedure of the SCM biodiesel production

The procedure involved charging a mixture of RCO and methanol into the supercritical reactor, mixing them to obtain a homogeneous mixture, closing the reactor, and adjusting the temperature and pressure to reach the supercritical fluid region. The reaction time varied from 1 to 3 hours, and after the specified reaction time, the reaction vessel was removed from the heating jacket, and the cooling process took place. The excess methanol was transferred to the condenser, and the product mixture was poured into a separation funnel to separate the fatty acid methyl esters (FAME) and glycerol phases. The FAME was further heated to remove any remaining water or methanol, and its weight was measured to determine the transesterification yield. After production was completed to ensure the quality of produced biodiesel, its properties such as viscosity, cloud point, and pour point were measured following corresponding ASTM and EN-ISO standards.

Results and Discussion

Biodiesel Yield by SCM Transesterification

SCM transesterification experiments were conducted as five batches at constant temperature and pressure of 240˚C and 8.3 Mpa, respectively which were just above the critical temperature and pressure of methanol. These minimum operating temperature and pressure were preferred to ensure safety, even though it would result in longer reaction times. The reaction time started from 1 hour for the first batch, then, increased by half an hour for the next batch and so on. The percent conversion of canola oil to biodiesel was determined using the equation below (Phan and Phan, 2008).

$$\% \, Yield = \frac{m_{ester}}{3 \times \frac{m_{oil}}{MW_{oil}} \times MW_{ester}}$$

where MW_{oil} and MW_{ester} are the averaged molecular weight of feedstock oil (RCO) and FAME (RCOME) produced, respectively.

Table 2. % Yield of RCO to RCOME by supercritical transesterification

Batch No. (reaction time)	% Conversion of FAME produced
Batch 1 (60 min)	86.4
Batch 2 (90 min)	89.0
Batch 3 (120 min)	97.9
Batch 4 (150 min)	98.2
Batch 5 (180 min)	98.8

The results showed that longer reaction times resulted in higher conversions, as shown in Table 2. The percent yield increased from 86.4% to 98.8% as the reaction time increased from 1 to 3 hours. The obtained conversions met the minimum ester content requirement of 96.5% specified by the EN 14214 standard. The results were compared with previous studies which are used similar conditions, for example, Lee et al. working with little higher temperature at 270 °C obtained a 96.4 % yield in 45 minutes (Lee et al., 2012). The comparison indicates that higher pressure and temperature can significantly reduce the reaction time required for biodiesel production

Characterization of Produced Biodiesel

The produced biodiesel samples for each batch were tested for their viscosity, cloud point, and pour point following either ASTM D6751 or EN 14214 standards. The viscosity values fell within the acceptable range specified by ASTM D446. The kinematic viscosities of the biodiesel produced via base-catalyzed transesterification (Al-Shanableh et al., 2023) and supercritical methanol transesterification were comparable. However, the supercritical method required significantly less time to complete the production process, including device preparation, reaction, and separation. The results of the viscosity, cloud point, and pour point tests are presented in Table 3. As the percent conversion of RCO to RCOME increased, its kinematic viscosity decreased.

Table 3. Viscosity, CP and PP test result for RCOME

	Kinematic Viscosity (mm^2/s)	Cloud Point (˚C)	Pour Point (˚C)
Base Catalyzed Transesterification *	4.582	-3.5	-10
Batch 1	5.966	4.3	-5.5
Batch 2	5.230	4.0	-6.0
Batch 3	4.760	-2.0	-8.8
Batch 4	4.592	-3.0	-9.0
Batch 5	4.580	-3.0	-9.0

*Al-Shanableh et al., 2023

The fuel properties of the biodiesel produced by the traditional method with the same feedstock-RCO were compared to Batch 5 biodiesel that was produced by in this study as shown in Table 4.

Table 4. The fuel properties of of base-catalyzed and SCM BD

	Method	Limits	RCOME by Base-catalyzed	RCOME by SCM-Batch #5
Kinematic viscosity at 40 ˚C	ASTM D 445	1.9-6.0	4.582	4.580
Higher heating value	ASTM D 4809	35.0	39.23	39.18
Free glycerin (wt %, max.)	EN 14105	0.02	0.003	0.003
Total glycerin (wt %, max.)	EN 14105	0.25	0.196	0.192
Mono glyceride (wt %,	EN 14105	0.80	0.64	0.61
Diglyceride (wt %, max.)	EN 14105	0.20	0.20	0.20
Triglyceride (wt %, max.)	EN 14105	0.20	0.1	0.1
Ester contents (wt %, max.)	EN 14103	96.5	97.0	98.8
Linoleic acid methyl esters	EN 14103	12.0	6.8	4.5
Iodine value (g I_2 / 100 g,	EN 14111	120	66	66
Cloud point (˚C)	D 2500		-3.5	-3
Pour point (˚C)	D 97		-10	-9
Cold filter plugging point	D 6371		-7.5	-7

Table 5. A comparison of base-catalyzed and SCM transesterification methods

	Base-Catalyzed Transesterification	SCM Transesterification
Reaction time (min)	60	180
Reaction temperature(^{o}C)	60	240
Reaction pressure (bar)	Atmospheric pressure	83
Separation from glycerol	Need min 8 hours	10 min
FFAs in feedstock	Need to be determined	No need to determine
Water in feedstock	Need minimum 2 hours for removal	No influence
Yield of FAME (%)	97.0	98.8
Purification of FAME	Difficult –Require water washing and drying min. 6 hours	none

Compared to base-catalyzed transesterification, the major disadvantage of SCM seems to be only high temperature and pressure as seen in Table 5. Once the system is built, production can be performed at higher temperatures and pressures, resulting in a higher BD conversion and a shorter reaction time. The short reaction time of SCM makes it more suitable for continuous production.

Conclusion

The study successfully demonstrated the production of biodiesel using supercritical methanol in a bench-scale reactor. The supercritical fluid method showed promising results in terms of efficiency and reduced production time compared to base-catalyzed transesterification. The one-step process using a bench-scale reactor yielded high conversion rates within a relatively short time. 98.8 % yield was obtained at 240˚C and 8.3 MPa, just above the critical temperature and pressure of methanol. Including reaction and separation, the complete process via supercritical transesterification took 180 minutes. The results indicate that the supercritical method has the potential for large-scale biodiesel production, particularly due to its shorter reaction time. Further research and optimization of the process parameters can lead to even higher conversions and improved overall efficiency in biodiesel production using supercritical methanol.

Scientific Ethics Declaration

The authors declare that the scientific ethical and legal responsibility of this article published in EPSTEM journal belongs to the authors.

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