

TRANSESTERIFICATION OF COCONUT OIL USING DIMETHYL CARBONATE AND TiO₂/SiO₂ HETEROGENEOUS CATALYST

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ABSTRACT

In this study, transesterification of coconut oil with dimethyl carbonate (DMC) for preparing biodiesel has been studied using TiO₂/SiO₂ as heterogeneous catalyst, with the main purpose to investigate the effect of molar ratio of DMC to oil. The product was analyzed by GC-MS to identify the fatty acid methyl esters (FAMEs) composting the biodiesel. The significant role of the DMC to oil ratio was observed in this study, in which the oil conversion was found to increase with increasing molar ratio of DMC : Oil, with the highest percent of conversion of 88.44%. The GC-MS analysis revealed the presence of methyl esters in accordance with the composition of coconut oil commonly reported. Formation of FAMEs was verified by ¹H-NMR spectroscopic analysis, which also suggested that some of the fatty acids remain unconverted into biodiesel. The biodiesel produced was found to have kinematic viscosity of 2.4 mm²/S at 40 °C, flash point of 103 °C, and cetane number of 54.

Keywords: coconut oil; transesterification; heterogeneous catalyst; dimethyl carbonate; fatty acid methyl ester

ABSTRAK

Dalam penelitian ini dilakukan transesterifikasi minyak kelapa menggunakan dimetil karbonat (DMC) dan katalis heterogen TiO₂/SiO₂ dengan tujuan utama mempelajari pengaruh nisbah DMC terhadap minyak. Biodiesel yang dihasilkan dianalisis dengan kromatografi gas-spektroskopi massa (GC-MS) untuk mengidentifikasi metil ester asam lemak (FAMEs) yang terkandung dalam biodiesel. Hasil penelitian menunjukkan bahwa nisbah DMC terhadap minyak memegang peranan penting, dimana semakin tinggi nisbah semakin besar persen konversi yang mampu dicapai, dengan nilai tertinggi sebesar 88,44%. Hasil analisis dengan GC-MS menunjukkan komposisi metil ester asam lemak yang terbentuk sesuai dengan komposisi minyak kelapa. Keberadaan metil ester diverifikasi dengan analisis menggunakan spektroskopi resonansi magnetik inti (¹H-NMR), yang juga menunjukkan bahwa belum seluruhnya asam lemak mampu diubah menjadi metil ester. Biodiesel yang dihasilkan memiliki viskositas kinematik sebesar 2,4 mm²/S pada suhu 40 °C, titik nyala 103 °C, dan angka setana 54.

Kata Kunci: minyak kelapa; transesterifikasi; katalis heterogen; dimetil karbonat; metil ester asam lemak

INTRODUCTION

Due to the depletion of fossil fuels and increasing concern about environmental issues associated with their use, interest in developing alternative energy sources has increased rapidly in recent years. Among them is biodiesel as an alternative to petrodiesel. This alternative energy source has become increasingly attractive worldwide because it is made from renewable raw materials, including vegetable oils and animal fats. In addition, it combines high performance with environmental benefits, making this fuel an ideal solution for global energy demands.

Traditionally, biodiesel is produced by transesterification of vegetable oil or fat with simple alcohols, most commonly methanol and ethanol, in the presence of either alkaline or strong acid catalysts. Acid-

catalyzed transesterification is usually carried out using strong acids, primarily HCl [1-2], H₂SO₄, [3-4] and HNO₃ [5-6]. This reaction is acknowledged to afford high yields but suffers from several disadvantages. To reach complete conversion, the reaction requires long process and relatively high temperature, when compared with base-catalyzed transesterification, because of its low reaction rate. In addition, the reaction is very sensitive to water contained in the reaction mixture because of its high reactivity toward protonated carbonyl group of triglyceride to produce carboxylic acid, suppressing the formation of alkyl ester. For this reason, application of acid catalysts requires the reaction system is free from water in order to limit the formation of the acid to achieve optimum yield.

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Compared to acid-catalyzed reaction, base-catalyzed reaction is known to proceed faster, needs less methanol, requires lower temperature, and affords conversion of 90% or higher. The most widely base catalysts used are alkaline metal hydroxides, such as KOH [7-8] and NaOH [1,9], at amounts of 1–2 mol %. The main disadvantage of base catalyst is formation of water by *in situ* reaction between hydroxide and methanol. The water produced reacts rapidly with alkyl esters to produce carboxylic acids, which in turn react with alkaline metals to form soap. These side reactions make the process inefficient by reducing alkyl ester yield.

Due to the aforementioned disadvantages of acid and base catalysts, development of heterogeneous catalysts has been considered as an alternative. Since in heterogeneous transesterification the catalyst is in different phase from the product and reactants, separation process is easier and simpler. In addition, the process eliminates the formation of soap encountered in the homogeneous processes. Several examples of the heterogeneous catalysts that have been investigated are metal oxides [10-11], zeolites [12-13] and active metals loaded on supports [14-16].

Among various metal oxides, TiO₂ based catalyst is a very attractive choice since various TiO₂ based catalysts have been applied for long time to carry out a variety of catalytic reactions. More specifically, TiO₂/SiO₂ catalyst has been reported to exhibit excellent catalytic activity in transesterification reactions of ethylacetate and diethylmalonate with various alcohols [17], however application of this catalyst for biodiesel production is still very limited. Another aspect of biodiesel production currently gains attention is application of non-alcohol alkyl compounds, one of them is dimethyl carbonate. This compound has been considered as reactant for transesterification process because of its advantageous physical properties compared with methanol, such as environmental inertness, chemical reactivity, and its application produces no glycerol [18]. Considering the two aspects described above, the current study was aimed to produce biodiesel from coconut oil, by taking into account the advantages offered by heterogeneous catalyst and dimethyl carbonate.

EXPERIMENTAL SECTION

Materials

The chemicals used in this study, dimethyl carbonate, titanium trichloride, potassium hydroxide, and nitric acid, are reagent grade obtained from Aldrich. Rice husk was obtained from local rice milling industry. Before use, the husk was soaked in distilled water overnight to

clean it from dirt and to separate the husk with high silica content (sinking husk) from that with low silica content (floating husk). The husk with high silica content was collected and oven dried at 110 °C overnight.

Instrumentation

The main equipments used in this study are GCMS-QP2010 SE SHIMADZU for identification of transesterification product, Agilent 500 MHz ¹H-NMR spectrometer for proton NMR analysis, Cannon-Fenske Opaque NVS 210 for viscosity determination, Pensky-Marten S Semi Automatic Model NPM 220 for flash point determination and Shatox Sx 200 for cetane number determination.

Procedure

Extraction of silica

In this study, extraction of silica from rice husk was carried out using alkalis extraction following the method described in previous studies [19-20]. Typically, 500 g of dried husk was transferred into Erlenmeyer flask and enough 500 mL of KOH solution (1.5% by weight) was added into the flasks. The mixture was then heated to boil it for 30 min. The mixture was let overnight and the filtrate, which contains dissolved silica, was separated by filtration. To transform the silica into gel, HNO₃ solution (10%) was added dropwise until the formation of gel was completed, and the gel obtained was rinsed with hot distilled water several times to wash out the excess of acid. The gel was oven dried at 110 °C for 8 h to produce dry silica. A specified amount of dry silica (60 g) was redissolved in 300 mL of 1.5% KOH solution to be used for catalyst preparation.

Preparation of catalyst

Preparation of catalyst was carried out adopting the method previously applied [21-22]. An aliquot of 100 mL silica sol, which contains 20 g of silica, was transferred into Erlenmeyer flask placed in ultrasound cleaner. A specified volume of 15% TiCl₃ in HCl solution, to give the Ti/silica ratio of 5%, was slowly added into the sol under ultrasound agitation, to produce gel. The gel was aged for three days, and then oven dried at 110 °C for 8 h to transform the gel into solid catalyst. The catalyst was ground into powder using mortar and pestle, and then subjected into sintering treatment at 700 °C for 6 h.

Transesterification experiment

Transesterification reactions were carried out in 500 mL flask equipped with a reflux condenser, following

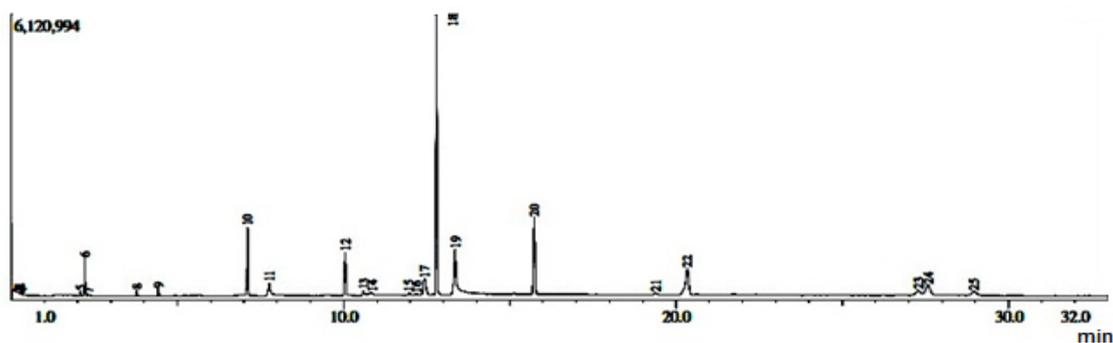


Fig 1. Typical example of GC chromatogram of the transesterification product

Table 1. The components of transesterification product identified

Peak number	Retention time (min)	Relative percentage	Compound name	Molecular formula
6	2.216	2.94	Dimethyl ketone	C ₃ H ₆ O
9	4.427	0.67	Methyl caproate	C ₇ H ₁₄ O ₂
10	7.111	7.06	Methyl caprylate	C ₉ H ₁₈ O ₂
11	7.772	2.47	Caprylic acid	C ₈ H ₁₆ O ₂
12	10.047	4.85	Methyl caprate	C ₁₁ H ₂₂ O ₂
13	10.603	0.62	Capric acid	C ₁₀ H ₂₀ O ₂
17	12.445	4.36	Hexadecanoic acid	C ₁₇ H ₃₄ O ₂
18	12.797	32.44	Methyl laurate	C ₁₃ H ₂₆ O ₂
19	13.354	8.98	Lauric acid	C ₁₂ H ₂₄ O ₂
20	15.736	12.58	Methyl myristate	C ₁₅ H ₃₀ O ₂
22	20.337	8.44	Methyl palmitate	C ₁₇ H ₃₄ O ₂
23	27.292	1.74	Linoleic acid	C ₁₈ H ₃₂ O ₂
24	27.578	3.97	Methyl oleate	C ₁₉ H ₃₆ O ₂
25	28.967	1.57	Methyl stearate	C ₁₉ H ₃₈ O ₂

the method described elsewhere [23-24]. The flask was immersed in water bath placed on top of magnetic stirrer with heating plate. The flask was filled with reaction mixture and heated to 80 °C for 6 h. After the completion of the experiment, the mixture was cooled to room temperature and transferred to a separatory funnel, and allowed for 2 h to separate the mixture into two layers. The two layers were separated and the biodiesel phase was collected. The excess of DMC was removed by evaporation and the volume of biodiesel was measured for percent conversion calculation.

Analysis of transesterification products

Analysis of transesterification products was carried out by gas chromatography-mass spectroscopy (GC-MS) technique on GCMS-QP2010 SE SHIMADZU, equipped with 30 m long and 0.32 mm internal diameter HP SMS 30 m column, operated in the EI mode at 70 eV. Carrier gas used was helium gas and nitrogen as make up gas to provide total flow rate of 60 mL/min. The components of the sample were tentatively identified by comparison of their mass spectra with those published in the MS Library System NIST62, Wiley 7, database. To verify the formation of FAMES, sample was analysis with ¹H-NMR spectroscopy, using Agilent 500 MHz.

To estimate the proportions of each of the compound identified, the amount of each compound expressed as the peak area relative to the sum of the peak areas of all identified compounds, was calculated as a percentage. However, since GC-MS is not a quantitative method and since response factors of each compound were not determined, these percentages were semi quantitative, at best, and should be considered in a relative rather than an absolute sense.

RESULT AND DISCUSSION

Analysis of Transesterification Products Using GC-MS

Typical example of the GC chromatogram of the sample obtained from transesterification experiments is presented in Fig. 1.

In general, the chromatogram displays very good peak shapes and the compounds are very well separated from each other. A total of 25 peaks are observed in the chromatogram, however, some of them could not be identified because their intensities are too low to be considered satisfactory.

The compounds identified according to Fig. 1 are presented in Table 1. As can be seen, a series methyl

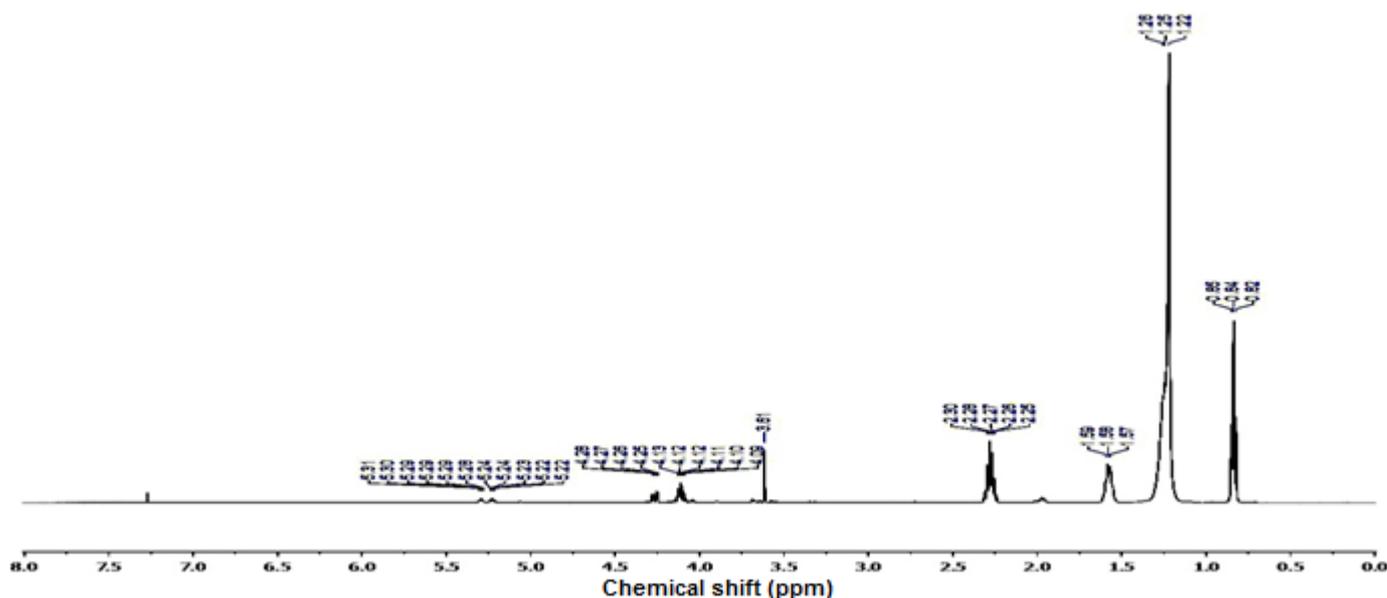


Fig 2. The $^1\text{H-NMR}$ spectrum of a typical biodiesel sample produced in this study

esters were identified. Identification of these methyl esters indicated that transesterification of fatty acids in the coconut oil took place as expected, which is also supported by the presence of dimethyl ketone in the product. The data also display that methyl laurate is the most prominent component of the sample, which is in accordance with the existence of lauric acid as the most abundant component of coconut oil, commonly reported.

In addition to methyl esters, several fatty acids were identified, which indicate that complete transesterification of the coconut oil has not been achieved under the experimental conditions applied. In this respect, further experiments to optimize the kinetic variables involved are required.

Analysis of Transesterification Products Using $^1\text{H-NMR}$ Spectroscopy

In addition to gas chromatography-mass spectrometry (GC-MS), another method that has been applied for biodiesel analysis is proton nuclear magnetic resonance ($^1\text{H-NMR}$) for its ability to provide complementary information regarding the molecular variability of the sample [25-27]. While the GC-MS provides detailed molecular weight information, the NMR technique is sensitive to unique molecular environments which yield unique spectra for different molecules. In this respect, the $^1\text{H-NMR}$ technique is very useful to verify whether the complete conversion of fatty acids to FAMES has been achieved and to indicate the presence of unsaturated as well as saturated methyl esters in the sample.

The analysis of the biodiesel produced in this study using $^1\text{H-NMR}$ technique was found to provide significant

molecular information related to biodiesel components commonly considered. The $^1\text{H-NMR}$ spectrum of a typical sample presented in Fig. 2 is characterized by the presence of peaks at different chemical shifts commonly reported for biodiesel [25-27].

Very evident existence of terminal alkyl methyl group, which is considered to be the most important structural characteristic of methyl ester, is displayed by the presence of peaks (triplets) at chemical shift around 0.9 ppm. These particular peaks confirmed that the conversion of fatty acids into FAMES was achieved. The formation of methyl ester is further supported by the presence of sharp peak at 3.7 ppm, which is assigned to ester methyl located next to the carbonyl carbon, the peaks at around 1.6 ppm associated with alpha methylene group, and the peaks at around 2.38 indicating the presence of beta methylene group in the biodiesel. The presence of peaks with low intensity located between 5.22 and 5.31 ppm are due to the proton located at or near double bond within the unsaturated methyl ester, confirming the presence of methyl oleate (18:1) as seen by the GC-MS analysis.

The presence of protons of $-\text{CH}_2-$ group is very evident in the spectrum, indicated by the peaks (triplets) located at chemical shift between 1.2–1.4 ppm which emerge as the signals with the highest intensity. These peaks of high intensity suggest the existence of long chain of $-\text{CH}_2-$ groups, in which the protons have similar resonance frequencies, and therefore, the total intensity of the peaks is the sum of the individual contributions from the protons of the $-\text{CH}_2-$ groups in the molecule. The peaks (multiplet) between 4.09 and 4.28 are due to the four hydrogens at positions 1 and 3

Table 2. Percent of conversion of coconut oil at different oil to DMC ratios

No.	Oil to DMC ratio	Percent of conversion
1	1:1.5	73.55
2	1:2.0	80.16
3	1:3.0	84.38
4	1:4.0	88.44

of the glyceride moiety of the triacylglyceride, indicating that some of the fatty acids remained unconverted, which is in agreement with the results of GC-MS analysis obtained.

Transesterification Yield

The yields of transesterification experiments in term of percent of conversion are presented in Table 2, to display the effect of oil to DMC ratio.

The results obtained clearly indicate the significant role of the oil to DMC ratio, in which the tendency of increased percent of conversion with increased relative amount of DMC used. As can be seen, the oil conversion was found to increase with increasing molar ratio of DMC : oil. These results demonstrated the importance role of the concentration of DMC to promote the extent of the reaction toward the formation of the products. Compared to the previous study using methanol [28], the percent conversion achieved in this study is comparable with that obtained with the ratio of oil to methanol of 1:15.

Characteristic of Biodiesel Produced

Additional analysis was carried out to determine three basic characteristics of the transesterification product, and the results are presented in Table 3. The standard values according to Indonesian standard for biodiesel (SNI 04-7182-2006) are included for comparison.

Compared to the standard values, the three characteristics are acceptable. However, determination of the rest of the parameters included in the standard is required for further evaluation of the applicability of the biodiesel produced using the method investigated in this current study.

CONCLUSION

The results obtained demonstrate that transesterification of coconut oil can be achieved using $\text{TiO}_2/\text{SiO}_2$ heterogeneous catalyst and DMC as substitute of methanol. Analysis of the biodiesel produced using GC-MS spectroscopy indicates that fatty acids were transformed into corresponding methyl esters. However, complete transesterification of the oil

Table 3. Some characteristics of biodiesel produced

Parameter	Biodiesel produced	Standard value (SNI)
Viscosity (mm^2/S), 40 °C	2.4	2.3 – 6.0
Flash Point, °C	103	min 100
Cetane Number	54	min 50

has not been achieved under the reaction conditions applied, suggesting the need for further research to optimize the reaction. The formation methyl esters are supported by the results of $^1\text{H-NMR}$ analysis, which also confirm that some of the fatty acids remain unconverted into biodiesel. The significant role of the DMC to oil ratio is observed in this study, in which the oil conversion was found to increase with increasing molar ratio of DMC : Oil. The values of three basic characteristics of the biodiesel produced are in agreement with those specified in the Indonesian standard for biodiesel, however, complete evaluation according to the standard is still required.

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