Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2017, 9(5):170-174

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Heterogeneous Catalyst from Graft-Cross Link Copolymer Chitosan on Trans-Esterification Palm Kernel Oil–Methanol with Fluidization Method

Suyanto[1*], Khusnul Ain[2], Hendra Pratama[1] and M Zakki Fahmi[1]

[1]Chemistry Department, Faculty of Sciences and Technology, Airlangga University, Surabaya, Indonesia
[2]Biomedical Engineering, Faculty of Sciences and Technology, Airlangga University, Surabaya, Indonesia

---

ABSTRACT

The aim of this research is to determine the power or ability catalytic heterogeneous catalyst chitosan derivatives are carboxy methyl chitosan-urea-glutaric acid (CMChi-UGLU) and 2,2-dichloro-carboxy methyl chitosan-urea pthalic acid (DCMChi-UTER) on the reaction of trans- esterification palm kernel oil (PKO) -methanol with fluidization method. In this research showed that both the catalyst may change in PKO triglycerides into methyl ester are methyl laurate, methyl caprate, methyl miristate, methyl palmitate, methyl oleate, methyl linoleate, and methyl stearate. The trans-esterification PKO-methanlo with CMChi-UGLU as catalyst give a total fatty acid methyl ester C_{14}-C_{24} (FAME) is 32.62% and conversion value 36.28%, while DCMChi-UTER as catalyst give total FAME is 11.93% and conversion value is 3.24%.

Keyword: CMChi-UGLU; DCMChi-UTER; Fluidization; Methyl ester

INTRODUCTION

Petrol and natural gas are non-renewable fuel, thus synthesis of fuel is one of alternative for daily needs. One of fuel synthesis is produced by methyl palmitate known as biodiesel which can be obtained by esterification fatty acid or via trans-esterification of triglycerides such as tripalmitine with alcohol namely methanol. The advantages of fuel biodiesel are used for diesel engine without engine modification, lower emission, high flash point, non toxic and biodegradable [1,2]. Mineral acid or alkali catalyst application causes corrosion [3], while using heterogeneous catalyst for esterification is easily recovered or separated, less corrosive, and reuse [4]. In order to that, this research heterogeneous catalyst CMChi-UGLU and DCMChi-UTER which chitosan derivative were used. These compounds are graft-cross link copolymer, which are insoluble in acid solution. In this research, trans-esterification was carried out by fluidization method. Fluidization is process or operation which makes particles like properties of fluid, by contacting particles in a bed with air or gas or liquid [5]. Trans-esterification of PKO-methanol with fluidization is expected to contact with heterogeneous catalyst-reactant will be more excellent.

MATERIALS AND METHODS

Materials

Materials used in this research were: chitosan (comersiel grade/IPB), PKO (Agro bukit central /Indonesia), methanol, urea, glutaric acid, phthalic acid, ethanol, acetone, chloroacetic acid and trichloro acetic acid (synthesis grade, sigma). Fluidized bed and air pump also used to fluidization process. Elucidation functional groups used FTIR (Shimadzu 8400S/Japan) and identification of variety of ester or biodiesel were done by GC-MS (Agilent 6890 N) and SEM (Zeiss EVO MA10) and EDX (Bruker X Flash Detetor 5010).

Synthesis Carboxymethyl Chitosan (CMChi)

Carboxymethyl chitosan was synthesized by modification of Chen-Park method [6,7]. Chitosan was added with 2% acetic acid and mixed to form solution, and then NaOH was added and heated at 50°C in an hour. This mixture was mixed reaction with chloroacetic acid in isopropanol and reflux for 50°C in 4 hours. The reaction stopped by adding ethanol and the product was characterized with FTIR.

Synthesis Carboxymethyl Chitosan-Urea-Glutaric Acid (CMChi-UGLU)

Carboxymethyl chitosan-urea-glutaric acid (CMChi-UGLU) was synthesized by modification of Chen-Park method [6]. Urea solution was mixed with glutaric acid by reflux this mixture for 3 hours at 100°C. Then CMChi was added to the product which produced CMChi-UGLU and the product were characterized with FTIR.

Synthesis 2,2-dichloro Carboxymethyl Chitosan-Urea-Phtaliclic Acid (DCMChi-UTER)

Synthesis 2,2-dichloro carboxymethyl chitosan-urea-phtaliclic acid (DCMChi-UTER) was conducted with the same procedure[6] as synthesis of CMChi-UGLU, but glutaric acid was replaced by phtalic acid and chloro acetic acid were replaced by trichloro acetic acid. Thus the product would be characterized with FTIR.

Esterification Free Fatty Acid (FFA)-Methanol

Before carrying out trans-esterification reaction, esterification reaction to lower the acid number was conducted, so that the level of free fatty acids in the oil would be less than 2% in order to avoid the formation of soap. The esterification carried out with reflux at a temperature of 75°C for 6 hours with methanol or oil molar ratio of 1/60 and catalyst sulfuric acid is 1% w/w to oil (50 grams PKO added 140.92 grams of methanol plus 0.5 grams of sulfuric acid). Then the residue of level of free fatty acids was determined by titration. Acid number was determined by [8]: 1 ml PKO was mixed with methanol then soaked and added methanol until limited sign.

1ml of this solution was filled in Erlenmeyer and then 1 drop phenol pthalin indicator was added. Acid number then determined by titration of solution with 0.0957 N NaOH and it stopped until pink color (three replication).

$$\text{Number of acid} = (N_{NaOH} \times V_{NaOH} \times 40) / m \quad \ldots\ldots\ldots\ldots (1)$$

Whereas N is normality, V is volume and m is mass of PKO.

Trans-Esterification PKO-Methanol

Fluidized bed made of a glass tube with a diameter of 5 cm and height 25 cm. At a height of 5 cm from the bottom of the tube fitted gauze to hold the catalyst granules. From the side tube fitted hole for inserting the plastic hose at the edges functioning air distributor mounted air to evenly divide air to entire column section [9]. Air flow rate into the column is set in such a manner, so fluidization velocity of catalyst particles caused this particle could be evenly throughout the bed at a speed of fluidization and circulation reach optimum state. After concentration of free fatty acids in the oil was less than 2%, the oil washed with demineralized aqua twice to remove the residual acid and glycerol. Fluidized bed was filled with catalyst (1% w/w to PKO oil) then PKO and methanol with molar ratio 1 : 60 was added. Air flow was provided by air pump from the bottom fluidized bed [9]. Amount of catalyst in this step 1% w/w to PKO oil and molar ratio PKO-methanol 1:60 and the reaction was held at 70°C for 1 hour [10]. Then catalyst was separated from the product by filtration, and methanol residue was evaporated by rotary evaporator. The ester product then characterized with GC-MS [3] and then conversion value and total fatty acid methyl ester (FAME) would be determined by [11] formula.

The conversion value of triglyceride to methyl ester determined by formula [11]:

$$C = [(\Sigma A - Ai)/Ai] \times [\, Ci.Vi/m] \times 100\% \quad \ldots\ldots\ldots (2),$$

where ΣA is peak total of methyl ester with number of C atom 14 to 24, Ai is peak area of internal standard, Ci is concentration of internal standard solution (mg/ml), Vi is volume of internal standard solution (ml), and m is mass of sample (mg).

RESULTS AND DISCUSSION

The synthesis of CMChi-UGLU were characterized with FTIR and obtained peaks at wave numbers 3388 and 1629 cm^{-1} which indicated a functional group CO (NH) and 1600 cm^{-1} indicated the group N (CO) N. Meanwhile the wave number of 2933 showed a - COOH group, this proved that CMChi-UGLU had been formed. Characterization DCMChi-UTER synthesized by FTIR showed wave number in cm^{-1} absorption peak at the wave number υ (cm^{-1}) 1641 and 3435 (-O = C-N-H); 1035 (- C-N urea); 2889 (-COOH), 1641 (NCON), 1149-1035 (COC), 3435 (OH), 1425 with 2 peaks (aromatic ring) and 746 (-C-Cl) [12] the existence of this group show, that DCMChi-UTER have formed (Figure 1).

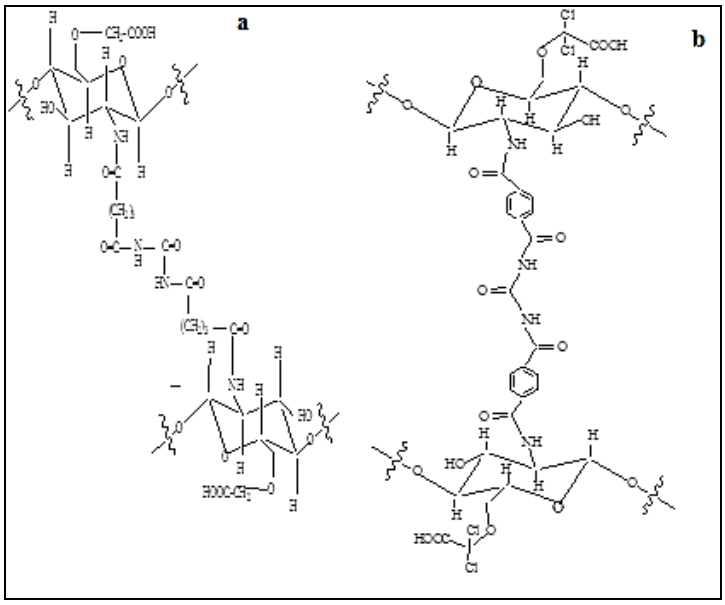

Figure 1: (a) Structure of CMChi-UGLU and (b) DCMChi-UTER

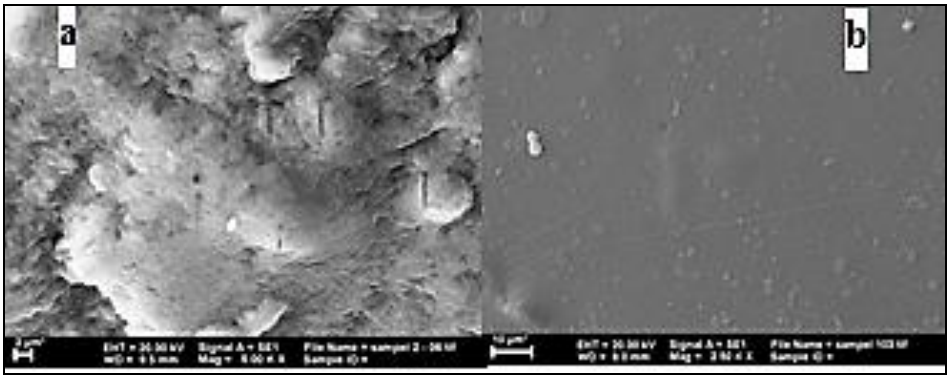

Figure 2: Morphology of (a) CMChi-UGLU and (b) CMChi-UTER

Concentration of Free Fatty Acid (FFA) in PKO is 9,178%, after esterification with methanol and used sulfuric acid as catalyst, so the FFA content decreased to 0.4% and then PKO in trans-esterification with catalyst CMChi-UGLU and carrying out by fluidization method, in order to obtain the results in Table 1.

Table 1: Spectra GC trans-esterification PKO-methanol using CMChi- UGLU as catalyst with fluidization method and methyl pentadecanoate as internal standard

Peak	Residence Time (Minutes)	Correction Area	% Total	Methyl Ester
1	2.106	63451	2.269	Methyl Caprate
2	3.137	1226895	43.877	Methyl Laurate
3	5.292	401503	14.359	Methyl Myristate
4	7.004	580173	20.749	Methyl Pentadecanoate
5	9.847	194485	6.955	Methyl Palmitate
6	14.913	281864	10.08	Methyl Oleate
7	15.639	34336	1.228	Methyl Stearate

The number of fatty acid methyl ester $C_{14} - C_{24}$ (FAME) = 14.359 + 6.955 + 10.080 + 1.228 = 32.622%, and conversion value in this trans-esterification determined by equation (2)

$$C = [(\Sigma A - Ai)/Ai] \times [Ci.Vi/m] \times 100\% = 912.188/580.173\ [(50, 6/5) \times 5: 250, 3] = 36.28\%$$

Trans-esterification of Palm Kernel Oil-methanol using DCMChi-UTER as catalyst with fluidization method result showed in Table 2.

Table 2: Results trans-esterification PKO-methanol using DCMChi-UTER as catalyst with fluidization method

Peak	Residence Time (Minutes)	Correction Area	% Total	Methyl Ester
1	1.655	2327352	0.55	Methyl Caprilate
2	2.151	4276259	1.011	Methyl Caprate
3	3.051	57523314	13.16	Methyl Laurate
4	3.866	1348221	0.319	Ethyl Laurate
5	5.513	19674206	4.652	Methyl Myristate
6	9.959	9139139	2.33	Methyl Palmitate
7	13.397	306988326	72.59	Methyl Margaratr
8	15.18	1634842	0.387	Methyl Linoleate
9	15.363	16117811	3.811	Methyl Oleate

The conversion value in this trans-esterification determined by equation (2)

$$C = [(\Sigma A - Ai)/Ai] \times [Ci.Vi/m] \times 100\% = 50.453.134/306.988.326\ [(50, 2/5) \times 5: 255] = 3.24\%$$

The amount of fatty acid methyl ester $C_{14} - C_{24}$ (FAME) = 11.931%.

From the above table and the total FAME is formed and see the huge number of conversion, it appears that the catalytic power CMChi-UGLU is better than DCMChi-UTER, it is suspected that the CMChi-UGLU contain more O atoms which have lone pair electrons than DCMChi-UTER. A lone pair electron is involved in the reaction. Initially, the catalyst will interact with methanol to form N- metoksi- DCMChi-UTER. The O atoms in the N-OCH_3 on this complex attacks triglycerides which resulting trans-esterification reaction on PKO. Morphology (Figure 2) CMChi-UGLU wavely it mean that surface area CMChi-UGLU wider than DCMChi-UTER so CMChi-UGLU better than DCMChi-UTER as fluidized catalyst on trans-esterification PKO-methanol with fluidization method (Figures 3 and 4).

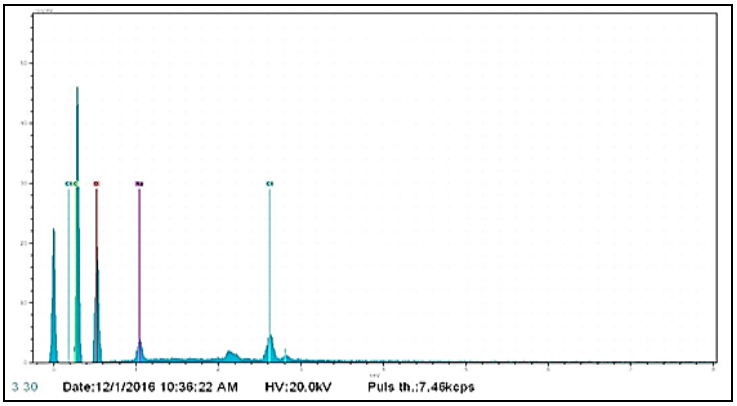

Figure 3: EDX of DCMChi-UTER, elemen O (red colour) = 30%

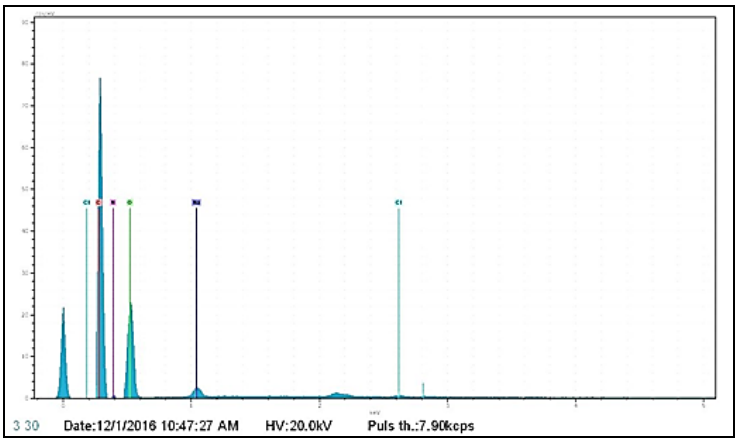

Figure 4: EDX CMChi-UGLU elemen O (green colour) = 50%

CONCLUSION

Carboxy methyl-urea-glutaric acid (CMChi-UGLU) and 2,2-dichloro carboxy methyl-urea-phthalic acid (DCMChi-UTER) used as catalyst on trans-esterification of PKO-methanol with fluidization method which is resulting a total fatty acid methyl ester C_{14}-C_{24} (FAME) is 32.62% and conversion value 36.28%, while DCMChi-UTER as catalyst give total FAME is 11.93% and conversion value is 3.24%.

ACKNOWLEDGEMENT

We thank the Directorate of Research and Community Service, General Directorate Strengthening Research and Development, Ministry of Research, Technology and Higher Education, Republic of Indonesia, which has been a given funding for this study.

REFERENCES

[1] FE Soetoredjo; A Ayucitra; A Ismaji; AL Maukar. *Appl Clay Sci*. **2011**, 53(2), 341-346.
[2] http://www.eng.uwo.ca/zeolite/Betty-Poster-Final.pdf
[3] KH Chung; DR Chang; BG Park. *Bioresource Technol*. **2008**, 99(16), 7438-7443.
[4] O İlgen; AN Akin. *Turk J Chem*. **2009**, 33(2), 281-287.
[5] D Kunii, O Levenspiel. Fluidization engineering. Elsevier, **2013**.
[6] XG Chen; HJ Park. *Carbohyd Polym*. **2003**, 53(4), 355-359.
[7] S Sun; A Wang. *Sep Purif Technol*. **2006**, 49(3), 197-204.
[8] S Sudarmadji, B Haryono, dan Suhardi. Analysis procedure for food material and agriculture, 4th edition, Liberty Publisher, Yogyakarta, Indonesia, **1997**, 85.
[9] D Suyanto. *J Chem Pharm Res*. **2015**, 7(1), 247-254.
[10] ZH Huaping; WU Zongbin; C Yuanxiong; P Zhang; DU Shijie; LI Xiaohua; MA Zongqiang. *Chinese J Catal*. **2006**, 27(5), 391-396.
[11] T Ruppel, T Huybrighs, CT Shelton. Fatty acid methyl esters in B100 biodiesel by gas chromatography (modified EN 14103). Application Note, Perkin Elmer. **2008**, 2012.
[12] DH Williams, I Fleming. Spectroscopic methods in organic chemistry. McGraw-Hill, New York, United States, **1980**.