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Chemical Engineering Conference



“Chemical Engineering Role for Sustainable Development”

Kuta, Bali
December 4-5th, 2013



INTERNATIONAL CONFERENCE AND WORKSHOP ON CHEMICAL ENGINEERING UNPAR 2013

CERTIFICATE OF ATTENDANCE

This is to certify that

Dr. Ir. Joelianingsih, M.T.

has presented oral paper during
International Conference and Workshop on Chemical Engineering 2013
with theme

“Chemical Engineering Role for Sustainable Development”

held in Kuta, Bali, Indonesia, December 4-5th, 2013

Chairman ICCE 2013



Dr. Henky Muliiana S.T. M.Eng.

PREFACE

Dear all participants,

First of all, we would like to welcome all of you into the 1st UNPAR's International Conference of Chemical Engineering and Process Safety Workshop where this event is also in conjunction with the 10th National Conference of Chemical Engineering. This year, on April 2013, we are celebrating our 20th anniversary. Therefore in this special year, we are extending our conference scope from national to international event. It is also our intention to introduce our Chemical Engineering Department in the International level.

We are choosing Chemical Engineering Role for Sustainable Development as the conference theme. We realize that chemical engineering plays an important role to ensure the sustainability in every aspects starting from alternative renewable feedstocks for energy and chemicals, alternative green processes until waste minimization. Strongly related with the sustainable process development, chemical engineer also have to deeply involved in the process safety in order to bring this sustainable technology in the industrial level. It is our wish that the conference and the workshop will provide an excellent forum for academia, industry and Indonesia's government to share information, discuss recent knowledge and technological advancement, as well as provide an up-to-date perspective on the sustainable development around the globe.

We are very pleased to have lectures given by our special keynote speakers. The topics are surely important and will stimulate a fruitful discussion about the chemical engineering role in many aspects for sustainable development. We would like to sincerely thanks our keynote speakers, Prof Djoko Said Damardjati from Indonesian Agency for Agricultural Research and Development (IAARD), Ministry of Agriculture, Indonesia, Prof Haryadi from Gadjah Mada University, Prof Yudi Samyudia from Curtin University, Prof. Leon Janssen, Prof H.J. Heeres, and Prof F. Picchioni from University of Groningen, Assoc. Prof. Kim Jaehoon from Sungkyunkwan University, and Prof. Xiao Dong Chen from Soochow University. We would like to give a special thanks to Bapak Ir Yos Triadmodjo, M.M., for his willingness to share and to bring his 30 years Industrial experiences in the Process Safety workshop.

We are also grateful to the Indonesian Center for Estate Crops Research and Development Indonesian Agency for Agricultural Research and Development (IAARD), Ministry of Agriculture, Indonesia and Research Centre for Chemistry, Indonesian Institute of Science (LIPI) for supporting our 1st International Conference and Workshop. Last but not least, I would like to express a very special gratitude to the scientific committee and the organizing committee for their time, efforts and contribution to this event.

And finally, I hope that you enjoy this event and wish you a pleasant stay in Kuta, Bali.

Sincerely,

Dr. Henky Muljana, ST., M. Eng
Chairman of the Organizing Committee,
Head of Chemical Engineering Department
Parahyangan Catholic University

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1. Introduction

The catalytic transesterification of vegetable oil used to produce biodiesel, is an important industrial process. Biodiesel is a promising fuel for substitution or blending with petroleum based diesel fuel, while these two kinds of fuel share similar physical and chemical properties. Some of the first industrial processes to produce biodiesel used either strong base or strong acid homogeneous catalyst for transesterification reaction, such as potassium and sodium hydroxide, sulfuric, hydrochloric or sulphonic acids. The homogeneous catalyst offer certain advantages such as high activity, easily reached reaction condition (25-130°C at atmospheric pressure) and less expensive, but face variety of technical difficulties. Homogeneous catalyst are normally carried out in batch mode processing. Furthermore, a drawback of homogeneous base-catalyzed transesterification is that the oil that contain significant amounts of free fatty acids could not be convert into biodiesel completely and remained as soap in high quantity. Separation of the product from the soap and spent waste catalyst appears to be technically challenging and brings additional cost to the product. It was reported that generally acid catalyzed reactions are performed at high alcohol to oil molar ratios, low to moderate temperatures and pressures, and high acid catalyst concentrations. Unfortunately, ester yields do not equally increase with molar ratio of reagents. Despite its insensitiveness to free fatty acids, acid-catalyzed transesterification is relatively slow reaction rate. However, Raka and Kusdhana² revealed that producing biodiesel fuel from rapeseed oil which was prepared in supercritical methanol (at 350 °C and 200 bar) had highly reduced reaction time. Unfortunately, such kind of reactor is not only high risk but also high capital and operating cost.

Yamashita et al.³ and Jofriyaningsih et al.⁴ have studied the production of non catalytic biodiesel oil supported by Bubble Column Reactor (BCR) at atmospheric condition. In the semi-batch system, Jofriyaningsih⁴ had varied the temperature reaction in the range between 250 and 290 °C with flow rate of methanol vapor set at 4 g/min. Transesterification reaction of triglycerides (TG) to form methyl

Biodiesel production from palm frying oil using sulphated zirconia catalyst in a bubble column reactorIs Sulistyati Purwaningsih^{a*}, Joelianingsih^a, Wahyudin^a^aChemical Engineering Department, Institut Teknologi of Indonesia, Jl. Raya Puspiptek Serpong, Tangerang Selatan 15320, Indonesia**Abstract**

Homogeneous catalysts are promising for the transesterification reaction of vegetable oil to produce biodiesel since this catalyst offer certain advantages such as high activity, easily reached reaction condition and less expensive; however homogeneous catalyst has some drawbacks such as high energy consumption, costly separation of catalyst from the reaction mixture and the purification of the product. The use of bubble column reactor (BCR) in producing biodiesel fuel without catalyst has been developed. In the BCR, the role of catalyst was replaced by high operating temperature, while the role of agitation was taken over by the formed vapor bubbles. The experimental result concluded that the higher the operating temperature, the higher the product conversion as well as the reaction yield, although it lowers the biodiesel's purity. Nowadays, heterogeneous catalysts have been more widely favoured over the homogeneous one since they are easily separated from reaction mixture and reused for many times. In this study, transesterification reaction of refined palm oil (palm frying oil) was conducted in a bubble column reactor using sulphated zirconia (SO_4/ZrO_2) as the solid heterogeneous catalyst. The experiment was carried out at 250 °C. At first, the influence of methanol flow rate towards vapor bubble formation was investigated, the experiments were then run catalytic and non-catalytically by varying the catalyst to reactant mass ratio. The experimental result showed at 5 mL/min of methanol flow rate, the amount of methanol vapor bubbles were continuously produced and uniformly distributed in the oil phase. This condition was then selected for the remaining study. It was noted that the highest yield of biodiesel product was achieved at 0.5 % (m/m) of catalyst concentration, meanwhile yield of product that run without catalyst was the lowest among all experimental results. However, at 1% (w/w) of catalyst to reactant mass ratio, the product phase was changed to solid.

Keywords: biodiesel; refined palm oil (palm frying oil); SO_4/ZrO_2 catalyst; bubble column reactor

1. Introduction

The catalytic alcoholysis of vegetable oil use to produce biodiesel, is an important industrial process. Biodiesel is a promising fuel for substitution or blending with petroleum based diesel fuel, while these two kinds of fuel share similar physical and chemical properties¹. Some of the first industrial processes to produce biodiesel used either strong base or strong acid homogeneous catalyst for transesterification reaction, such as potassium and sodium hydroxides, sulfuric, hydrochloric or sulphonic acids. The homogeneous catalyst offer certain advantages such as high activity, easily reached reaction condition (25-130°C at atmospheric pressure) and less expensive, but face variety of technical difficulties¹. Homogeneous catalysts are normally carried out in batch-mode processing. Furthermore, a drawback of homogeneous base-catalyzed transesterification is that the oil that contain significant amounts of free fatty acids could not be convert into biodiesel completely and remained as soap in high quantity². Separation of the product from the soap and spent waste catalyst appears to be technically challenging and brings additional cost to the product. It was reported that generally acid catalyzed reactions are performed at high alcohol to oil molar ratios, low to moderate temperatures and pressures, and high acid catalyst concentrations. Unfortunately, ester yields do not equally increase with molar ratio of reactans. Despite its insensitiveness to free fatty acids, acid-catalyzed trans-esterificataion is relatively slow reaction rate³. However, Saka and Kusdiana⁴ revealed that producing biodiesel fuel from rapeseed oil which was prepared in super-critical methanol (at 350 °C and 200 Bar) had highly reduced reaction time. Unfortunately, such kind of reactor is not only high risk but also high capital and operating cost.

Yamazaki et al.⁵ and Joelianingsih et al.^{6,7} have studied the production of non catalytic biodiesel oil employed by Bubble Column Reactor (BCR) at atmospheric condition. In the semi-batch system, Joelianingsih⁷ had varied the temperature reaction in the range between 250 and 290 °C with flow rate of methanol vapor set at 4 g/min. Transesterification reaction of triglycerides (TG) to form methyl

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ester (ME) in the BCR showed that this reactor acts as reactive distillation (RD); the reactor is not only as a reaction place, but also as a product separator as well. The RD concept works appropriately on equilibrium reaction such as in vegetable oil transesterification reaction, because straight and continuous separation of reaction product will drive the equilibrium to the product side and raise the conversion. According to Yamazaki et al.⁵ and Joelianingsih et al.⁶, in the BCR, the role of catalyst was replaced by high operating temperature, while the role of agitation was taken over by the formed vapor bubbles. Their experimental result concluded that the higher the operating temperature, the higher the product conversion as well as the reaction yields although it lowers the biodiesel's purity. It was also revealed that BCR that runs with high temperature condition will cause more monoglyceride (MG) formed as impurity in the product. According to the Indonesian National Standard⁸, the ME content in biodiesel should be less than 96.5% (m/m). Many studies have been reported that utilization solid or heterogeneous catalyst can be done to improve quality and conversion of biodiesel product¹.

Producing biodiesel oil incorporated heterogeneous catalyst has the potential to offer some relief to the biodiesel producers by improving their ability to process other cheaper feedstocks and to use a shortened and less expensive manufacturing process¹. In addition, compared to the homogeneous one, this catalyst can be easily separated from reaction mixture and reused for many times. Moreover, using heterogeneous catalyst, biodiesel processing can be run continuously. Several solid acid catalysts have been reported to have the potential to replace strong liquid acid. These catalysts are zeolites, heteropoly acids, functionalized zirconia & silica, and some metals oxide³. Zeolites normally can be synthesized with extensive variation of acidic properties. However due to their uniform pore structure, the hydrophobicity of the catalyst is still in the stage of trial and error^{3,9}. Previous study¹⁰, reported that sulphated zirconia ($\text{SO}_4\text{-ZrO}_2$) has been utilized as a catalyst for transesterification vegetable oil to produce biodiesel. Study by Kiss¹ revealed that this catalyst was the most active catalyst for esterification. Petchmala et al.¹¹ reported that transesterification of palm oil with $\text{SO}_4\text{-ZrO}_2$ catalyst in super-critical methanol at 250°C and within 10 minutes reaction, its conversion reached to 90 %.

Based on the above information, in this study, experiment was carried atmospherically in a set of BCR apparatus incorporated with $\text{SO}_4\text{-ZrO}_2$ as a catalyst. Previous study⁵ revealed that transesterification reaction carried out in the BCR, run non catalytically at atmospheric pressure and at 250 °C temperature, produced biodiesel oil with high purity (almost reach the standard value), but its conversion was very low (55%). However, the superiority of BCR over other type of reactors is based on the capability act as RD proces. Even though the rate of the reaction is very slow, the product is directly separated from the reactants and produces higher purity of ME. In addition, reaction can be proceed continuously although with low capacity. It is expected by combining the BCR technology with the advantage of sulphated zirconia as the catalyst in transesterification of vegetable oil¹¹, will increase quality and productivity of the biodiesel.

2. Experimental methods

2.1 Materials

Palm Frying Oil (PFO, Bimoli brand) was purchased at Alfa-Mart grocery store. The fatty acids composition of palm frying oil was determined by gas chromatography (GC) equipped with a flame ionization detector and a cyanopropylmethyl silicone column (60 m × 0.25 mm internal diameter and film thickness of 0.25 μm). The carrier gas was helium at 1 mL.min⁻¹. The oven temperature was initially held at 160 °C for 5 minutes then increased to 220 °C. This analysis was conducted at the Integrated Laboratory of Bogor Agricultural University. Methanol (MeOH) with 99.8 % purity (analytical grade) was produced by PT. Smart-Lab. Indonesia. Sulphated zirconia ($\text{SO}_4\text{-ZrO}_2$) catalyst.

2.2 Preparation of catalyst

Sulphated zirconia ($\text{SO}_4\text{-ZrO}_2$) catalyst was prepared by Center of Physics Research - The Indonesian Institute of Sciences, Puspiptek Serpong South Tangerang. As for catalyst preparation, 100 gram of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ was dissolved into 1000 mL of aquadest water. Ammonium hydroxide solution was added dropwise into well-stirred solution of ZrOCl_2 until pH reach to 9 at room temperature till ZrO_2 solid formed. The resulting precipitate was removed by filtration and then washed by aquadest

until free of chlor. The solid was then dried in the oven at 120°C, for 16 hours. The sulphated zirconia was then prepared by impregnation of H₂SO₄ over Zr(OH)₄, by immersing in 1.0 N solution of H₂SO₄ (1 gram sample in 15 mL H₂SO₄) for 30 min. The solid was then filtered and dried at 120°C. Next, solid sample was calcined (650°C, 3.5 hr). Differential Thermal Analyzer (DTA) was applied to determine calcination temperature of catalyst. The sulphated zirconia catalyst was characterized using the Fourier Transform Infra Red (FTIR) analyzer, the XRD and the Brunauer-Emmett-Teller (BET) value. The FTIR analysis was conducted prior impregnation the ZrO₂ with sulphate solution and after calcined at the ITI Chemical Engineering laboratory. The crystal structure was determined using X Ray Diffractometer at the Center of Integrated laboratory of University of Islam Negeri Syarif Hidayatullah Jakarta, while the BET analysis was carried out at the BATAN laboratory, Puspiptek Serpong.

2.3 Apparatus

A photograph and a schematic diagram of a BCR apparatus are presented in Fig. 1. The apparatus was equipped with a methanol tank, vaporizer, reactor, heater, and condenser columns.

2.3. Experimental procedures

Initially, the reactor was filled with PFO until reach the minimum mark level. Then another 250 ml of palm oil was filled into reactor, put the reactor lid and bring it into tight. Secondly, the vaporizer was filled with MeOH till the maximum mark level followed by filling up the MeOH tank. Next, switched the reactor heater on and held until reached the setting temperature. Afterwards, the superheater was turned on until temperature reached to 250 °C, followed by running the water cooler. Then, switched the MeOH vaporizer on and adjusted its vapor flow rate, followed by turning MeOH pump on and adjusted its pumping rate according to the vapor rate. Reaction time was counted after the vapor bubble uniformly formed and evenly distributed in the reactor. Finally, samples were taken within 20 minutes interval time, and were analyzed using GC.



Fig 1(a). The photograph of biodiesel apparatus set up

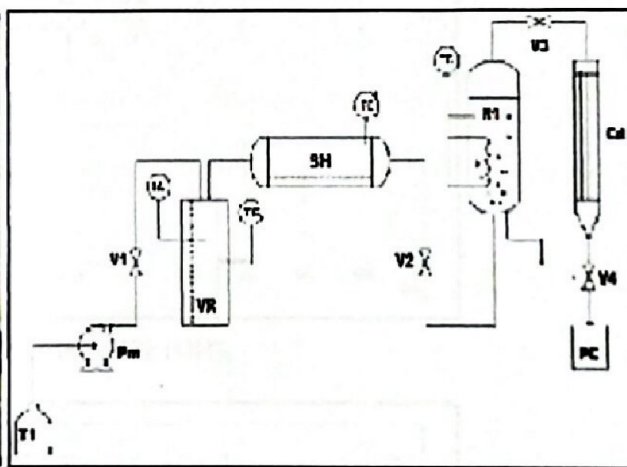


Fig 1(b). The schematic diagram of biodiesel experiment apparatus.

T1: MeOH tank, Pm: MeOH, pump, V1-V4: valves, VR: vaporizer, LC: level controller, TC: temperature controller, SH; superheater, R1: reactor, Cd: condenser, PC: product collector.

2.4. Product analysis

The biodiesel products analysis was carried out using a gas chromatograph, Shimadzu 2010 model with a flame ionization detector (FID), using helium as a carrier gas. The GC featured a capillary column (RTX-1 restex nonpolar phase; Cross bond[®] dimethyl polysiloxane, 30 M, 0.32 mm ID, 0.5µM). Method of analysis follows the modified EN 14105¹².

3. Results and discussion

3.1. Fatty Acid composition of palm frying oil material

The major fatty acid composition of PFO was tabulated in Table 1 and its result was compared to fatty acid composition of several palm oils analyzed by Petchmala et al.¹¹ and Kataren¹³.

Table 1. Comparison of Fatty Acid Composition

Fatty Acids	Fatty Acids Composition (% w/m)		
	Sample (avg)	Reference ¹¹	Reference ¹³
Miristic Acid	1.2	1.0	1.1 – 2.5
Palmitic Acid	43.9	45.6	40 – 46
Stearic Acid	3.9	3.8	3.6 – 4.7
Oleic Acid	41.7	33.3	39 – 45
Linoleic Acid	9.3	7.7	7 – 11

It can be observed that the fatty acid composition of PFO sample in this experiment is in accordance with the results of previous studies^{11,13}.

3.2. Catalyst characterization

Sulphated zirconia ($\text{SO}_4\text{-ZrO}_2$) catalyst that was prepared from the impregnation of H_2SO_4 over $\text{Zr}(\text{OH})_4$ resulted in 48 % (w/w) yield. The FTIR analysis prior H_2SO_4 impregnation and after H_2SO_4 impregnation followed by catalyst calcination were presented in figures 2 and 3.

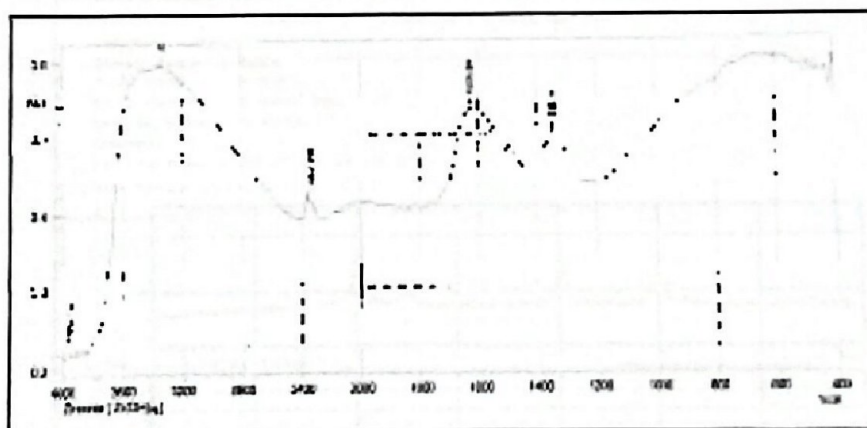


Fig 2. FTIR Spectrum of $\text{Zr}(\text{OH})_4$

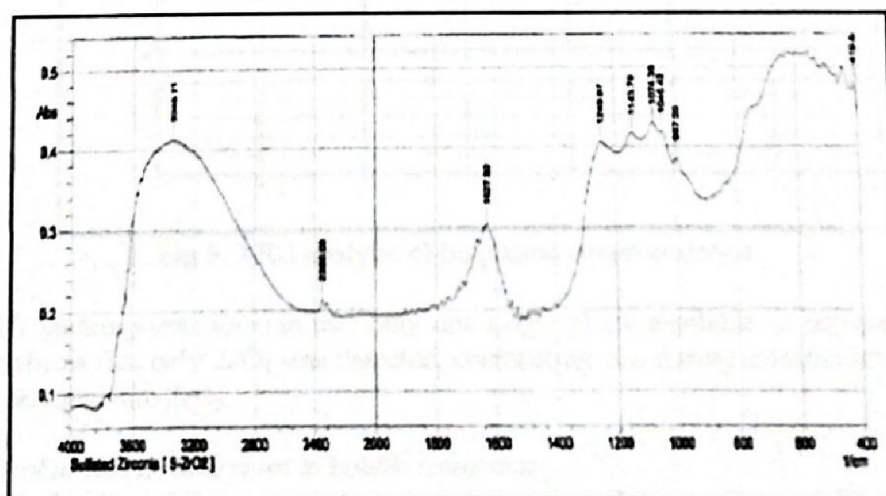


Fig 3. FTIR spectrum of $\text{SO}_4\text{-ZrO}_2$

Fig.2 indicates the spectrum of FTIR analysis of $Zr(OH)_4$ prior to H_2SO_4 impregnation and Fig. 3 shows the spectrum of FTIR analysis of SO_4-ZrO_2 . It was noted that there is a difference absorbance profile between these two figures at the range of $1000 - 1280\text{ cm}^{-1}$ wave lengths. According to Stuart¹⁴ the SO_2 and SO groups of sulphur compounds produce strong infra red band at wave length of $1000-1400\text{ cm}^{-1}$. It can be concluded that H_2SO_4 impregnation over the $Zr(OH)_4$ occurred, since sulphates group were identified at $997,20; 1045,42; 1074,35; 1143,79$ and $1249,87\text{ cm}^{-1}$ wave lengths.

The specific surface area of catalyst was determined by the BET method and found to be $53.26\text{ m}^2/\text{g}$. This result is represented in fig 4.

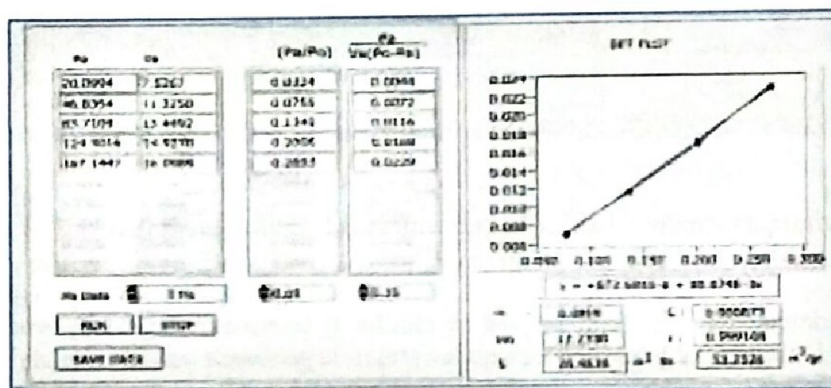


Fig 4. Analysis of surface area of SO_4-ZrO_2 catalyst

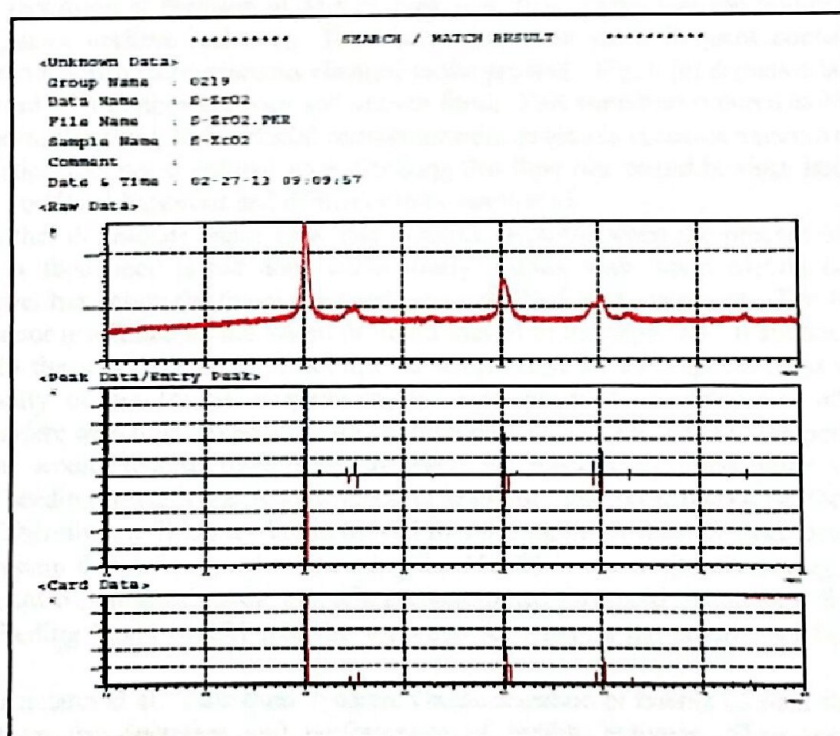


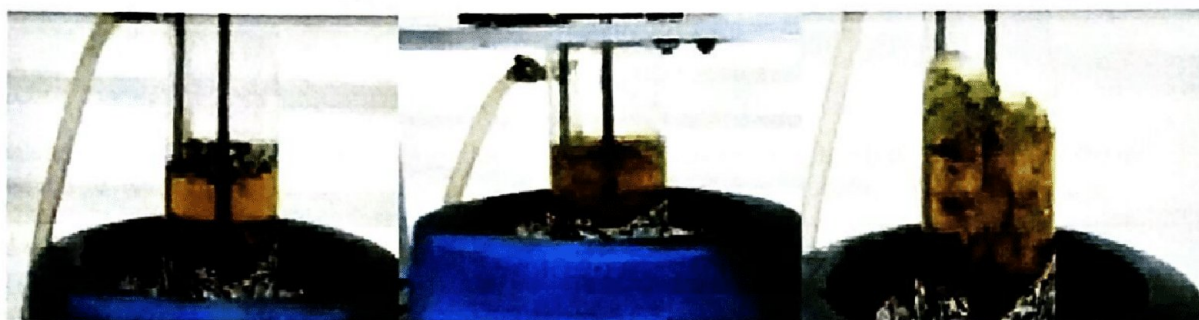
Fig 5. XRD analysis of Sulphated zirconiacatalyst

While XRD measurement showed that only one single phase available as depicted on Figure 5. This result confirms that only ZrO_2 was detected, considering that during calcinations process all the $Zr(OH)_4$ was changed into ZrO_2 .

3.3. The effect of methanol flow rates in bubble formation

The effect of methanol flow rates in bubble formation are shown in Figure 6. These figures show the flow rate differences in bubble formation. The bubble sact as substitutes for stirring the biodiesel

manufacturing process in which the reaction occurs at the contact interface of the bubbles. The methanol flow rates affect the amount and uniformity of the formed bubbles.



(a) (b) (c)
Fig 6. Bubble formation at methanol flow rate of 3,5 and 7 ml/min respectively

Fig. 6 (a) shows bubble formation at 3 ml/min of MeOH flow rate. The number of bubbles produced was slight and uneven. Resulting in interfacial contact between MeOH and oil is not optimal due to the lack of MeOH vapor flows into the reactor column. Consequently, the reactants which supposed to be changed into the product become even and less likely to be a product. Fig. 6 (b) indicates bubble formation at 5ml/min of MeOH flow rate. It is shown that the number of bubbles formed are much more uniform and even. Therefore, there were more frequent contact interface between the reactants which more reactants changed to the product. Fig. 6 (c) depicts a large amount of bubbles produced with in homogeneous and uneven form. This condition occurred as MeOH flow rate run at 7 ml/min. Resulting in interfacial contact between reactants becomes excessively fast and the product formation was not at optimal state. Utilizing this flow rate would be risky because of the numerous bubbles outburst happened and difficulty to be controlled.

It is observed that the MeOH vapor flow rate becomes unstable when the process of filling the liquid methanol as fresh feed is not done continuously. Filling with liquid MeOH is conducted when the liquid level has below the line of fluid indicator specified in the vaporizer. The formation of bubbles in the reactor is affected by the height of liquid MeOH in the vaporizer. If sudden refilling of liquid MeOH into the vaporizer occurred because of temperature of the vaporizer has reached the temperature stability of the MeOH evaporation, the cold physical characteristics of the liquid methanol will interfere with high temperature distribution process. The MeOH with temperature below evaporation point would require more time to reach its evaporation temperature causing the methanol's flow heading towards the reactor tends to wane or even none (based on the number of bubbles formed). Therefore, refilling the liquid MeOH into the vaporizer must be done continuously by generating such system that refilling and evaporating the MeOH to occur simultaneously, in order to maintain the amount of liquid methanol at a stable predetermined threshold. Additional flow meter is required before feeding liquid MeOH into the vaporizer to maintain the continuous flow of liquid MeOH

According to Kantarci et al.¹⁵, the fluid dynamic characterization of bubble column reactors has a significant effect on the operation and performance of bubble columns. They noted that the performance of bubble columns strictly depend on the regime prevailing in the column that can be classified and maintained according to the superficial gas velocity employed in the column. The methanol vapor superficial velocity obtained in this study was presented in Table 2.

Table 2. Superficial velocity of methanol vapor

Flow rate ($\frac{\text{ml}}{\text{min}}$)	Vapor Velocity ($\frac{\text{cm}}{\text{s}}$)
3	1,370
5	2,300
7	3,219

Kantarci et al.¹⁵ reported that the bubbly flow regime, also called the homogeneous flow regime is obtained at low superficial gas velocities, approximately less than 5 cm/s. This flow regime is characterized by bubbles of relatively uniform small sizes. In addition, a uniform bubble distribution and relatively gentle mixing is observed over the entire cross-sectional area of the column. Based on the above table, it was showed that the superficial velocities of methanol vapor employed in this study were in agreement with Kantarci et al.¹⁵. Based on the vizualisation of above figures obtained, and supported by literature data, the flow rate of 5ml/min of methanol was then selected for further studies.





3.4. The effect of catalyst to reactant mass ratio in biodiesel yield

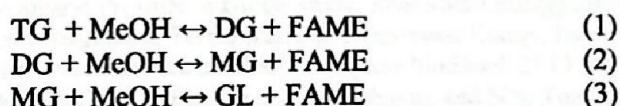
Experimental study was conducted with and without catalyst. Amount of catalyst were varied in the range of 0.1 – 1.0 % (w/w) catalyst to reactant ratio when sulphated zirconia catalyst was employed. Experimental result is presented inTable3.

It was shown that average yield of product accumulation of biodiesel run catalytically is higher than that of non catalytically (4.41% after 100 min run). Previous study conducted by Joelianingsih et al⁷ at thesame temperature (250°C), non catalytically, revealed that product yield was 1.25% and 10.96 %(w/w) after 60 and 180 min run respectively. There is a significance difference if these data are compared to this non-catalytically experiment result. The yield obtained in previous study⁷ was total yield of product in the vapor and liquid phases. Their experiment was conducted in a four-necked flask equipped with a condenser and a pipe for MeOH vapor feed, and the TLC/FID was used to analyze content of product. In this experiment, the yield obtained was yield in the vapor phase only. The BCR form is different to the reactor used in the previous study⁷. In addition, the GC was used to analyze the product in this experiment. Some differences mentioned above that might cause product yield run non-catalytically in this experiment lower than the previous study.

It can be observed also that the biodiesel product yield obtained run with catalyst were significantly low compared to the previous studies^{6,7,11}. Petchmala et al.¹¹ indicated that the specific surface area and calcination temperature of sulphated zirconia catalyst play an important role in transesterification reaction of vegetable oil. The BET surface area of sulfated circonia employed in this study was only 52.26 m²/g, with calcination temperature at 650 °C, while Petchmala et al.¹¹ concluded that the most active catalyst of their synthesized sulphated zirconia catalyst has the BET value of 234,9 m²/g and calcination temperature at 500 °C. The specific surface area of sulphated zirconia considerably decreases as calcination temperature is increased from 500 to 700 °C, since the amount of active sites of catalyst was reduced. In addition, the low yield obtained in this study might be due to the short contact time between oil and methanol vapor, resulting the reactions to be incomplete. The mechanism reactions of transesterification of PFO can be presented as follows:

Table 3. Experiment results of biodiesel production (methanol flow rate at 5 ml/min, reactor temperature at 250°C, time 100 min)

Catalyst to reactant ratio, % (w/w)	Product yield, %	Product picture
0.00	4.41	
0.10	6.09	
0.50	7.91	
1.00	5.53	



The third reaction, in which MG with methanol turns to Fatty Acid Methyl Esters (FAME)/biodiesel and glycerol (GL), is considered the slowest reaction among all above reactions, because MG, as an intermediate compound, is the most stable compound compared to triglyceride and diglyceride⁶, and resulted that the amount of MG formed was excessive.

It is shown from Table 3 that the reaction run with 0.5 % (w/w) catalyst produces the highest yield than the run using 0.1 % and 1.0% (w/w) catalyst. Catalytic experiment run with 0.1% (w/w) sulphated zirconia resulted in 6.9 % of product yield, while with 0.5 % (w/w) catalyst, yield obtained was 7.91 %. Several literatures^{3,9,11} revealed that the highest yield of biodiesel products was achieved at catalyst to reactants mass ratios between 0.1 and 0.5 %. These findings support our experimental results.

Since method of product analysis in this experiment follows the modified EN 14105¹², in which in the list of EN 14105 parameters standard noticed to calculate the impurities of biodiesel product, such as free GL, MG, DG, TG, and total GL, instead of purity of biodiesel product, so that in this study, purity of the product did not directly analyzed. However, it could be calculated using equation (1) to (3) with several assumptions.

Utilization of 1% catalyst to reactant mass ratio in this study causes biodiesel product to change into solid phase with the acquisition of a low yield. The low yield of product indicated that more MG

present in the biodiesel. According to literature¹⁷, melting and solidification points of MGs are higher than room temperature. This condition might be caused by the biodiesel product phase that changed into solid at room temperature. The result study confirms employee of 1% (w/w) catalysts to reactant ratio is unappropriate in transesterification of vegetable oil for biodiesel production as revealed by literatures^{3,11}.

Conclusion

Biodiesel production by transesterification of palm frying oil carried out in bubble column reactor in the presence of SO_4/ZrO_2 catalyst, unfortunately, beyond the expectation, because all experimental results showed lower biodiesel yield than previous studies. The highest yield was 7.91% run with 0.5 % (w/w) catalyst to reactant mass ratio.

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References

1. Yan S, DiMaggioC., Mohan S.KimM., Stalley S.O., and Simon Ng, K.Y., Advancements in Heterogeneous Catalyst for Biodiesel Synthesis, *Top Catal* 2010: 53,721-736.
2. Furuta S., Matsuhashi H., and Arata K. ,Biodiesel Fuel Production with Solid Superacid Catalysis in Fixed Bed Reactor under Atmospheric Pressure. *Catal. Commun.*2004:5,721-723.
3. HelwaniZ., M.R.Othman, N.Aziz, J. Kim and W.J.N. Fernando., Solid Heterogeneous Catalyst for Transesterification of Triglycerides with Methanol: A Review. *Applied Catalyst A:General*, 2009:363, 1-10.
4. Saka ,S. and D. Kusdiana., Biodiesel Fuel from Rapeseed Oil as Prepared in Supercritical Methanol. *Fuel*, 2001: 80, 225-231
5. Yamazaki R, Iwamoto S, Nabetani H, Osakada K, Miyawaki O, Sagara Y.,. Non catalytic alcoholysis of oils for biodiesel fuel production by semi-batch process. *Jpn J.Food Eng.* 2007; 8,11-19.
6. Joelianingsih, H. Nabetani, S. Hagiwara, Y. Sagara Y, T.H. Soerawidjaya, A.H. Tambunan, K. Abdullah. , Performance of a Bubble Colum Reactor for the Non-catalytic Methyl Esterification of Free Fatty Acids at Atmospheric Pressure. *J. Chem. Eng. Japan.* 2007: 40 (9),780-785.
7. Joelianingsih, H. Maeda, H. Nabetani, Y. Sagara Y, T.H. Soerawidjaya, A.H. Tambunan, K. Abdullah. Biodiesel Fuels from Palm Oil via the Non-Catalytic Transesterification in a Bubble Column Reactor at Atmospheric Pressure: a kinetic study. *Renewable Energy* 2008.: 33 (7). pp 1629-1636.
8. Dirjen Energi baru, Terbarukan dan Konservasi Energi, Indonesia ministry of energy and mineral resources, Standar dan mutu bahan bakar nabati jenis biodiesel, 2013 ,SK No.. 723 K/10/DJE/2013
9. Chopade ,S.G., K.S. Kulkarni, A.D. Kulkarni, and N.S. Topare.. Solid Heterogeneous Catalyst for Production of Biodiesel From Trans-esterification of Triglycerides with Methanol: A Review. *Acta Chlm.Pharm.Indica.*2012: 2(1), 8-14
10. Omota f., Dimian A.C., and Bliiek A. Fatty acid Esterification by Reactive Distillation Part2-Kinetica-based design for Sulphated Zirconia Catalyst. *Chem.Eng.Sci.* 2003: 58(14).3175-3185
11. Petchmala, A., Laosiripojana, N., Jongsomjit, B., Goto, M., Panpranot, J., Mekasuwan-dumrong, O., and Shotipruk, A. Transesterification of Palm Oil and Esterication of Palm Fatty Acid in Near- and Super-Critical Methanol with $\text{SO}_4\text{-ZrO}_2$ Catalysts, *Fuel* 2010:89, 2387-2392.
12. Joelianingsih, Indra, I., and Purwaningsih, I.S. Modification Method of EN14105 for Determination of Free Glycerol and Mono-Di-TriglyceridesContents in Biodiesel, International Seminar on Biorenewable Resources Utilization for Energy and Chemicals 2013 Bandung, 10-11 October.
13. Ketaren S., *Pengantar teknologi minyak dan lemak pangan*, 1st ed.,Jakarta,UI-Press, 1986
14. Stuart, B. *InfraredSpectroscopy : Fundamentals and Applications*, John Wiley & Son, 2004
15. Kantarci N., Borak F., Ulgen K.O. Bubble Column Reactor-Review, *J. Process Biochemistry* 2007: 40, 2263-2283.
16. Warabi, Y., Kusdiana, D., and Saka, S., Reactivity of Triglycerides and Fatty Acids of Rapeseed Oil in Supercritical Alcohols, *Bioresource Technology*2004 :91, 283-287.
17. Gunstone, F.D., Harwood, J.L., and Padley, F.B. *The Lipid Handbook*, 2nd ed. Cambrigde , Chapman & Hall, University Press,1994.