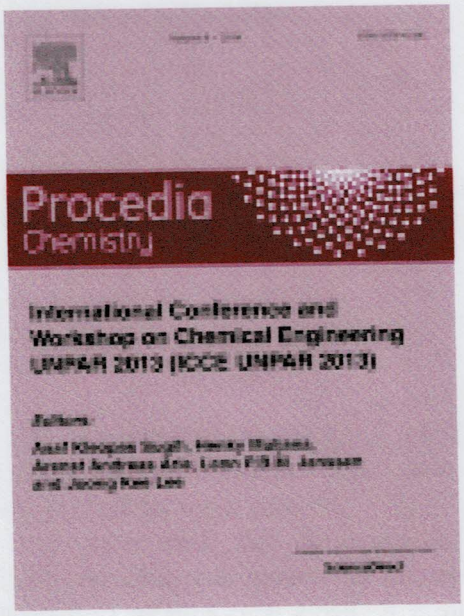


Imprint: ELSEVIER
ISSN: 1876-6196

Procedia Chemistry
Volume 9, Pages 1-294 (2014)

International Conference and Workshop on Chemical Engineering UNPAR 2013 (ICCE UNPAR 2013)

Edited by Asaf Kleopas Sugih, Henky Muljana, Arenst Andreas Arie, Leon P.B.M. Janssen and Joong Kee Lee

Available online at www.sciencedirect.com

ScienceDirect

ELSEVIER

Procedia Chemistry 9 (2014) 1 – 2

Procedia Chemistry

International Conference and Workshop on Chemical Engineering UNPAR 2013, ICCE UNPAR 2013

Preface

First of all, we would like to welcome you into the special issue of Procedia Chemistry. In this issue, a number of papers from the 1st UNPAR's International Conference of Chemical Engineering and Process Safety Workshop were selected. This year, we are organizing the 1st International Conference in conjuction with the 10th National Conference of Chemical Engineering as we are celebrating our 20th anniversary. In this special year, we are extending our conference scope from national to international event. It is our intention to introduce our Chemical Engineering Department in the International level. We would like also to give a contribution on the development and dissemination of knowledge, particularly in the chemical engineering field, by publishing a number of selected papers in Procedia Chemistry.

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 selected papers in this special issue will provide an up-to-date information and 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 fruitfull 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

1876-6196 © 2014 Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/3.0/).
Peer-review under responsibility of the Organizing Committee of ICCE UNPAR 2013
doi:10.1016/j.proche.2014.05.001

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. We would like to thank PT Lautan Luas for financial support. Last but not least, I would like to express a very special gratitude to the scientific committee, the organizing committee and Elsevier for the contribution to this conference and this special issue.

Sincerely,

Dr.Henky Muljana, ST.,M.Eng
Chairman of the Organizing Comitteee,
Head of Chemical Engineering Department
Parahyangan Catholic University (UNPAR)

© 2014 Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/3.0/).
Peer-review under responsibility of the Organizing Committee of ICCE UNPAR 2013

International Conference on Chemical Engineering 2013
in conjunction with The 10th UNPAR National Chemical Engineering Conference
Kuta-Bali, Indonesia

November 7th, 2013

FULL PAPER REVIEW RESULT

Dear,
Dr Joelianingsih

We would like to thank you for choosing International Conference and Workshop on Chemical Engineering UNPAR 2013 as a platform for publishing your scientific work. We would like to inform you your full paper entitled "**Reactivity of Palm Fatty Acids for the Non-catalytic Esterification in a Bubble Column Reactor at Atmospheric Pressure**" has been accepted in the sub topic **New and Renewable Energy** and will be presented as **Oral** presentation at the conference.

Your full paper has been reviewed and the comments form the reviewers are as follow

Reviewer 1 :

1. Tables should be written with a same font type and size.
2. The resolution of the figures should be increased if the paper is to be published in Proc. Chem.
3. There are still some grammatical and typing errors which should be corrected, for example:

- Page 6 line 4 : "13, 15, 17 (0,1,2)"? Is it correct, or should it be: MA: C14:0, PA: C16:0, SA: C18:0, OA: C18:1, etc.?
- Page 10 line 9-10 : should be ".. Table 5, for the saturated fatty acids, reactivity increases with…"

Reviewer 2 :

Page 1, Abstract, line 9, should be: "pseudo first order rate"?
Page 3, Introduction: The introduction is too long, please compress or reduce by around 30%
Page 5, Results and Discussions: Please discuss the results given in Table 1 and 2
Page 6, Equation 1: Please add equilibrium reaction sign. The reaction is an equilibrium reaction, but due to the constant removal of the products, it may be considered an irreversible reaction.
Page 7, equation 5: pseudo first order rate constant

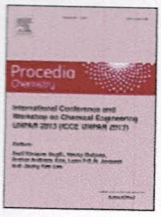
We kindly request that you will revise the full paper manuscript. The revision of the full paper will determine whether the full paper will be published in our Proceeding or Procedia Chemistry. Revision must be submitted before November 20th, 2013 . Please submit your revision on time as we have to submit the whole proceeding to Procedia Chemistry at the latest the end of November 2013.

Best regards,
Committee of International Conference and Workshop on Chemical Engineering 2013
in conjunction with the 10th UNPAR National Chemical Engineering Conference

Dr. Henky Muljana, ST., M.Eng
Conference Chairman

Journals | Books Shopping cart Sign in | Help
You have **Guest** access to ScienceDirect Find out more...
Search all fields | Author name | --This Journal/Book-- | Volume | Issue | Page | Advanced search

The ScienceDirect interface was updated on Saturday, September 6. View our blog for more information



Procedia Chemistry

Open Access | About this Journal | Submit your Article

Get new article feed
Subscribe to new article alerts
Add to Favorites

Copyright © 2014 Elsevier B.V. All rights reserved

Procedia Chemistry
Volume 9, Pages 1-294 (2014)
International Conference and Workshop on Chemical Engineering UNPAR 2013 (ICCE UNPAR 2013)

Edited by Asaf Kleopas Sugih, Henky Muljana, Arenst Andreas Arie, Leon P.B.M. Janssen and Joong Kee Lee

< Previous vol/iss No next vol/iss

Volumes 1 - 9 (2009 - 2014)

Volume 9
pp. 1-294 (2014)
International Conference and Workshop on Chemical Engineering UNPAR 2013 (ICCE UNPAR 2013)

Volume 8
pp. 1-348 (2013)
YOuth in the COnservation of CUltural Heritage, YOCOCU 2012

Volume 7
pp. 1-814 (2012)
ATALANTE 2012 International Conference on Nuclear Chemistry for Sustainable Fuel Cycles

Volume 6
pp. 1-210 (2012)
2nd International Conference on Bio-Sensing Technology

Volume 4
pp. 1-366 (2012)
The International Conference on Innovation in Polymer Science and Technology

Volume 3, Issue 1
pp. 1-366 (2011)
22nd Solvay Conference on Chemistry

Volume 2, Issue 1
pp. 1-180 (January 2010)
5th Symposium by Nordic Separation Science Society (NoSSS 2009)

Volume 1, Issue 2
pp. 1547-1590 (November 2009)
The 22nd Conference of the European Colloid and Interface Society, ECIS 2008

Volume 1, Issue 1
pp. 1-1546 (September 2009)
Proceedings of the Eurosensors XXIII conference

Articles 1 - 34

Export | Open Access articles

Preface Open Access
Pages 1-2
Henky Muljana
PDF (127 K)

The Preparation of Dye Sensitized Solar Cell (DSSC) from TiO_2 and Tamarillo Extract Original Research Article Open Access
Pages 3-10
Diah Susanti, Maula Nafi, Hariyati Purwaningsih, Rindang Fajarin, George Endri Kusuma
Abstract PDF (1718 K)

Spectrum Activity and Lauric Acid Release Behaviour of Antimicrobial Starch-based Film Original Research Article Open Access
Pages 11-22
Eraricar Salleh, Ida Idayu Muhammad, Qadly Ameen Pahlawi
Abstract PDF (3467 K)

Starch based Active Packaging Film Reinforced with Empty Fruit Bunch (EFB) Cellulose Nanofiber Original Research Article Open Access
Pages 23-33
Mohd Harfiz Salehudin, Eraricar Salleh, Siti Nur Hana Mamat, Ida Idayu Muhamad
Abstract PDF (36515 K)

The Utilization of Solid Substrates on *Monascus* Fermentation for Anticholesterol Agent Production Original Research Article Open Access
Pages 34-39
Sri Priatni, Sophi Damayanti, Vienna Saraswaty, Diah Ratnaningrum, Marlia Singgih
Abstract PDF (967 K)

Toxicity Measurement of Imidazolium Ionic Liquids Using Acute Toxicity Test Original Research Article Open Access
Pages 40-52
Mohanad El-Harbawi
Abstract PDF (1157 K)

The Characteristics of Green Calcium Oxide Derived from Aquatic Materials Original Research Article Open Access
Pages 53-61
Soipatta Soisuwan, Jirapom Phommachant, Wilasinee Wisaijorn, Piyasan Praserthdam
Abstract PDF (23729 K)

Study on the Kinetics of Vitamin C Degradation in Fresh Strawberry Juices Original Research Article Open Access
Pages 62-68
Lanny Sapei, Lie Hwa
Abstract PDF (2091 K)

Calcium Carbonate Scale Formation in Pipes: Effect of Flow Rates, Temperature, and Malic Acid as Additives on the Mass and Morphology of the Scale Original Research Article Open Access
Pages 69-76
S. Muryanto, A.P. Bayuseno, H. Ma'mun, M. Usamah, Jotho
Abstract PDF (1043 K)

< Previous vol/iss No next vol/iss

A Simple and Effective Model for Modeling of Convective Drying of Sewage Sludge: The Reaction Engineering Approach (REA) Original Research Article — Open Access
Pages 77-87
Aditya Putranto, Xiao Dong Chen
Abstract PDF (268 K)

Catalytic Conversion of Empty Fruit Bunch of Palm Oil for Producing Lactic Acid Original Research Article — Open Access
Pages 88-93
J.P. Sitompul, R.F. Simangunsong, A.A. Asrizal, H. Alisyahbana, H.W. Lee, C.B. Rasrendra
Abstract PDF (493 K)

The Extraction and Activity Test of Bioactive Compounds in *Phaleria Macrocarpa* as Antioxidants Original Research Article — Open Access
Pages 94-101
David Andrean, Susiana Prasetyo, Anastasia Prima Kristijarti, Tedi Hudaya
Abstract PDF (718 K)

Kinetics of Calcium Oxalate Reduction in Taro (*Colocasia Esculenta*) Corm Chips during Treatments Using Baking Soda Solution Original Research Article — Open Access
Pages 102-112
Andri Cahyo Kumoro, Rr. Dewi Artanti Putri, Catarina Sri Budiyati, Diah Susetyo Retnowati, Ratnawati
Abstract PDF (243 K)

Improving Shelf-life of Cavendish Banana Using Chitosan Edible Coating Original Research Article — Open Access
Pages 113-120
Natalia Suseno, Emma Savitri, Lanny Sapei, Karsono S. Padmawijaya
Abstract PDF (213 K)

Removal of Reactive Dye by Adsorption over Chemical Pretreatment Coal based Bottom Ash Original Research Article — Open Access
Pages 121-130
Chutima Jarusiripot
Abstract PDF (1196 K)

Understanding the Relationship between Organic Structure and Mineralization Rate of TiO_2-mediated Photocatalysis Original Research Article — Open Access
Pages 131-138
Wenny Irawaty, Felycia Edi Soetaredjo, Aning Ayucitra
Abstract PDF (838 K)

Synthesis of Renewable Diesel through Hydrodeoxygenation Using Pd/zeolite Catalysts Original Research Article — Open Access
Pages 139-150
Bambang Heru Susanto, Mohammad Nasikin, Sukirno, Andri Wiyo
Abstract PDF (1797 K)

The Effect of Alkaline Addition in Hydrothermal Pretreatment of Empty Fruit Bunches on Enzymatic Hydrolysis Efficiencies Original Research Article — Open Access
Pages 151-157
M.S. Siti Aisyah, Yoshimitsu Uemura, Suzana Yusup
Abstract PDF (790 K)

Bio-oil from Jackfruit Peel Waste Original Research Article — Open Access
Pages 158-164
Jennifer Pieter Soetardji, Cynthia Widjaja, Yovita Djojorahardjo, Felycia Edi Soetaredjo, Suryadi Ismadji
Abstract PDF (433 K)

Synthesis of Biodiesel from Palm Oil in Capillary Millichannel Reactor: Effect of Temperature, Methanol to Oil Molar Ratio, and KOH Concentration on FAME Yield Original Research Article — Open Access
Pages 165-171
Wan Norita Wan Ab Rashid, Yoshimitsu Uemura, Katsuki Kusakabe, Noridah B. Osman, Bawadi Abdullah
Abstract PDF (338 K)

Effect of Bio-based Catalyst in Biodiesel Synthesis Original Research Article — Open Access
Pages 172-181
Lieke Riadi, Edy Purwanto, Hendrik Kurniawan, Ria Oktaviana
Abstract PDF (424 K)

Reactivity of Palm Fatty Acids for the Non-catalytic Esterification in a Bubble Column Reactor at Atmospheric Pressure Original Research Article — Open Access
Pages 182-193
Joelianingsih, Armansyah H. Tambunan, Hiroshi Nabetani
Abstract PDF (238 K)

Palm Kernel Shell Original Research Article
Pages 194-201
Shazleen Saadon, Yoshimitsu Uemura, Nurlidia Mansor
Abstract PDF (648 K)

Syngas Production from Lignite Coal Using K_2CO_3 Catalytic Steam Gasification with Controlled Heating Rate in Pyrolysis Step Original Research Article Open Access
Pages 202-209
Dijan Supramono, Dewi Tristantini, Agustina Rahayu, Ricky Kristanda Suwignjo, David Hartono Chendra
Abstract PDF (543 K)

Dry Degumming of Corn-oil for Biodiesel Using a Tubular Ceramic Membrane Original Research Article Open Access
Pages 210-219
Yusuf Wibisono, Wahyunanto Agung Nugroho, Tsair-Wang Chung
Abstract PDF (304 K)

The Effect of Chitin Alkaline Deacetylation at Different Condition on Particle Properties Original Research Article Open Access
Pages 220-225
Cléo T.G.V.M.T. Pires, Joice A.P. Vilela, Claudio Airoldi
Abstract PDF (705 K)

State of the Art in the Development of Adaptive Soft Sensors based on Just-in-Time Models Original Research Article Open Access
Pages 226-234
Agus Saptoro
Abstract PDF (377 K)

Formulation of Nanoencapsulated Catechin with Chitosan as Encapsulation Material Original Research Article Open Access
Pages 235-241
Sari Intan Kailaku, Ira Mulyawanti, Andi Nur Alamsyah
Abstract PDF (2549 K)

The Influence of Temperature and Ethanol Concentration in Monacolin K Extraction from Monascus Fermented Rice Original Research Article Open Access
Pages 242-247
Marlia Singgih, Vienna Saraswaty, Diah Ratnaningrum, Sri Priatni, Sophi Damayanti
Abstract PDF (507 K)

Effects of Temperature, Pressure, Preheating Time and Pressing Time on Rubber Seed Oil Extraction Using Hydraulic Press Original Research Article Open Access
Pages 248-256
Herry Santoso, Iryanto, Maria Inggrid
Abstract PDF (1242 K)

Preparation of Fenofibrate Microparticles Using Top-down and Bottom-up Processes Original Research Article Open Access
Pages 257-264
Stevanus Hiendrawan, Bambang Veriansyah, Raymond R. Tjandrawinata
Abstract PDF (3930 K)

Application of Supercritical Fluid Extraction on Food Processing: Black-eyed Pea (*Vigna Unguiculata*) and Peanut (*Arachis Hypogaea*) Original Research Article Open Access
Pages 265-272
Karmelita Anggrianto, Rinaldi Salea, Bambang Veriansyah, Raymond R. Tjandrawinata
Abstract PDF (489 K)

Durability Assessment and Physical Properties Investigation of Modified Petung Bamboo (Dendrocalamus asper) as Resulted on Acetylation, Assisted by Supercritical CO_2 Original Research Article Open Access
Pages 273-283
Silviana, S. Kareth, M. Petermann
Abstract PDF (258 K)

Modeling of LGV Supply Chain System for Land Transportation Sector Original Research Article Open Access
Pages 284-294
Mirza Mahendra, Yuswan Muharam, Sutrasno Kartohardjono, Fiqi Giffari
Abstract PDF (1077 K)

About ScienceDirect Contact and support Information for advertisers Terms and conditions Privacy policy

Available online at www.sciencedirect.com

SciVerse ScienceDirect

Procedia Chemistry00 (2014) 000–000

Procedia Chemistry

www.elsevier.com/locate/procedia

International Conference and Workshop on Chemical Engineering UNPAR 2013, ICCE UNPAR 2013

Reactivity of palm fatty acids for the non-catalytic esterification in a bubble column reactor at atmospheric pressure

Joelianingsih[a*], Armansyah H Tambunan[b], Hiroshi Nabetani[c]

[a]*Chemical Engineering Study Program,Institut Teknologi Indonesia, Jl. Raya Puspiptek Serpong Tangerang Selatan-15320 ,Indonesia*
[b]*Graduate School, Agricultural Engineering Science, Bogor Agricultural University, Darmaga Campus, Bogor 16002, Indonesia.*
[c]*Food Engineering Division, National Food Research Institute, NARO,2-1-12, Kannondai, Tsukuba-shi, Ibaraki, 305-8642, Japan.*

Abstract

A bubble column reactor has been developed to produce fatty acids methyl esters by blowing superheated methanol continuously into triglycerides or fatty acids without using any catalysts at atmospheric pressure. In this paper, reactivity of variety fatty acids in non-catalytic methyl esterification using a bubble column reactor was investigated. Five kinds of fatty acids in palm oil (palm fatty acids), namely myristic acid, palmitic acid, stearic acid, oleic acid and linoleic acid were used as substrates. The reactivity of palm fatty acids was studied at 533 K in a semi-batch reactor system to produce variety of fatty acid methyl esters namely methyl myristate, methyl palmitate, methyl stearate, methyl oleate and methyl linoleate. The initial mass of fatty acid in the reactor was 200 g. The reaction started by blowing superheated methanol vapour continuously into the reactor at 4 g/min of methanol. After 60 min of reaction time, conversion of myristic acid, palmitic acid, stearic acid, oleic acid and linoleic acid at 523 K was 29, 38, 43, 48 and 47 (% mol/mol), respectively. While, the pseudo first order rate constant (*k*') of myristic acid, palmitic acid, stearic acid, oleic acid and linoleic acid was 0.0065, 0.0080, 0.0081, 0.0090 and 0.0095 min^{-1}, respectively. In methyl esterification of palm fatty acids, reactivity of saturated fatty acids (myristic acid, palmitic acid, stearic acid) is lower than unsaturated fatty acids (oleic acid and linoleic acid), meanwhile in the saturated fatty acids, reactivity increased with the length of fatty acids alkyl chains.

Keywords: Fatty acids, methyl esterification, biodiesel, non-catalytic, superheated methanol

© 2014 The Authors. Published by Elsevier B.V.
Selection and peer-review under responsibility of the Organizing Committee of ICCE UNPAR 2013.

* Corresponding author. Tel.: +62-021-756-1092; fax:. +62-021-756-1092
E-mail address: joelianingsih@iti.ac.id

1876-6196© 2014 The Authors. Published by Elsevier B.V.
Selection and peer-review under responsibility of the Organizing Committee of ICCE UNPAR 2013.

Nomenclature

$C_{FA,0}$	fatty acids concentration at initial point of the reaction, [% mol/mol]
$C_{FA,\,t}$	fatty acids concentration at t reaction time, [% mol/mol]
C_M	methanol concentration, [% mol/mol]
dC_{FA}	change in fatty acids concentration, [% mol/mol]
dt	change in reaction time , [min]
k	reaction rate constant defined by Eq. (3), [min(mol/mol)$^{-1}$]
k'	the pseudo first order rate constant defined by Eq. (4) and (5), [min^{-1}]
r_{FA}	reaction rate of fatty acids, [(mol/mol) min^{-1}]
R^2	coefficient of determination, [-]
t	reaction time, [min]
T_{bn}	normal boiling point, [K]
α	conversion of the reaction, [% mol/mol]

1. Introduction

Biodiesel has been defined as the monoalkyl esters of long-chain fatty acids derived from renewable feedstocks, such as vegetable oils and animal fats, for use in compression-ignition (diesel) engines[1]. Biodiesel, consisting of fatty acids methyl esters (FAME) can be produced by transesterification of triglycerides (TG) and/or esterification of fatty acids (FA) with short-chain alcohol, mainly methanol. At present, most of the methods for transesterification reaction are using alkaline catalyst such as potassium hydroxide (KOH), sodium hydroxide (NaOH), sodium methylate ($NaOCH_3$) and potassium methylate ($KOCH_3$). The reaction occurs at moderate temperatures around 333 K and at atmospheric pressure with a short reaction time of around one hour[2]. However, this method has drawbacks such as difficulties in the recovery of glycerol (GL), the need for removal of the residual catalyst and the formation of saponified product (soaps) due to the excess of free fatty acids (FFA). This separation/purification adds operating and capital cost to biodiesel production.

The production of biodiesel from low-cost raw materials, which generally contain high amounts of FFA. The production of biodiesel from this kind of raw materials comprises a two-stage process, which requires an initial acid-catalyzed esterification of the FFA, followed by a base-catalyzed transesterification of the triglycerides. Commonly, the acid H_2SO_4 is the catalyst on the first step of this process. It must be said, however, that major drawbacks such as substantial reactor corrosion and the great generation of wastes, including the salts formed due to neutralization of the mineral acid[3].

To deal with the problems posed by impurities and post-process separation, many alternative processes have been suggested. These include pre-treatment with an esterification reaction with an acid catalyst to lower FFA[4], reactions with enzymes[5,6], direct reactions with a heterogeneous catalyst for easier separation[7,8] and non-catalytic reactions in supercritical methanol[9,10]. This last process is very interesting since the reactions occur without a catalyst and is less sensitive to water and free fatty acid than conventional homogeneous catalyst. The reaction was found to complete in a very short time (4 − 10 min). However, the reaction requires temperatures of 623 − 850 K and pressures of 43 − 105 MPa, which are not practical for application in industry.

Han et al.[11] used CO_2 as co-solvent to decrease the operating temperature, pressure and molar ratio of alcohol to vegetable oil. It was demonstrated that, with an optimal reaction temperature of 553 K, methanol to oil molar ratio of 24 and CO_2 to methanol molar ratio 0.1, a 98% yield of FAME was observed in 10 min at a reaction pressure of 14.3 MPa. Kusdiana, & Saka[12] had studied methyl esterification of FFA of rapeseed oil treated in supercritical methanol. Warabi et al[13] have reported about alkyl esterification of FA in various supercritical alcohols (573, 6 − 20 MPa). The reaction temperature could be decreased but the reaction pressure was still high. The reactor costs will be expensive for their pressurized reactions and might lead to high energy consumption.

Yamazaki et al.[14] have developed a bubble column reactor (BCR) to produce FAME by blowing bubbles of superheated methanol vapour into oil (TG) without using any catalysts. Kinetics of the non-catalytic transesterification of palm oil at atmospheric pressure has been reported by Joelianingsih et al.[15] The effects of reaction temperatures (523, 543, and 563 K) on the rate constant, conversion, yield of FAME and composition of the reaction product under semi-batch mode operation were investigated. The performance of the BCR for the non-

catalytic methyl esterification of oleic acid has also been reported by Joelianingsih et al.[16] However, reactivity of variety FA via the non-catalytic methyl esterification in BCR has not been reported. The objective of this study is to investigate reactivity of five kinds of FA commonly found in palm oil (myristic acid, palmitic acid, stearic acid, oleic acid and linoleic acid) in semi-batch reactor system.

2. Materials and methods

2.1 Materials

Oleic acid (OA), technical grade of minimum 90% w/w purity, as a substrate, was purchased from Sigma-Aldrich Inc. Myristic acid (MA) of minimum 98% w/w purity, palmitic acid (PA) of minimum 95% w/w purity, stearic acid (SA) of minimum 95% w/w purity, linoleic acid (LA) of minimum 88% w/w purity, and methanol HPLC grade, used as substrates, were purchased from Wako Pure Chemical Industries, Ltd.

Benzene and hexane (all HPLC grade), used in the thin layer chromatography/flame ionization detector (TLC/FID) analysis were purchased from Wako Pure Chemical Industries, Ltd. Benzene was used as the developing solution, and hexane as the solvent. Squalane ($C_{30}H_{62}$) as the internal standard was purchased from Sigma-Aldrich Japan K.K. Fatty acids (MA, PA, SA, OA, LA) and FAME (methyl myristate, methyl palmitate, methyl stearate, methyl oleate, and methyl linoleate), used as standards were purchased from Sigma Chemical Co.

2.2 Reactor for the non-catalytic methyl esterification

Fig.1 shows the schematic flow diagram of a reactor used in this experiment. This system has been used in our previous work for non- catalytic methyl transesterification[15]. The BCR was a four-necked flask (capacity, 500 mL) equipped with a condenser, a pipe for methanol vapour feed and a temperature controller (TC).The reactor was placed in a mantle heater. The glass dehydration column was filled with molecular sieves. A pump with a variable speed motor (model NPD − 461, Nihon Seimitsu Kagaku Co., Ltd.) was used to control the charging rate of methanol. A tin bath was placed on an electric heater. Temperature of the tin bath was monitored by a temperature indicator (TI). Temperatures of the superheated methanol supplied to the reactor and liquid in the reactor were controlled with the two TCs.

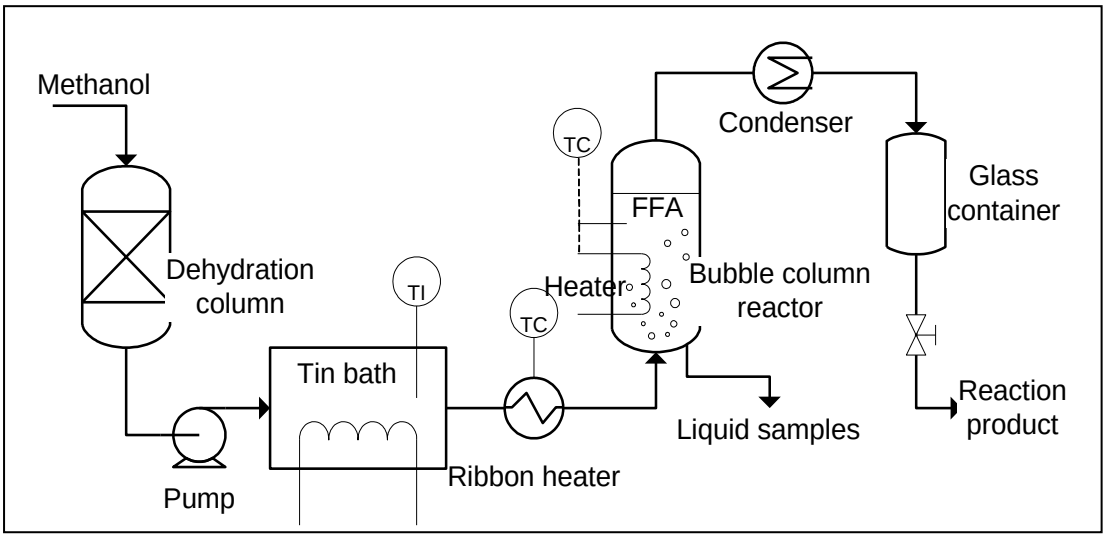


Fig. 1. The schematic flow diagram of the reactor used in esterification experiment.

The reactor was initially charged with 200 g of FA and heated to the desired temperature. Liquid methanol was pumped out of the dehydration column to the tin bath for vapourization. The methanol vapour was passed through a ribbon heater and the reaction started by blowing superheated methanol bubbles continuously into the reactor at 4 g/min of methanol. The temperature of superheated methanol feed was set up to the reaction temperature. The reacted products in the gas phase were condensed and collected in the glass container. The reaction products were taken from the glass container every 20 min and then weighed (samples A). During the reaction course (100 min), 5 samples were collected. Liquid samples in the reactor were taken 20 − 30 mg every 20 min to be analyze FAME and FA contents using TLC/FID. To study reactivity of palm fatty acids; MA, PA, SA, OA and LA were used as substrates and reaction was conducted at the same reaction temperature (523 K).

2.3 Methyl esterification procedure and conditions

The reactor was initially charged with 200 g of FA and heated to the desired temperature. Liquid methanol was pumped out of the dehydration column to the tin bath for vapourization. The methanol vapour was passed through a ribbon heater and the reaction started by blowing superheated methanol bubbles continuously into the reactor at 4 g/min of methanol. The temperature of superheated methanol feed was set up to the reaction temperature. Reacted products in the gas phase were condensed and collected in the glass container. The reaction products were taken from the glass container every 20 min and then weighed (samples A). During the reaction course (100 min), 5 samples were collected. Liquid samples in the reactor were taken 20 − 30 mg every 20 min to be analyze FAME and FA contents using TLC/FID. To study reactivity of palm fatty acids; MA, PA, SA, OA and LA were used as substrates and reaction was conducted at the same reaction temperature (523 K).

2.4 Analysis

Methanol and water contents in the gaseous products (sample A) were evapourated using a rotary evapourator and then the gaseous products without methanol and water were obtained (samples B). The samples B were weighed and their FA and FAME content were analyzed using TLC/FID.

TLC/FID was used to analyze the content of FA and FAME in the samples B and the liquid samples in the reactor. Analyses were performed with an Iatroscan MK-5 Analyzer (Iatron Laboratories, Inc.). The flame ionization detector used hydrogen and air with flow rates of 160 and 2000 mL/min, respectively. Type SIII Chromarods were used as thin layers. Before being spotted, rods were scanned as blank on the instrument to obtain the proper degree of hydration. The samples B and the liquid samples (20 − 30 mg) were diluted with 1 mL solvent (hexane containing 5 mg/mL of squalane) and 1 µL of the solution was spotted on each rod. Five replicates were used for each solution. The rods were developed for 30 min (they were stored in a glass chamber in which the atmosphere was saturated with benzene vapour), oven dried at 333 − 338 K for 5 min and then analyzed by the Iatroscan. The mass fraction of methyl oleate and oleic acid in the samples B and the liquid samples taken from the reactor was calculated based on the concentration of an internal standard.

3. Results and discussion

The feedstock for biodiesel is usually a mix of different type of FA. Therefore, the knowledge of how different FA affects the reaction is important. This might also have an effect on the properties of fuel produced. Depending upon climate and soil conditions, different nations are looking into different vegetable oils for diesel fuels. For example, soya bean oil in the United States, rapeseed and sunflower oils in Europe, coconut oil in The Philippines, and palm oil in Southeast Asia (mainly Malaysia and Indonesia) considered as substitutes for diesel fuels[17].

The fatty acids composition of refined palm oil is myristic acid (0.5–5.9), palmitic acid (32–47), stearic acid (2–8), oleic acid (34–44),and linoleic acid (7–12) %w/w[15]. Reactivity of five kinds of FA in palm oil for the non-catalytic esterification in semi-batch reactor system is described as follows.

3.1 The content of FAME in gaseous and liquid product

The content of FAME (% w/w) of methyl myristate (MM), methyl palmitate (MP), methyl stearate (MS), methyl oleate (MO) and methyl linoleate (ML) in the total mass (accumulated) of samples B (gaseous product) and

liquid in the reactor and the total mass of each fraction at 523K are shown in Tables 1 and 2, respectively. The principle of a BCR for transesterification of TG is the similar with a reactive distillation (RD), where the reaction products in the gas phase (GL and FAME) is continuously removed from the reactive zone while TG as the reactant still exist in the reactive zone (liquid phase)[15]. The application of reactive distillation for the esterification reaction in BCR at a temperature of 523 has a weakness that is nearly the same volatility between the FA and FAME. Therefore, FA and FAME distribute in the gas and liquid phase with a small difference in the composition. If the difference in boiling temperature of FA and FAME (ΔT_{bn}) is smaller, then the difference of FAME content in the gas and liquid phase will be smaller as presented in Tables 1 and 2. Table 3 shows the normal boiling point (the boiling point of component at atmospheric pressure (T_{bn}) for pure FA and FAME of myristic, palmitic, stearic, oleic and linoleic [18,19].

Table 1. The total mass of gaseous product and content of FAME in each reaction experiment.

	Myristic		Palmitic		Stearic		Oleic		Linoleic	
t (min)	Total mass of sample B (g)	FAME content (%w/w)	Total mass of sample B (g)	FAME content (%w/w)	Total mass of sample B (g)	FAME content (%w/w)	Total mass of sample B (g)	FAME content (%w/w)	Total mass of sample B (g)	FAME content (%w/w)
0	0	0	0	0	0	0	0	0	0	0
20	63.73	23	41.86	26	26.87	22	25.07	12	24.77	27
40	125.62	33	88.75	37	54.82	35	56.05	44	55.60	44
60	185.20	32	135.59	44	84.25	42	90.00	52	88.94	51
80			177.69	46	113.09	47	124.59	58	122.63	57
100					142.26	51	159.96	61	156.51	61

Table 2. The total mass of liquid in the reactor and content of FAME in each reaction experiment.

	Myristic		Palmitic		Stearic		Oleic		Linoleic	
t (min)	Mass of liquid (g)	FAME content (%w/w)	Mass of liquid (g)	FAME content (%w/w)	Mass of liquid (g)	FAME content (%w/w)	Mass of liquid (g)	FAME content (%w/w)	Mass of liquid (g)	FAME content (%w/w)
0	200.08	0	200.82	0	200.79	0	199.82	0	199.9	0
20	136.35	16	158.96	21	173.92	24	174.75	14	175.13	21
40	74.46	18	112.07	30	145.97	38	143.77	34	144.30	39
60	14.88	11	65.23	39	116.54	46	109.82	46	11.96	46
80			23.13	45	87.70	50	75.23	51	77.27	53
100					58.53	51	39.86	56	43.39	51

From the data in Table 2, it can be seen that the longer the carbon chain of fatty acids will have a residence time in the reactor longer. This is because the longer the carbon chain of fatty acids will have a normal boiling temperature higher so that it becomes more difficult to evaporate. As a result, the purity of FAME in the gas phase will also be higher as presented in Table 1.

Table 3. The normal boiling points and molecular weight of variety FA and FAME.

	Normal boiling point, T_{bn} (K)		ΔT_{bn}	Molecular weight (g/gmol)	
Component	FA [1]	FAME [2]	(K)	FA	FAME
Myristic	591.0	568.0	23.0	228.376	242.403
Palmitic	626.8	611.0	15.8	256.430	270.457
Stearic	643.0	625.0	18.0	284.484	298.511
Oleic	633.0	622.0	11.0	282.468	296.495
Linoleic	475.0 *	639.0		280.452	294.479

[1] Gunstone et al.[18] [2] Yuan et al.[19] * Measured at1.4 mmHg

3.2 Reactivity of palm fatty acids in the BCR

Reactivity of fatty acids is determined based on the conversion and the reaction rate constant. Fatty acids react with methanol to form FAME by the following esterification reaction as presented in Eq. (1).

$$\text{R-COOH} + \text{CH}_3\text{OH} \overset{k}{\leftrightarrow} \text{R-COOCH}_3 + \text{H}_2\text{O} \quad (1)$$

where R is an alkyl group with chain length MA: C14:0, PA: C16:0, SA: C18:0, OA: C18:1

Conversion of the reaction (α) is defined by Eq. (2).

$$\alpha = (C_{FA,0} - C_{FA,t}) / C_{FA,0} \times 100\% \quad (2)$$

where $C_{FA,0}$ and $C_{FA,t}$ are concentrations of FA in the total system at the initial time of the reaction and after the reaction time of *t*, respectively.

The concentration expressed in % mol/mol of MA, PA, SA, OA and LA in the total system (samples B and liquid in the reactor) at 523 K are presented in Table 4 and conversion of MA, PA, SA, OA and LA at 523 K is shown in Fig. 2. Molecular weight data of variety FA and FAME are shown in Table 3.

Table 4. The concentration of FA in the total system (gas and liquid).

	The concentration of FA (% mol/mol) in the total system				
t (min)	MA	PA	SA	OA	LA
0	100	100	100	100	100
20	83	79	77	86	79
40	74	68	64	64	61
60	71	62	57	52	53
80		55	53	46	46
100			50	42	43

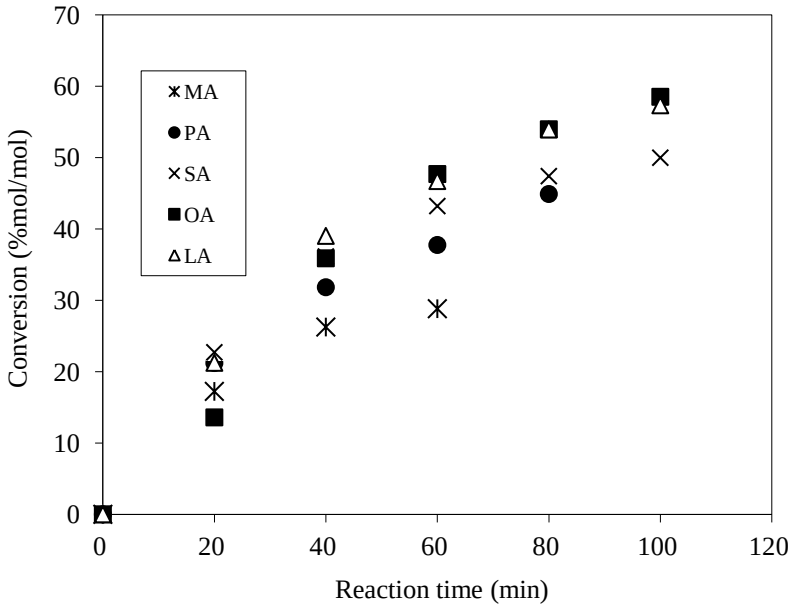


Fig.2. Conversion of the reaction of palm fatty acids at 523 K.

Another method to evaluate the reactivity of palm fatty acid is to calculate the rate constant of the reaction. In a semi-batch mode of operation where methanol (MeOH) is continuously passed through a reactor containing FA, the concentration of MeOH in the gas does not change appreciably. With the passage of reaction time (t) the concentration of FA (C_{FA}) will fall, but the concentration of MeOH (C_M) will remain unchanged. If the kinetics is a first order with respect to both FA and MeOH, the reaction rate based on the decreased concentration of FA can be given by Eq. (3)[20].

$$- r_{FA} = - \mathrm{d}C_{FA} / \mathrm{d}t = k\, C_{FA}\, C_M \tag{3}$$

Rearranging and integrating, noting that C_M is constant, the equation will be:

$$- \ln (C_{FA,t} / C_{FA,0}) = k' \, t \tag{4}$$

$$\text{where} \quad k' = k\, C_M \ \text{(the pseudo first order rate constant)} \tag{5}$$

Figures 3, 4, 5, 6, 7 show the relationship between the normalized concentration of FA ($C_{FA,t} / C_{FA,0}$) and reaction times for MA, PA, SA, OA and LA, respectively at the same reaction temperature (523 K).

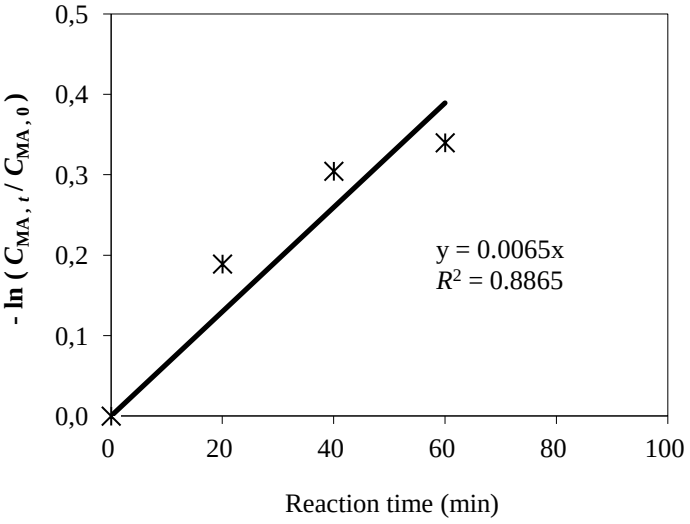


Fig.3. First order reaction model of MA esterification at 523 K.

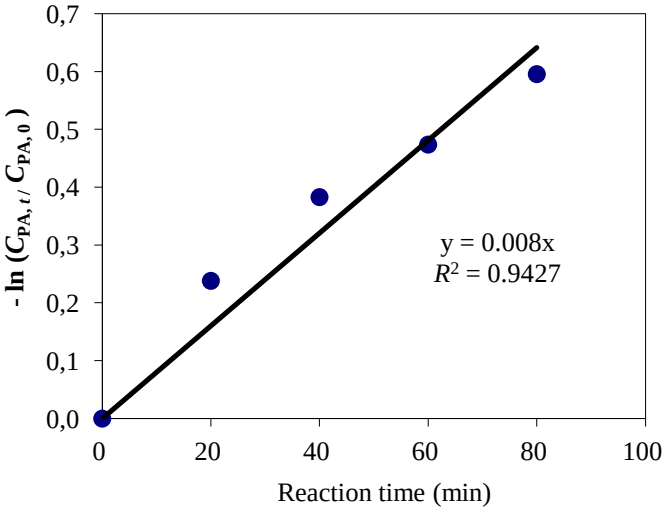


Fig. 4. First order reaction model of PA esterification at 523 K.

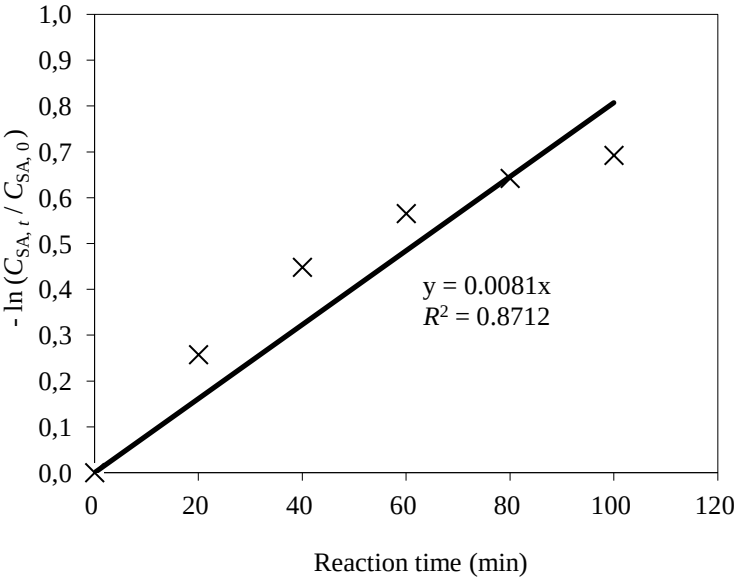


Fig.5. First order reaction model of SA esterification at 523 K.

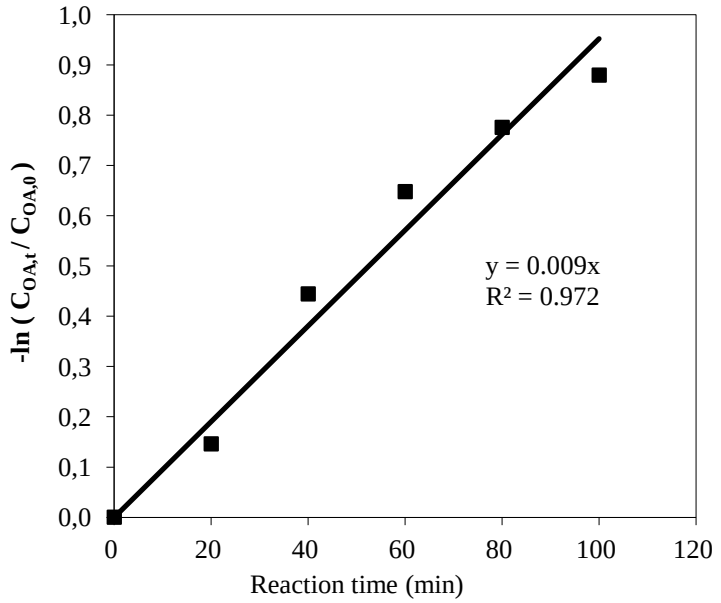


Fig.6. First order reaction model of OA esterification at 523 K.

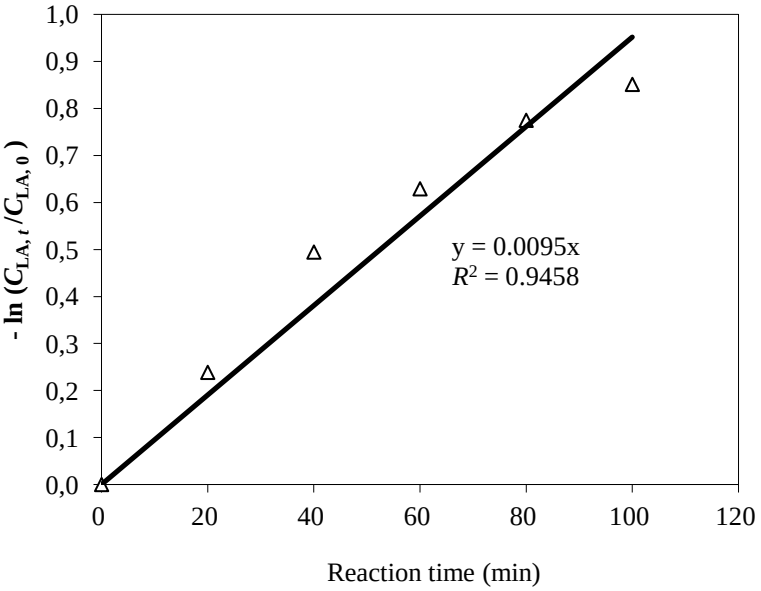


Fig.7. First order reaction model of LA esterification at 523 K.

The gradient of the linear regression of the -ln ($C_{FA,t}$ / $C_{FA,0}$) curve with respect to the reaction time is regarded as the pseudo first order rate constant (k') according to Eq. (4). Table 5 gives the value of the pseudo first order rate constant (k') and coefficient of determination (R^2) for each fatty acid.

Table 5. The rate constant of fatty acids methyl esterification.

Fatty Acids	k' (min^{-1})	R^2
MA	0.0065	0.8865
PA	0.0080	0.9427
SA	0.0081	0.8712
OA	0.0090	0.9720
LA	0.0095	0.9458

A substrate (fatty acid) is more reactive if the conversion of the reaction in semi-batch process is higher at the same reaction time and temperature, also the rate constant of the reaction is higher at the same reaction temperature. As shown in Fig. 2, conversion of the reaction of saturated fatty acids such as myristic, palmitic and stearic acids is lower than the unsaturated fatty acids such as oleic and linoleic acids. After 60 min of reaction time, conversion of myristic acid, palmitic acid, stearic acid, oleic acid and linoleic acid at 523 K were 29, 38, 43, 48 and 47 (% mol/mol), respectively. The reaction rate constant of the saturated fatty acids is lower than the unsaturated fatty acid as presented in Table 5. Thereby the saturated fatty acids show lower reactivity than the unsaturated fatty acid.

These experiment results also consistent with results the reported by Aranda et al.[21] Their study of activation energy by semi-empirical methods revealed that the activation energy of palmitic acid (272 kJ/mol) is higher than that of oleic acid (176 kJ/mol), which means that the reactivity of palmitic acid is lower than the oleic acid. This might be assigned to the polarity of the double bond of oleic acid, which increases the reactivity of the carboxylic moiety. Warabi et al.[12] confirmed that saturated fatty acids (palmitic and stearic acid) have slightly lower reactivity than unsaturated ones (oleic, linoleic, linolenic) especially with ones containing more than one double bond. Based on the reaction rate constant value as shown in Table 5, linoleic acid has slightly higher reactivity than oleic acid.

Liu et al.[22] studied the effect of chain length in short chain carboxylic acids (acetic, propionic, butyric, hexanoic and caprylic acid) with methanol. The carboxylic acid reactivity decreased with increasing alkyl chain length. Their study is at temperature of 333 K and uses a commercial Nafion/silica composite solid acid catalyst (SAC-13) with initial concentration of carboxylic acid at 3M and 6M of methanol. They suspected that this trend was caused by two effects: an inductive effect and a steric effect[23]. The inductive effect is that electron-releasing ability increases with alkyl chain length, which helps the protonation of the carbonyl oxygen. At the same times the electrophilicity of the carbonyl carbon decreases, resulting in more difficulty for nucleophillic attack by alcohol. The steric effect is that smaller carboxylic acids are easier for alcohol to attack. These two effects support the lower conversion obtained with higher number of alkyl chain length of carboxylic acid [22]. Warabi et al.[13], reported that their result also shows a slight difference between palmitic acid (C16:0) and stearic acid (C18:0), with the reaction being faster with shorter chain length.

Based on the conversion of the reaction as shown in Fig. 2 and the reaction rate constant in Table 5, for the saturated fatty acids; reactivity increase with the length of fatty acids alkyl chains. These results contradict with the results reported by previous investigators [13, 22, 23].

As described in section 3.1, application of reactive distillation for the esterification reaction in BCR at a temperature of 523 K has a weakness that is nearly the same volatility between the FA and FAME. Conversion of the FA could not achieve 100% because FA evapourated as a product in the gas phase before reacting. There is a competition between reaction and evapouration of FA. In the saturated fatty acids, the normal boiling point increase with the length of fatty acids alkyl chains. The longer chain length of the FA makes the residence time in the reactor (reaction time) becomes longer, so that the conversion of the reaction and reaction rate constant was higher.

4. Conclusions

Five kinds of fatty acid in palm oil could be methyl esterified in a BCR under atmospheric pressure at 523 K in the absence of a catalyst. After 60 min of reaction time, conversion of MA, PA, SA, OA, and LA was 29, 38, 43, 48 and 47 (% mol/mol), respectively. Meanwhile, the value of the reaction rate constant (*k*') of MA, PA, SA, OA, and LA was 0.0065, 0.0080, 0.0081, 0.0090 and 0.0095 min^{-1}, respectively. In methyl esterification of variety of FA, reactivity of saturated FA is lower than unsaturated FA, meanwhile in the saturated FA, reactivity increased with the length of FA alkyl chains.

Acknowledgement

The authors are grateful for the financial support received from to the Ditlitabmas - Directorate General of Higher Education, Ministry of National Education Indonesia through National Strategic Research Fund" under contract No.158/SP2H/PL/DIT.LITABMAS/V/2013.

References

1. Krawczyk T. Biodiesel-alternative fuel makes inroads but hurdles remain. *Inform* 1996; **7**:801-29.
2. Singh A, He B, Thompson J, Van Gerpen J. Process optimization of biodiesel production using alkaline catalysts. *Appl. Eng. Agric*. 2006; **22**:597–600.
3. Cardoso AL, Gonzaga Neves SC, Da Silva MJ. Esterification of oleic acid for biodiesel production catalyzed by $SnCl_2$: A kinetic investigation. *Energies* 2008; **1**:79-92.
4. Wang Y, Ou S, Pengzhan Liu, Zhang Z. Preparation of biodiesel from waste cooking oil via two-step catalyzed process. *Energ. Convers. Manage*. 2007; **48**:184–8.

5. Shimada Y, Watanabe W, Sugihara A, Tominaga Y. Enzymatic alcoholysis for biodiesel fuel production and application of the reaction to oil processing. *J. Mol. Catal. B: Enzym* 2002; **17**:133-42.
6. Pogaku R, Raman JK, Ravikumar G. Evaluation of activation energy and thermodynamic properties of enzyme-catalysed transesterification reactions. *Adv. Chem. Eng. Sci*. 2012; **2**:150-4.
7. Xin Deng, Zhen Fang, Yun-hu Liu, Chang-Liu Yu. Production of biodiesel from Jatropha oil catalyzed by nanosized solid basic catalyst. *Energy* 2011; **36** :777-84.
8. Lei Niu, Lijing Gao, Guomin Xiao, Baosong Fu. Study on biodiesel from cotton seed oil by using heterogeneous super acid catalyst SO_4^{2-}/ZrO_2. *Asia-Pac. J. Chem. Eng*. 2012;**7** : S222-8.
9. Saka S, Kusdiana D. Biodiesel fuel from rapeseed oil as prepared in supercritical methanol. *Fuel* 2001; **80**:225-31.
10. Demirbas A. Biodiesel from vegetable oils via transesterification in supercritical methanol. *Energ. Convers. Manage.* 2002;**43**:2349-56.
11. Han H, Cao W, Zhang J. Preparation of biodiesel from soybean oil using supercritical methanol and CO_2 as co-solvent. *Process Biochem* 2005;**40**:3148-51.
12. Kusdiana D, Saka S. Methyl esterification of free fatty acids of rapeseed oil as treated in supercritical methanol. *J. Chem. Eng. Jpn.* 200;**34**(3):383-7.
13. Warabi Y, Kusdiana D, Saka S. Reactivity of triglycerides and fatty acids of rapeseed oil in supercritical alcohols. *Bioresour. Technol*. 2004; **91**:283-7.
14. Yamazaki R, Iwamoto S, Nabetani H, Osakada K, Miyawaki O, Sagara Y. Non catalytic alcoholysis of oils for biodiesel fuel production by semi-bach process, *Jpn. J. Food Eng.*2007; **8**:11-19.
15. Joelianingsih, Maeda H, Nabetani H, Sagara Y, Soerawidjaya TH, Tambunan AH, Abdullah K. Biodiesel fuels from palm oil via the non-catalytic transesterification in a bubble column reactor at atmospheric pressure: a kinetic study. *Renew. Energ*. 2008;**33**:1629-36.
16. Joelianingsih, Nabetani H, Hagiwara S, Sagara Y, Soerawidjaya TH, Tambunan AH, Abdullah K, Performance of a bubble column reactor for the non-catalytic methyl esterification of free fatty acids at atmospheric pressure. *J. Chem. Eng. Jpn*. 2007; **40**(9):780-5.
17. Srivastava A, Prasad R. Triglycerides-based diesel fuels. *Renew. Sust. Energ. Rev*. 2000 ;**4**:111-33.
18. Gunstone FD, Harwood JL, Padley FB. *The lipid handbook.* 2nd ed. London:Chapman & Hall;1994.
19. Yuan W, Hansen AC, Zhang Q. Vapour pressure and normal boiling point predictions for pure methyl esters and biodiesel fuel. *Fuel* 2005;**84**:943-50.
20. Levenspiel O. *Chemical reaction engineering*. 2nd ed. New York: Wiley;1972.
21. Aranda DA, Santos RT, Tapanes NC, Ramos AL, Antunes QA. Acid-catalyzed homogeneous esterification reaction for biodiesel production from palm fatty acids. *Catal. Lett*. 2008;**122**: 20–5.
22. Liu Y, Lotero E, Goodwin JG Jr. Effect of carbon chain length on esterification of carboxylic acids with methanol using acid catalysis. *J. Catal*. 2006;**243**:221–8.
23. He H, Sun S, Wang T, Zhu S. Transesterification kinetics of soybean oil for production of biodiesel in supercritical methanol. *J. Am. Oil Chem. Soc.*2007;**84**:399–404.