

PROCEEDING

BOOK I



bio energy chemicals materials

BIOENCHE 2013

International Seminar on Chemical Engineering
In conjunction with
Seminar Teknik Kimia Soehadi Reksowardojo (STKSR) 2013

“Biorenewable Resources Utilization for Energy, Chemicals, and Materials”

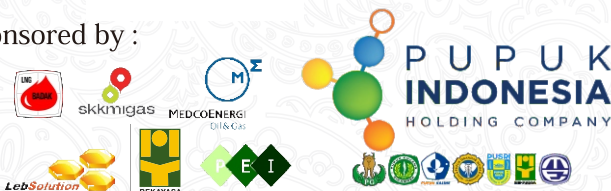
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October 10-11, Bandung, Indonesia

International Seminar on Biorenewable Resources Utilization for Energy and Chemicals 2013
In conjunction with Chemical Engineering Seminar of Soehadi Reksowardojo 2013

PREFACE

This BioEnChe-STKSR2013 proceeding contains of the collections of research works presented in International Conference of Bio Energy Chemicals and Materials 2013 (BioEnChe 2013) that was held in Institut Teknologi Bandung. The conference is in conjunction with annual Chemical Engineering Seminar of Soehadi Reksowardojo (Seminar Teknik Kimia Soehadi Reksowardojo, STKSR 2013).

The international conference provides an opportunity to publicize research works which done or in ongoing ones in many research institution. As the use of fossil base energy and other derivate become harmful for human life, the uses of renewable resource become more interest in our daily life. Therefore, the science and technology for utilization of those resources become enhanced to get more effective and efficient process to produce their products.

We have expectation in this occasion is not only a good place to exchange and discuss the progress of their research in bioenergy, biochemical and biomaterials, but also a venue to collect and to disseminate the most updated technologies and the researches of regional issue and public interest in order to contribute to the community and to draw support from the industrial and the governmental sectors. As this conference has main theme of biorenewable resources utilization for bioenergy, biochemical and material, hopefully this conference will contribute to enhance the utilization of renewable resources for many uses.

We would like to grateful to all participants and sponsors who has contributed to the conference, to the organizing committee for their commitment in their busy days so that the conference is possible to be held and conducted successfully.

Thank you,

Dr. Tirto Prakoso, MEng.
Conference Chairman



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BIOENCHE 2013

October 10-11, Bandung, Indonesia

International Seminar on Biorenewable Resources Utilization for Energy and Chemicals 2013
In conjunction with Chemical Engineering Seminar of Soehadi Reksowardojo 2013

TABLE OF CONTENT

PREFACE	i
TABLE OF CONTENTS	ii
COMMITTEE	x
PROGRAM	xi
KEYNOTE PRESENTATION	1
• The Bioethanol Perspective as Fuel and its Production from the Lignocellulosic Biomass by Hyung Keun Song	1
• The Challenges of Bioenergy Development in Indonesia by Tatang H. Soerawidjaja	11
• Combustion Characteristic of Envo-Diesel in Oil Burner by Prof. Dr. Mohammad Nazri Bin Mohd Jaafar	17
• Innovative Japanese Waste-to-Green Product Technologies: Viable Options for Fuel Cost Reduction and Sustainable Waste Management by Prof. Kunio Yoshikawa	32
QUESTION AND ANSWER	47
PAPERS	49



bio energy chemicals materials
BIOENCHE 2013

October 10-11, Bandung, Indonesia

International Seminar on Biorenewable Resources Utilization for Energy and Chemicals 2013
In conjunction with Chemical Engineering Seminar of Soehadi Reksowardojo 2013

BOOK I

BIODIESEL

CODE	TITLE	AUTHORS	
BD.03	The Effect of Pre-Washing Step Using CaO in Biodiesel Dry Washing using Rice Husk Ash Adsorbent	Ade Kurniawan, Indra Perdana, Arief Budiman	51
BD.04	Kinetic Study Of Ultrasound Assisted Transesterification From Waste Cooking Oil	Haris Nu'man Aulia, Widayat, Setia Budi Sasongko	63
BD.05	Synthesis of biodiesel using carbon based-solid catalyst	Febri Raharningrum, Yano Suryapradana, Arif Hidayat, Arief Budiman	77
BD.07	Biodiesel from Low-cost Feedstock and Renewable Resource	Putri Restu Dewati, Dyah Retno Sawitri, Ade Kurniawan, Arief Budiman	85
BD.09	A Kinetics Study of Fatty Acid Esterification over Sulfated Zeolite-Zirconium Catalyst for Biodiesel Production	Ratna Dewi Kusumaningtyas, Masduki, Arif Hidayat, Rochmadi, Suryo Purwono, Arief Budiman	97
BD.13	Kinetics of Palm Oil Transesterification Using Double Promoted Catalyst CaO/KI/g-Al ₂ O ₃ in Refluxed Methanol	Nyoman Puspa Asri, Kusno Budikaryono, Suprpto, Achmad Roesyadi	113
BD.17	Studies of FAME Production and Fractionation from Coconut Oil	J.P. Sitompul, R. Muhtadi, Rinjani, H. Shudri, D. Lestari, Dinarti, R.W. Kurnianto, H.W. Lee, T.H. Soerawidjaja	129
BD.19	Utilization of Palm Oil Mill Effluent for <i>Chlorella vulgaris</i> Cultivation Medium under Mixotrophic Condition as Feedstock of Biofuel	M. M. Azimatun-Nur, and H. Hadiyanto	141
BD.20	Biodiesel Production From Rubber Seeds (<i>Hevea brasiliensis</i>) with In Situ and Acid Catalyst Method by Using Ultrasonic Assisted	Widayat, Agam Duma Kalista Wibowo, M Sigit Samsena, Louis Adi Wiguno	153
BD.21	EN14105 Modification Method for Determination of Free Glycerol and Mono-Di-Triglyceride Content in Biodiesel	Joelianingsih, Imansyah Indra, and Is Sulistyati	169



bio energy chemicals materials
BIOENCHE 2013

October 10-11, Bandung, Indonesia

International Seminar on Biorenewable Resources Utilization for Energy and Chemicals 2013
In conjunction with Chemical Engineering Seminar of Soehadi Reksowardojo 2013

CODE	TITLE	AUTHORS	
BD.23	Experiment on Hydroxy (HHO) Gas Addition on Performance and Exhaust Gas Emissions of a Compression Ignition Engine Fuelled with Rubber Seed Methyl Ester	Iman K. Reksowardojo, Ratnak Sok, Tirta Prakoso, Toshio Shudo, Wiranto Arismunandar, Sovanna Pan	181

BIOETHANOL

CODE	TITLE	AUTHORS	
BE.02	Bioethanol Production Comparison of Elephant Grass and Liquid Waste Plant Wheat Boga Sari	Ni Ketut Sari, C. Pujiastuti, I Nyoman Abdi	191
BEP.01	Analysis on Chemical Components of Woods to Predict Ethanol Production Values	Wahyu Dwianto, Fitria, Ika Wahyuni, Danang Sudarwoko Adi, Rumi Kaida, Takahisa Hayashi	209

BIOMASS GASIFICATION

CODE	TITLE	AUTHORS	
BMG.01/ BMGP.01	IMPLEMENTATION OF BIOMASS GASIFICATION TECHNOLOGY IN NATURAL RUBBER PROCESSING SECTOR	Didin Suwardin	217
BMG.04	Design, Simulation and Experiments of Circulating Fluidized Bed Reactor for Biomass Gasification	Dr. Haifa Wahyu, Ir. Imam Djunaedi, Ir. M. Affendi, Ir. Sugiyatno, MT	227
BMG.05	Scaling-up and Implementation of Circulating Fluidized Bed Gasifier for Biomass Gasification in Siak Region	Dr. Haifa Wahyu	243



bio energy chemicals materials
BIOENCHE 2013

October 10-11, Bandung, Indonesia

International Seminar on Biorenewable Resources Utilization for Energy and Chemicals 2013
In conjunction with Chemical Engineering Seminar of Soehadi Reksowardojo 2013

BIOHYDROGEN

CODE	TITLE	AUTHORS	
BH.01	Effect of Agitation Condition on BioHydrogen Production in Stirred Tank Reactor	Tantular Nurtono, Christina Wahyu Kartikowati, Wa Ode Cakranirwana, Widiyastuti, Sugeng Winardi	255
BH.02	Dynamic Separation of Hydrogen from Producer Gas Using Pd-Ag Membrane	Yogi Wibisono Budhi, Rusdi, Irwan Noezar, Allan A.B. Padama, and Hideaki Kasai	265

BIOHYROCARBON

CODE	TITLE	AUTHORS	
BHC.02	Synthesis Bioaviation Turbine Jet Fuel from Ozonolysis of Jathropa curcas Oil Methyl Ester	Irwan Kurnia, and Tirta Prakoso	281
BHC.03	Electrochemical Hydrogenation of Terpene Hydrocarbons	Tedi Hudaya, Antonius Rionardi, Tatang Hernas Soerawidjaja	293

BIOMASS TO LIQUIFACTION

CODE	TITLE	AUTHORS	
BL.02	Preparation of fermentable sugars from coconut coir dust lignocelluloses by pretreatment of ionic liquid 1,3-methylmethylimidazolium dimethyl phosphate	Hanny F. Sangian, Junaidy Kristian, Sukma Rahma, Silvya Yusnica Agnesty, Setyo Gunawan, Arief Widjaja	303
BL.03	Degradation of Chitosan by Ultrasonication and Hydrothermal in The Presence of Acetic Acid as Degradation Agent	S.R.Juliastuti, E.Savitri, F.Kurniawansyah, Sumarno and A. Roesyadi	325
BL.04	Effect of oxalic acid catalyst on hydrolysis of cellulose in NaCl ionic liquid	N.E. Mayangsari and Sumarno	337
BL.05	PRETREATMENT OF SEAWEED WASTE BIOMASS USING IONIC LIQUIDS TO ENHANCE ENZYMATIC SACCHARIFICATION	Uju, Masahiro Goto and Noriho Kamiya	347



bio energy chemicals materials
BIOENCHE 2013

October 10-11, Bandung, Indonesia

International Seminar on Biorenewable Resources Utilization for Energy and Chemicals 2013
In conjunction with Chemical Engineering Seminar of Soehadi Reksowardojo 2013

BOOK II

BIOMATERIALS

CODE	TITLE	AUTHORS	
BM.04	Microbial Nanomagnetic Particle Production: Effects of Carbon and Iron Sources	M.T.A.P. Kresnowati, Andy Wiranata Wijaya, and Andry	353
BM.05	Production of Natural Composite with Alkaline Treatment Using Empty Fruit Bunch Ash Extract Solution	Helena Rouhillahi, Zulfansyah, Hari Rionaldo, Warman Fatra	363
BM.06	Binderless Molded Pulp from Cornstalk as Degradable Packaging	Muhammad Shiddiq Abdul Aziz, Zulfansyah, Hari Rionaldo, Warman Fatra	373
BM.07	Alkaline Treatment of Oil Palm Frond Fiber by Using Extract of Oil Palm Empty Fruit Bunch Ash for Use in Natural Fiber Reinforced Composite	Randi Sanjaya, Zulfansyah, Hari Rionaldo, Warman Fatra	391
BM.08	The crystallinity behaviour of composite polylactid acid based reinforced by bamboo fiber which is treated using different chemical treatment	Laili Novita Sari, Lisman Suryanegara, Mochamad Chalid	401
BM.09	The Effect of Diethylene Glycol Dibenzoate and Triacetine to The Thermal Properties and Crystallinity of Polylactic Acid	Lisman Suryanegara, Adam Febriyanto Nugraha, Mochamad Chalid	411
BM.10	ACROLEIN SYNTHESIS FROM GLYCEROL	Akhmad Zainal Abidin, Rani Guslianti Afandi	425
BM.11	Utilization of Cassava Starch in Manufacturing of Superabsorbent Polymer Composite to Reduce Cost and Time of Production	T. Puspasari and A.Z. Abidin	435
BM.12	Direct Polycondensation of Biodegradable PLA Synthesis over Al ₂ O ₃ and ZnO Catalyst	H. W. Lee, R. Insyani, D. Prasetyo, H. Prajitno, C.B. Rasrendra, J. P. Sitompul	445
BMP.01	Preparation of Natural Rubber / Ionic Liquid Composites for Polymer Electrolytes	Edy Marwanta and Ahmad Fauzantoro	455



bio energy chemicals materials
BIOENCHE 2013

October 10-11, Bandung, Indonesia

International Seminar on Biorenewable Resources Utilization for Energy and Chemicals 2013
In conjunction with Chemical Engineering Seminar of Soehadi Reksowardojo 2013

**BIOCHEMICAL PROCESS
SIMULATION**

CODE	TITLE	AUTHORS	
BPS.02	Process Modeling of b-galactosidase Enzyme Plant by <i>Kluyveromyces Lactis</i> Using Superpro Designer	Enrico Gianino, Tan Mellisa, Andry	463
BPS.03	Kinetic Modeling of Volatile Fatty Acids Feeding by Batch Culture on Polyhydroxyalkanoate Production	Martha Aznury, Azis Trianto, Tjandra Setiadi, Adi Pancoro,	475
BPS.04	Determination of Model Kinetics for Forced Unsteady State Operation of Catalytic CH ₄ Oxidation	Mohammad Effendy, Yogi Wibisono Budhi, Yazid Bindar, Subagio	491

BIOREFINERY

CODE	TITLE	AUTHORS	
BR.02	The Effect of Carbon dioxide Gas As Blowing Agent in Polyurethane Foam Based Castor Oil	Sumarno, S. Anisah, Y.M. Sakti and P.N. Trisanti	509
BR.03	Microbial Production of Xylitol from Palm Oil Empty Fruit Bunches: Effects of Inoculum Size and Initial pH	M.T.A.P. Kresnowati, Tjandra Setiadi, Tan Mellisa Tantra, and David	517
BR.07/ BRP.02	SYNTHESIS OF BIOSURFACTANTS BY <i>Pseudomonas aeruginosa</i> USING OZONIZED CHEESE WHEY FOR ENHANCED OIL RECOVERY	Miftahul Jannah, Misri Gozan, Cut Nanda Sari	529
BR.08/ BRP.03	Production of Biosurfactant from <i>Pseudomonas aeruginosa</i> using Ozonized Biodiesel Waste as Substrate for Enhanced Oil Recovery	Izzah Nur Fatimah, Misri Gozan, Abdul Haris	541
BRP.04	The Utilization of Sorghum Bagasse (Sorghum Bicolor) as Pulp and Paper Raw Materials Using Kraft Pulping	Widya Fatriasari, Supriyanto, Apri Heri Iswanto	553



bio energy chemicals materials
BIOENCHE 2013

October 10-11, Bandung, Indonesia

International Seminar on Biorenewable Resources Utilization for Energy and Chemicals 2013
In conjunction with Chemical Engineering Seminar of Soehadi Reksowardojo 2013

FUEL CELL

CODE	TITLE	AUTHORS	
FC.01	The Influence of Oxygen Flow Rate and Current Collector Types in the Hydrogen Fuel Cell Performance	Harita N Chamidy, Riniati	571
FC.03	Preparation of Mixed Matrix Polysulfone-Based Anion Exchange Membranes with Silica Loading	Khoiruddin, I. G. Wenten	583
FC.04	Characterization of Electrochemical Impedance Spectroscopy Approach Based on Equivalent Circuit for Molten Carbonate Fuel Cell (MCFC)	Rein Nasution and Hary Devianto	597
FC.05	Electrochemical Characterization Of Cathode For Molten Carbonate Fuel Cell (MCFC) Produced By Dry Casting	Hary Devianto Ph.D, Muhammad Ardian Nur, and Ribka Priscilla Sinaga	607
FC.06	Microbial Fuel Cell for Desalination Application without External Energy using <i>Saccharomyces cerevisiae</i>	Bagas Muhamad Kartiko, Tania Surya Utami, Albert Santoso, Dita Amalia Wijanarko	615
FCP.01	ACTIVE NATURAL ZEOLITE UTILIZATION FOR MICROBIAL FUEL CELL MEMBRANE MODIFICATION	Agusta Samodra Putra, Sri Handayani, Wahyudin, Ismojo	625
FCP.02	INFLUENCE OF CLAY/SULFONATED POLYETHER-ETHER KETONE AS POLYMER ELECTROLYTE MEMBRANE FOR MICROBIAL FUEL CELL	Sri Handayani, Wahyudin, Ismojo, Agusta Samodra Putra	631

OTHERS

CODE	TITLE	AUTHORS	
OT.03	Characterization of Sweet Potato Flour Dough and Its Baking Performances for Daily Bread Food	Yazid Bindar, Enriko P.T. Siregar dan Jhon P. S. L. S. Sinaga	641



bio energy chemicals materials
BIOENCHE 2013

October 10-11, Bandung, Indonesia

International Seminar on Biorenewable Resources Utilization for Energy and Chemicals 2013
In conjunction with Chemical Engineering Seminar of Soehadi Reksowardojo 2013

CODE	TITLE	AUTHORS	
OT.04	Effectiveness of Tannin as Corrosion Inhibitor for Carbon Steel in Sulphuric Acid Solution	Fahmi Atriadi, Dr. Ir. Isdiriyani Nurdin	655
OT.06	The Effect of Preparation Method on the Inclusion of Ketoprofen-Cyclodextrin by Using Supercritical Fluid	Sumarno, P.N Trisanti, and R. Tetrisyanda	671
OT.07	Calcined Kaolin Phases as Precursor Synthesis NaY Zeolite	Endang Sri Rahayu, Subagjo, Tjokorde Walmiki Samadhi, Melia Laniwati Gunawan	679
OT.08	Evaluation of Flare Gas and Flue Gas Injection for EOR	Tjokorde Walmiki Samadhi, Stephanie L.U. Sutoko, Utjok W.R. Siagian	691
OT.11	Forced Unsteady State Operation of Catalytic CO Oxidation during Cold Start-up Period	Yogi Wibisono Budhi, Sri Baardianti A.M., Wiwin Lukman F., Subagjo	701
OT.14	Sol-Gel synthesis of Titanium Dioxide Nanoparticles	Bram Dwijaya, Yoshiaki Uchida, Egashira Yasuyuki, and Norikazu Nishiyama	715
OT.15	Synthesis and Characterization of Geopolymer from Paiton Fly Ash	Tjokorde Walmiki Samadhi, I Dewa Gede Arsa Putrawan, Nurhidayati Muan, and Pambudi P. Pratama	719
OT.16	Effect Of High Concentrated PEG Addition On PVC Ultrafiltration Membrane Performance	Ritha Yustiana & I Gede Wenten	729
OT.18	The Utilization of Mature Coconut Water for Packaged Drink Using Ultrafiltration Membrane	Dr. Lienda Aliwarga Handojo, Muhamad Faris Firmansyah, and Made Ian Maheswara Supriyatna	741
OT.20	Evaluation of Lean Gas Effect to Demethanizer Column Performance	Arfianto A, Devianto H, Sasongko D	757
OT.21	The Effect of High Additive Concentration to Membrane Performace During Peat Water Filtration	P.T.P. Aryanti, S.R. Joscariita, A. K. Wardani and I G. Wenten	773
OT.22	Energy Conservation by Optimization in PT Badak NGL CO2 Removal Plant	Mohammad Arief Setiawan, Akbar Surya Laksamana	787

Biodiesel Production From Rubber Seeds (*Hevea brasiliensis*) with In Situ and Acid Catalyst Method by Using Ultrasonic Assisted

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Abstract. Biodiesel production from the non-edible raw materials become very important because will not collide with human needs. Furthermore, this research studies to biodiesel production with ultrasonic assisted by in situ method. The raw material uses rubber seed and ultrasonic process use ultrasonic cleaner. The objective of this research was to study the influence of catalyst concentration and ratio of raw materials to methanol. The process was done at 60°C for 30 minutes reaction time. The results showed that maximum yield of Fatty Acid Methyl Ester (FAME) was 34.74% by using sulphuric acid 0.1% as catalyst and rubber seed ratio to methanol 1:1.75 (w/v).

Keywords: *Biodiesel, rubber seeds, in situ, (trans)esterification, Fatty Acid Methyl Ester (FAME), Ultrasonic*

1. Introduction

Biodiesel, a liquid fuel is consisting of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats. It can be used as a substitute for diesel fuel [1]. Some of the advantages of using biodiesel fuel are its renewability, easy biodegradability, non-toxicity and safer handling due to its higher flash point compared to those of fossil fuels [2]. In addition, biodiesel fuel is also primarily free of sulfur and aromatics, producing more tolerable exhaust gas emissions than conventional fossil diesel [3].

Currently, more than 95% of the world biodiesel is produced from edible oils which are easily available on large scale from the agricultural industry. However, continuous and large-scale production of biodiesel from edible oils has recently been of great concern because they compete with food materials - the food versus fuel dispute. There are concerns that biodiesel feedstock may compete with food supply in the long-term. Non-edible plant oils have been found to be promising crude oils for the production of biodiesel. The use of non-edible oils when compared with edible oils is very significant in developing countries because of the tremendous demand for edible oils as food, and they

are far too expensive to be used as fuel at present [4,5]. Indonesia is a country with a largest rubber land area of the world's with vast acreage totaled 3.4 million hectares, with rubber production reached 2.6 million tons in 2009 [6]. With regard to plant rubber, rubber seeds are not much utilized, whereas oil levels are high enough for about 40-50% [7]. Utilization of rubber seeds as raw material of biodiesel production enough potential in Indonesia. The oil contains triglyceride which can be converted into biodiesel by transesterification reaction. Transesterification is reaction between triglyceride and alcohol and produces alkyl ester with glycerol as by-product. Transesterification reaction was presented in Figure 1.

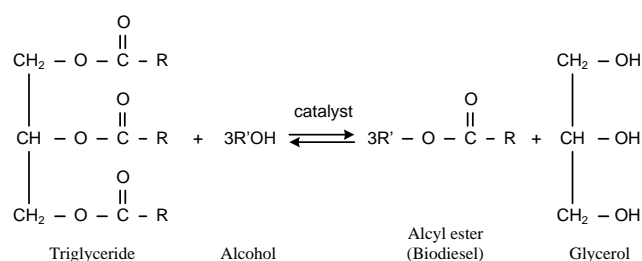


Fig. 1. Transesterification reaction of biodiesel production

Using conventional methods, oil is directly treated with an alcohol in the presence of a catalyst. Therefore, the total process involves various oil treatments such as its extraction, purification, (trans)esterification. The in situ biodiesel production is a novel approach for producing biodiesel from oil bearing materials such as oilseeds or seed cakes and acidified or alkalinized alcohol, developed by Harrington and D'Arcy-Evans [8]. In this method, the alcohol acts as an extracting solvent and a (trans)esterification reagent, so both oil extraction and transesterification reaction proceed in one step. Usually, the oil bearing material is directly treated at ambient temperature and pressure with an alcohol solution of the catalyst. The method eliminates the need for the isolation and possibly refining of seed oils, so the biodiesel production process could reduce costs and maximize the product yield, this technology is known as reactive extraction. Once the oil is extracted out from seeds, it is converted to esters. In this way, it is possible to reduce processing time, solvent amount and total cost. However, it requires a higher amount of alcohol than traditional processes [9]. Several researchers have studied in situ biodiesel production from non-edible oil bearing materials in the absence of a catalyst [10] and the presence of an acid [11], a base [12] or an enzyme [13] catalyst.

The use of ultrasound in the biodiesel production from seed cakes by base-catalyzed methanolysis reaction shortens reaction time and enhances total FAME yields under milder reaction conditions, compared to the conventional method [14]. The total FAME yields from cotton, sunflower and sesame seeds are increased from 46 to 85.5%, 67.2 to 93%, and 43.2 to 83.5%, respectively. In situ methanolysis of cotton [12] and sunflower [15] seeds produces FAME in yields significantly greater than those obtained from the conventional reaction with pre-extracted seed oils. The base-catalyzed in situ methanolysis and ethanolysis require only 20 and 40 min, respectively, for complete conversion using ultrasonication. Generally, Ultrasound is also effective in increasing the FAME yield in the acid-catalyzed in situ production of biodiesel from rice bran with low FFA content [16].

The objective of this research was to study influence of catalyst concentration and ratio of raw materials to methanol on yield of biodiesel from rubber seed by in situ method with ultrasonic assisted.

2. Methodology

2.1. Materials

Rubber seed were procured from rubber plantation Kendal Indonesia. Methanol has industrial grade. Sulphuric acid has analytical grade from Merck, Germany. Sulphuric acid used as catalystr. KOH, ethanol, KI

The reactor used consists of a three-necked flask equipped with stirring. Ultrasonic radiation obtained from the ultrasonic cleaner. Radiation propagating through water that loaded in the ultrasonic bath cleaner. This equipment like as presented in Fig 2.

2.2. Experimental procedure

Rubber seed were peeled and the kernels were crushed, macerated and dried in an oven at 55°C for 2 hours. One hundred grams kernels were inserted into a flask assembled by stirrer (see figure 2) and put it in ultrasonic bath. Then methanol which has been mixed with a catalyst was added and stirred as well as heated at 60°C for 30 minutes at atmospheric pressure. First stage, concentration of H₂SO₄ varied in 0.1-1% v/v and ratio rubber seed to methanol (1:2 w:v). The best catalyst concentration obtained then used on the second stage. Second stage, the ratio rubber seed to methanol varied in 1:1.5-1:3 (w/v) with the best concentration of H₂SO₄ catalyst 0.1% w/v. After the extraction-reaction in ultrasonic bath was completed then the product was filtered and methanol was

separated with distillation. Biodiesel product was measured for weight, viscosity and density.

2.3. Analysis methods

Biodiesel product was analyzed for physical properties and methyl ester concentration. Concentration of methyl ester in biodiesel product was analyzed by Gas Chromatography (GC). The liquid product concentration was analysed by using gas chromatography (HP 5890, with OV-17 column and FID detector). The analysis process used internal standard method. The operation used nitrogen as gas carries with flowrate of 28 ml/minute, programming temperature and detector temperature of 275 °C. The programming temperature was used initial temperature of 125°C that kept constant for 3 minute, furthermore the temperature increased with rate of 15/minute until 275°C. The standard product was used methyl ester from Pertamina Company and benzyl alcohol as internal standard.

Weight of product was used to calculate for biodiesel yield. Yield of FAME was calculated by using this equation [17]:

$$\text{Yield of FAME} = \frac{\text{weight of the product (g)} \times \text{content of FAME (\%)}}{\text{weight of potential FAME in seed}} \times 100\% \quad (1)$$

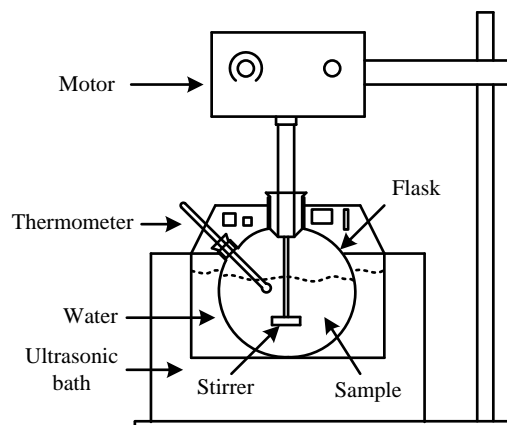


Fig. 2. Experimental tool sets

3. Result and discussion

Before doing the research, first the rubber seed kernel was analyzed of fat/oil content. The oil content was 26.85% lower than that expressed by Ketaren, [18] which was about 40-50% and Stosic & Kaykay, [19] was 39%, this was because the low quality of rubber seed. In this research the reaction temperature was used at 60°C because according to Leung and Guo [20] and Eevera et al. [21] found that when the reaction temperature increases beyond the optimal temperature, the yield of the biodiesel product decreases due to acceleration of the saponification reaction of triglycerides. Depending on the oil used, the optimal temperature ranges from 50 to 60°C. The reaction temperature must be less than the boiling point of alcohol in order to ensure minimum vaporization. When the reaction temperature closes or exceeds the boiling point of methanol (68°C), the methanol will vaporize and form a large number of bubbles which may inhibit the reaction [22].

To increase the extraction-reaction rate, vigorous mixing was utilized to increase the rate of collision between the reactants and to homogenize the reaction mixture. The alcohol (methanol) and the triglyceride source (vegetable oil/animal fat) are immiscible and tend to form two layers. Vigorous mixing increases the mass transfer rate by dispersing the alcohol as fine droplets in the triglyceride phase, thereby increasing the contact surface area between the two immiscible reactants [23].

Besides using in situ method by agitation, extraction-reaction process also assisted by ultrasonic irradiation because, it has proven to be a useful tool in enhancing the reaction rates in many reacting systems. During the application in transesterification, ultrasonication provides the mechanical energy for mixing and the activation energy needed to start the transesterification reaction [24]. Furthermore, ultrasonication increases the chemical reaction speed, the efficient molar ratio of methanol to oil, the yield of transesterification of vegetable oils and animal fats into biodiesel with less energy consumption than for the conventional mechanical stirring method [25].

In order to understand the way in which cavitation collapse can affect chemical transformations, we must consider the possible effects of this collapse in these systems. In the case of homogeneous liquid phase reactions (this research was using a homogenous catalyst), there are two major effects. First, the cavity that is formed is unlikely to enclose a vacuum (in the form of void)—it will almost certainly contain vapor from the liquid medium or dissolved volatile reagents or gases. During the collapse, these vapors will be subjected to extreme conditions of high temperatures and pressures, causing molecules to fragment and generate highly reactive radical species. These radicals may then

react either within the collapsing bubble or after migration into the bulk liquid. Secondly, the sudden collapse of the bubble also results in an inrush of the liquid to fill the void producing shear forces in the surrounding bulk liquid capable of breaking the chemical bonds of any materials, which are dissolved in the fluid or disturb the boundary layer facilitating the transport. When considering the reaction conditions for a cavitation process, the choice of the solvent and bulk operating temperature are significant factors and often interrelated. Any increase in the solvent vapor pressure decreases the maximum bubble collapse temperature and pressure [26].

The cavitation activation in heterogeneous systems is mainly as a consequence of the mechanical effects of cavitation. In a heterogeneous solid/liquid system such as in situ method, the collapse of the cavitation bubble results in significant structural and mechanical defects. Collapse near the surface produces an asymmetrical inrush of the fluid to fill the void forming a liquid jet targeted at the surface. This effect is equivalent to high-pressure/high velocity liquid jets and is the reason why ultrasound is used for cleaning solid surfaces [26].

In situ method involves extraction-reaction process. Extraction enhancement by ultrasound has been attributed to the propagation of ultrasound pressure waves, and resulting cavitation phenomena. High shear forces cause increased mass transfer of extractants [27]. The implosion of cavitation bubbles generates macro-turbulence, high-velocity inter-particle collisions and perturbation in micro-porous particles of the biomass which accelerates the eddy diffusion and internal diffusion. Moreover, the cavitation near the liquid–solid interface sends a fast moving stream of liquid through the cavity at the surface. Cavitation on the product surface causes impingement by micro-jets that result in surface peeling, erosion and particle breakdown so that the oil will easily come out from the kernel particles. This effect provides exposure of new surfaces further increasing mass transfer of the oil into the reaction systems [28].

In heterogeneous liquid/liquid reactions between oil and alcohol, cavitation collapse at or near the interface will cause disruption and mixing, resulting in the formation of very fine emulsions. When very fine emulsions are formed, the surface area available for the reaction between the two phases is significantly increased, thus increasing the rates of reaction. The emulsions formed using cavitation, are usually smaller in size and more stable, than those obtained using conventional techniques and often require little or no surfactant to maintain the stability. This is very beneficial particularly in the case of phase-transfer catalysed reactions or biphasic systems [26].

When applying indirect ultrasound for the in situ biodiesel production it is preferable to use additional mechanical stirring, which provides enough mixing for the maximum exposure of the reactant to the reaction medium during sonication [16]. Therefore in this research was combined between agitation and ultrasonic irradiation for the in situ biodiesel production from rubber seed.

III.1. Effect of catalyst concentration

Density and viscosity are physics properties that depend with composition in solution. In (trans)esterification reaction was produce methyl ester and glycerol. So, the in situ process can be obtained methyl ester, glycerol, and unreacted vegetable oil as products. Based on Figure 3, along with the increase in the concentration of catalyst, either the density or kinematic viscosity of biodiesel did not change significantly. The density of biodiesel varies from 0.904 to 0.965 g/mL but its value was slightly above the biodiesel standard (SNI 04-7182-2006) which has range (0.85-0.89 g/mL). The lowest density was obtained at 0.1% of H_2SO_4 and the highest was obtained at 0.25% of H_2SO_4 . From 0.5 to 1% catalyst concentration, density of biodiesel tends to be constant. The density of fuel has some effect on the break up of the fuel injected into the cylinder. In addition, more fuel is injected by mass as the fuel density increases [29]. The injected fuel amount, injection timing and injection spray pattern are directly affected by these parameters [30]. With increasing density, the diameter of the fuel droplets increases. Since the inertia of the big droplets is big, their penetrations in the combustion chamber will be higher, as well [31]. When a fuel with lower density and viscosity is injected, improved atomization and better mixture formation can be attained [29].

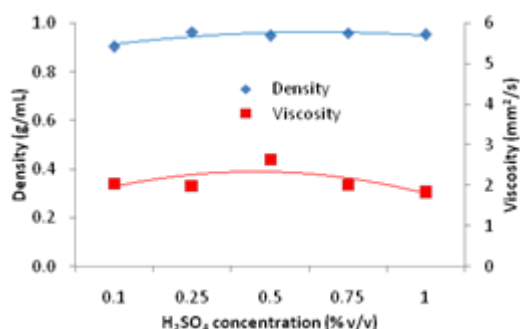


Fig 3. Effect of catalyst concentration (% v/v) of H_2SO_4 on density & kinematic viscosity of biodiesel

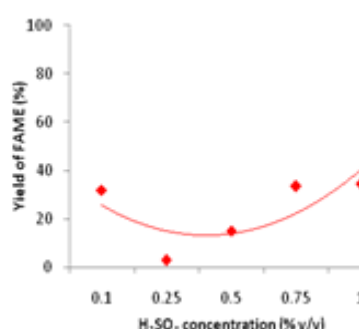


Fig. 4. Effect of catalyst concentration on yield of FAME

For the kinematic viscosity of biodiesel, from 0.1 to 1% catalyst concentration tends to be constant with the lowest and the highest value of 1.81 and 2.65 mm²/s respectively. The highest kinematic viscosity was obtained on catalyst concentration of 0.5% and afterwards decreased slightly and tends to be constant. When compared to SNI standard of biodiesel, the range of kinematic viscosity are 2.3–6.0 mm²/s, therefore almost all of the kinematic viscosity resulted still below with SNI standard. The viscosity of an engine fuel is one of the most critical fuel features. It plays a dominant role in the fuel spray, mixture formation and combustion process. The high viscosity interferes with the injection process and leads to insufficient fuel atomization. Moreover, the mean diameter of the fuel droplets from the injector and their penetration increases with increasing fuel viscosity [31]. The inefficient mixing of fuel with air contributes to incomplete combustion in the engine. In addition to all these, high viscosity can cause early injection due to high line pressure, which moves the combustion of the fuel closer to top dead center, increasing the maximum pressure and temperature in the combustion chamber [30, 31].

Based on Figure 4 that yield of FAME increased along with the increased of catalyst concentration, but tend to be constant from the catalyst concentration of 0.75% and beyond which the highest yield of FAME was 34.74% at 1% of catalyst. The low of FAME yield due to the low quality of rubber seeds that have a low oil levels and maybe the fact is that the acid-catalyzed reaction is about 4000 times slower than the base-catalyzed reaction [32]. However, acid-catalyzed transesterifications hold an important advantage with respect to base-catalyzed ones: the performance of the acid catalyst is not strongly affected by the presence of FFAs in the feedstock. In fact, acid catalysts can simultaneously catalyze both the esterification and transesterification process. Thus, a great advantage with acid catalysts is that they can directly produce biodiesel from low-cost lipid feedstock such as rubber seed.

Rubber seeds will quickly rots if its skin already peeled, but this can be avoided with dry it quickly and samples to be more durable and can be stored in a long time. As mentioned by Ramadhas., et al. [7] from physical appearance the higher catalyst concentration, the darker also biodiesel produced. Therefore the addition of a suitable catalyst concentration is important to the physical appearance of biodiesel. If used in higher catalyst concentration is feared could create a high acid content. Higher acid content can cause severe corrosion in fuel supply system of an engine [33].

III.2 Effect of rubber seed ratio to methanol

Based on Figure 5 with acid catalyst, by varying the ratio of rubber seeds to methanol, did not affect the density of biodiesel significantly or tend to constant. The biodiesel product had density in the range from 0.89 to 0.98 g/mL which was slightly higher than that from SNI standard. Biodiesel density meet with SNI standard are at the ratio of 1:1.25 and 1:3 w:v (0.89 g/mL). Meanwhile, if using base catalyst, the density tend to constant also, the lowest biodiesel density at 0.9 g/mL with ratio of 1:1.75 w:v and the highest biodiesel density at 0.96 g/mL with ratio of 1:2.5 w:v. All values of density on the biodiesel product with base catalyst were higher than that from SNI standard so that acid catalyst was the best catalyst in this case.

Viscosity of any fuel is related to its chemical structure. Viscosity increases with the increase in the chain length and decreases with the increase in the number of double bonds (unsaturated level) [34, 35]. When using an acid catalyst, obtained the highest kinematic viscosity at ratio of 1:1.75 w:v (3.98 mm²/s) and the lowest at the ratio of 1:2 w:v (2.04 mm²/s). By using an acid catalyst, there were several kinematic viscosities which less than biodiesel SNI standard (2.3 mm²/s). For kinematic viscosity under 2.3 mm²/s, it means more dilute than that biodiesel standard and value its worth even closer with diesel standard viscosity (SNI) at range of 1.6-5.8 mm²/s so that this becomes no problem. In spite of, low viscosity causes rapid wear of engine parts such as injection pump and fuel injector as expressed by Chigier [36]. Viscosity of methyl ester from rubber seed oil is lower at higher temperatures and almost equal to the diesel fuel. This helps the combustion as air entrainment increases, as spray cone angle increases due to reduction in viscosity [37].

Overall, the kinematic viscosity of biodiesel products by using base catalyst met with biodiesel SNI standard. The highest kinematic viscosity of biodiesel products was obtained at the ratio of 1:3 w:v (5.54 mm²/s) and the lowest ratio was obtained at the ratio of 1:1.75 w:v (3.65 mm²/s)

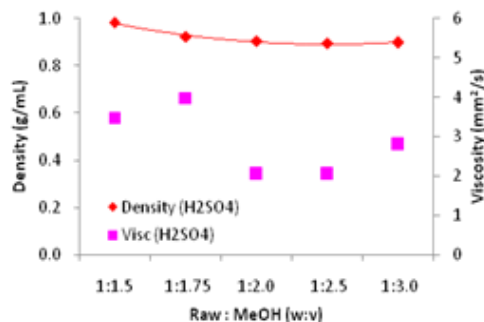


Fig. 5. Effect of raw material ratio to methanol on density & viscosity of biodiesel

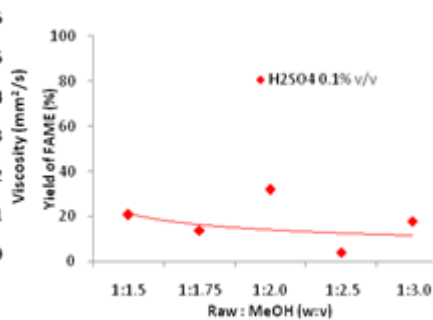


Fig. 6. Effect of raw material ratio to methanol on yield of FAME

Based on Figure 6, while using acid catalyst, it would be obtained the highest yield of FAME at 31.86% on the ratio of 1:2 w:v, but if the ratio was raised, the yield would decrease. Whereas, if using base catalyst, it would be obtained the highest yield at 35% on the ratio of 1:1.75 w:v and this is the highest yield on this research. If the ratio was raised, the yield would decrease also. The amount of methanol, however, should not be too exaggerated, as expressed by Ramadhas., et al [7], methanol on ester layers can lower the flash point of biodiesel. Therefore the purification process and removal of methanol with distillation or washing should be perfect.

III.3 Biodiesel analysis

Based on Figure 7 by varying the concentration of the acid catalyst from 0.1 to 1% v/v, it did not change significantly on acid value and tend to be constant at biodiesel products with the lowest acid value of 0.39 mg/KOH/g biodiesel at 1% H₂SO₄ and the highest acid value of 0.83 mg/KOH/g biodiesel at 0.75% H₂SO₄. Acid value on biodiesel product had met with biodiesel SNI standard (max. 0.8 mg KOH/g).

Based on figure 8 for the effect of raw materials ratio to methanol, also produced a constant acid value from ratio of 1:1.5 to 1:3 either with base or acid catalysts. For acid catalysts was produced the lowest acid value of 0.58 mg KOH/g at ratio of 1:2 and the highest of 0.87 mg KOH/g at ratio of 1:1.5. For base catalyst was produced the lowest acid value of 0.46 mg KOH/g at ratio of 1:1.75 and the highest of 0.78 mg KOH/g at ratio of 1:1.5. Therefore almost all

of the acid value on biodiesel product had met with biodiesel SNI standard (max. 0.8 mg KOH/g).

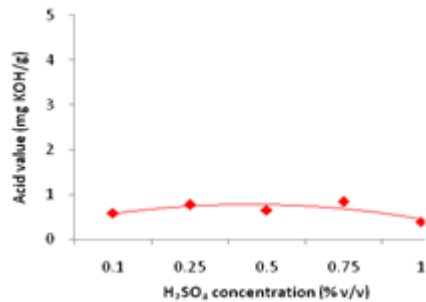


Fig 7. Effect of catalyst concentration on acid value

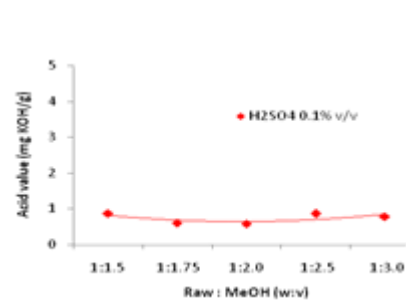
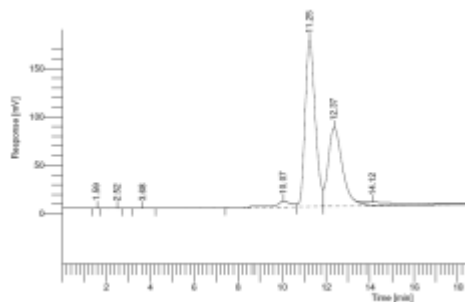
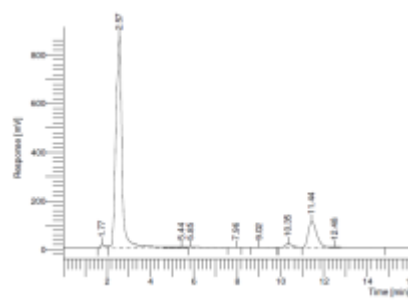


Fig. 8. Effect of rubber seed ratio to methanol on acid value



a. standart



b. product sampel

Fig 9. GC chromatogram of biodiesel on H₂SO₄ concentration of 1% (v/v) and ratio of 1:2 (w:v)

Figure 9.b. shown fatty acid methyl ester (FAME) was detected on retention time of 5.44-12.48 minutes. Biodiesel standard has chromatogram on retention time of 5-14. From the GC analysis, it was estimated that 5.44 minutes was methyl palmitate (C_{16:0}), 5.85 minutes was methyl palmitoleic (C_{16:1}), 7.96 minutes was methyl heptadecanoic (C_{17:0}), 9.02 minutes was methyl stearic (C_{18:0}), 10.35 minutes was methyl linoleic (C_{18:2}), 11.44 minutes was methyl linolenic (C_{18:3}) and 12.48 minutes was methyl eicosenoic (C_{20:1}).

4. Conclusion

Based on the research results, concluded that the concentration of acid catalyst was obtained the highest FAME yield of 34.74% at ratio of 1:2 w:v with H₂SO₄ 1% v/v. the experiment conducted in 60oC, 40 kHz frequency of ultrasonic cleaner, atmosphere condition and 30 minute. The characteristic of biodiesel product still on biodiesel standards according to the Indonesian government /SNI. Furthermore, in situ methods with ultrasonic assisted can used for biodiesel production especially from rubber seed.

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Question and Answer

1. What is consideration when producing biodiesel from waste cooking oil?
A1: (Bpk Tatang) the conversion must be higher than 96.5%.
A2: Effect of oil to ethanol molar ratio
2. How about catalyst? Can it be regenerated, how many times?
A1: catalyst can be regenerated by 3 times.
3. Why did you use rubber seed oil, seed is seasonal and have non-commercial and non-sustainable?
A1: because of non-edible and have high energy content.
A2: rubber seed oil has high iodine and acid number.
because of non-edible and have



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