PROGRAM RUNDOWN

Tuesday, December 2, 2014	
Time	Agenda
08.00 – 08.20	Open registration desk
8.20 – 8.50	1. Opening Ceremony (MC) 2. Welcoming remark from Organizing Committee 3. Opening Addresses by JSUs, JICA, His 4. Welcoming remark by UNRI Rector 5. Official Opening by UGM Rector
08.50 – 09.00	Traditional welcoming dance by UGM student
09.00 – 10.30	**Plenary Panel I** **Advance topics in natural resources technology** 1. Professor Hirofumi Hinode (Tokyo Institute of Technology Japan) 2. Professor Hajime Tamon (Kyoto University Japan) 3. Professor Tatsuya Okubo (University of Tokyo) 4. Professor Luis Razon (De La Salle University – The Philippines)
10.30 – 10.45	Morning Coffee
10.45 – 12.00	**Plenary Panel II** **ASEAN Industrial Challenges: Innovation, Technology, and Sustainability** 1. General Manager on Technology and Product Development for PT. Pertamina Gas Directorate, 2. Direktur R & D PT. Soho Farmasi Industri 3. Pusat Penelitian Kelapa Sawit Medan
12.00 – 13.00	Lunch Break
13.00 – 15.00	- **Technical Sessions I** (up to 7 parallel rooms) - Field Management Meeting for JSUs and MIs
15.00 – 15.30	Afternoon Coffee
15.30 – 17.30	**Technical Sessions II** (up to 7 parallel rooms)
19.00 – 21.00	Collegial Banquet and Award Ceremony

Wednesday, December 3, 2014	
Time	Agenda
08.00 – 08.15	Registration
08.15 – 08.20	Opening salutation
08.20 – 10.00	**Plenary Panel III:** **Chemical Engineering Education Challenges and Opportunities** 1. Chairman of Indonesian Association of Chemical Engineering Profession (BKKPII) 2. The Former Rector of ASEAN Institute of Technology (AIT), 3. Chairman of Chemical Engineering Department, Universiti Malaya, Malaysia
10.00 – 10.15	Morning Coffee
11.15 – 11.45	**Information from AUN/SEED-Net secretariat about development of program**
11.45 – 12.00	Farewell Address to Foreign Delegations by Chemical Engineering UGM Chairman
12.00 – 13.00	Lunch
13.00 – night	City Tour

PAPER CODE

- EE - Energy and Efficiency
- MM - Mathematical Modeling
- ST - Separation Technology
- M - Materials
- FBE - Food and Bioprocess Engineering
- OPP - Oleochemical and Petrochemical Processes
- WE - Water and Environment
- PCR - Particles-Catalysis-and Reaction Engineering
- N - Nanotechnology

TECHNICAL SESSION

TECHNICAL SESSIONS I (13.00 – 14.30)

Room I (ARIMBI ROOM, Ground Floor)
Moderator : Yano Surya Pradana

Time	Code	Title	Presenter
13.00	M-05	Oil Palm Fruit Bunch Fibre Conversion to High Refined Cellulose Using Nitric Acid and Sodium Hydroxide as The Delignificating Agents	Supranto
13.15	M-04	Synthesis of Pumice-TiO_2 Composite for Phenol and E.Coli Removal	Hendarsa, Agung Sri
13.30	M-07	Flas'on (Fly Ash as Sound Absorbent Concrete): Production Sound Absorbent Concrete for Solve Noise Problem in Industrial Area	M Dwiki
13.45	M-08	Silica Gel Derived from Palm Oil Mill Fly Ash	Panca Setia Utama
14.00	M-09	Effect of Anodization Time and Temperature on The Morphology of TiO_2 Nanotube Arrays for Photocatalytic Hydrogen Production from Glycerol-Water Solution	Ratnawati
14.15	M-12	The Crystalline Phase and Particle Size of $NaTaO_3$ Nanomaterials Synthesized by Hydrothermal Method	Nguyen Thi Lan

Room 2 (SHINTA ROOM, Ground Floor)

Moderator : Zuchra Helwani

Time	Code	Title	Presenter
13.00	FBE-01	Preliminary Study on Cocoa Beans Drying Process: The Effects of Fermentation and Water Content on Fungal Growth and Aflatoxin Production	Agus Supriatna
13.15	FBE-02	Fermented Cassava Flour Production in A Circulated Reactor	Anggina, Meitha
13.30	FBE-03	Kinetic Study of Xylitol Fermentation	Efri Mardawati
13.45	FBE-08	Hydrolysis of Tofu Solid Waste Using Cow Rumen Enzyme to Produce Glucose for Bioethanol Production Using *Saccharomyces sereviseae* as An Alternative Energy	Tutri Reski Nadia
14.00	FBE-12	Effect of Addition of Concentration of Crude Production Cellulase *Aspergillus niger* Media on The Application of Rice Straw as Biodeingking	Yanty Maryanty
14.15	FBE-10	Mapping the Effects of Starter Culture Addition on Cocoa Bean Fermentation	Hanny Febriami

Room 3 (RAMA ROOM, Ground Floor)

Moderator : Syaiful Bahri

Time	Code	Title	Presenter
13.00	ST-01	Dissolution Rates of Mangosteen (*Garcinia mangostana L.*) Pericarps Extract Granules in Synthetic Human Gastrointestinal Fluid	Andri Cahyo Kumolo
13.15	ST-06	The Pretreatment and Optimization Studies on the Extraction of Phaleria macrocarpa Fruit as Natural Antioxidant Source Using Ethanol-Water Mixture	Winawaty, Yayah
13.30	ST-08	Demulsification of Oil-Formation Water Emulsion Mixture with Variable of Temperature, Either Single or Double Demulsifier, Concentration, and Level of Experiment Liquid	Bardi Murachman
13.45	ST-02	Mathematical Modeling of Micronutrient Recovery from Vegetable Oil by Silica-based Adsorption: Vitamin E from Palm Fatty Acid Distillate	AD Susanti
14.00	ST-05	Adsorption of Chemicals by Reservoir Rock in The Enhanced Oil Recovery Process	Suryo Purwono
14.15	ST-04	Adsorption of Lead in Fixed-Bed Column Using Sodium Carbonate Treated Rice Husk	Sovattei, CHEA

Room 4 (NAKULA ROOM, 1st Floor)

Moderator : Yusnimar Sahan

Time	Code	Title	Presenter
13.00	PCR-01	γ-MnO_2 Nanoparticles Activation of Peroxymonosulfate for Catalytic Phenol Degradation in Aqueous Solutions	Edy Saputra
13.15	PCR-04	Pyrolysis of Waste Tyresas an Intermediate Chemical for Jet Fuel Production	Puspitasari, Mitha
13.30	PCR-06	Natural Zeolite for Transesterification Step Catalysts in Biodiesel Production From Palm Off Grade	S. Ulfayana
13.45	PCR-07	Non-Catalytic Thermal Cracking of Bio-Oil to Organic Liquid Product (OLP)	Sunarno
14.00	PCR-08	Hydrolysis Pretreatment of *Tetraselmis chuii* into Glucose by Using Diluted Sulfuric Acid	Syelvia Putri Utami
14.15	PCR-09	Effect of Preparation Method in Activating Active Sites and Catalytic Activity of SO42-/ZrO_2in Biodiesel Production	Yahaya Muhammad, Sani

Room 5 (ARJUNA ROOM, 1st Floor)
Moderator : Sang Kompiang Wirawan

Time	Code	Paper	Presenter
13.00	MM-01	CFD Analysis on Sand Settling Behaviour in A Sand Removal Vessel from Produced Water of An Oil Production Surface Facility	Idral Amri
13.15	MM-02	Optimization of Nutrient Recovery in A Fluidized Bed by Response Surface Methodology	Ralf Rafael
13.30	MM-03	Regression Modeling of Thermal Degradation Kinetics, of Concentrated, Aqueous Piperazinein Carbon Dioxide Capture	Shaukat Mazari
13.45	MM-04	Effect of An Additional Internal Baffle inside A Sand Removal Vessel on Sand Settling Efficiency from Produced Water of An Oil Production Surface Facility Using CFD Simulation Method	Yazid
14.00	MM-05	Multivariate Statistical Modellingof Sub-Micron Ibuprofen Particle Forming Using Rapid Expansion of Supercritical Solution (RESS)	Le Thi Kim Phung
14.15	MM-06	Design and Control of Natural Gas Dehydration Unit Using TEG Under Plantwide Process Control : The Thermodynamic Models and Steady State Simulation	Sony Ardian

TECHNICAL SESSIONS II (15.00 – 16.45)

Room 1 (ARIMBI ROOM, Ground Floor)

Moderator : Panca Setia Utama

Time	Code	Title of Paper	Presenter
15.00	M-10	The Effect of Chemical and Physical Activation on Preparation of Activated Carbon from Corn Cobs	Yuliusman
15.15	M-02	Study on Utilization of Coconut Oil as a Plasticizer for the Palm Oil Fly Ash/Carbon Black Reinforced Thermoset Rubber Products	Zuchra Helwani
15.30	M-01	Sol-Gel Processes in the Synthesis of Solar Selective Absorber Thin Film Coatings for Photothermal Collector: Challenges and Strategies	Amun Amri
15.45	M-03	Synthesis of Nanostructured Manganese Oxides Based Materials and Application for Supercapacitor	Thanh Tung, Mai
16.00	M-06	Novel Process to Utilize Wasted Cullet in Glass Industry as Ecomaterial	Trung Kien, Pham
16.15	M-11	Distribution Mineral Matter and Depositional Environment of Coal Seams from Samarinda Area, Lower Kutai Basin, Indonesia	Chaw Thuzar Win
16.30	ST-12	Mass Transfer at Concentration Cane Juice in A Falling Film Evaporator with Air Flow	Suhadi
16.45	ST-14	Mass Transfer at Concentration Cane Juice in A Falling Film Evaporator at Vacuum Conditions	Suhadi

Room 2 (SHINTA ROOM, Ground Floor)
Moderator : Syelvia Putri Utami

Time	Code	Paper	Presenter
15.00	FBE-09	Bioconversion Hampas Sago to Bioethanol with Ragi Tapai	Ulfah, M
15.15	FBE-06	The Effects of Incubation Time and Kieserite Concentration to Yield on The Isolation of Patchouli Oil by Fermentation Method Using *Phanerocheate chrysoperium*	Sri Rulianah
15.30	FBE-04	Sequential-Co-Culture of White-Rot Fungus and Yeast on Pretreated Sugarcane Bagasse for Ethanol Production	Li Wan, Yoon
15.45	FBE-07	Remazol Brilliant Blue R Dye Decolourizationby Laccase Produced by *Pleurotus sajor-caju* Via Solid-State Fermentation	Teck Nam
16.00	FBE-13	Effect of Additives on Delignification and Fermentation of Sugarcane Bagasse for Ethanol Production by A White–Rot Fungus, *Phlebia* Sp. Mg–60	Khuong Le Duy
16.15	FBE-11	Strategy for the Bioconversion of Palm Oil Mill Effluent into Valuable Polyhydroxyalkanoates	Wee Shen, Lee
16.30	FBE-05	Development and Characterization of Low Volume Aerobic Bioreactor	Samuel Sianturi
16.45	WE-02	Analyzation of Supported Medias for Wastewater Treatment by Anaerobic Fermentation	Yanisa Laoong-U-Thai

Room 3 (RAMA ROOM, Ground Floor)

Moderator : Suryo Purwono

Time	Code	Paper	Presenter
15.00	EE-01	Hydrogen Production System with Plasma Electrolysis Method in Natrium Carbonate-Acetate Acid Solution	Nelson
15.15	EE-02	Production of Biohydrogen and Bioacetic Acid by Using Isolates of *Bacillus circulans*	Mahreni
15.30	ST-03	Ion Exchanged Zeolite X for H_2S Adsorption at Room Temperature	Nguyen Quang Long
15.45	ST-09	Extraction of Rice Bran Oil from Rice Bran Using Isopropyl Alcohol (IPA)	Sang Kompiang Wirawan
16.00	ST-07	Pulsed Electric Field (PEF) Assisted Extraction of Microalgae *Teraselmis Chuii Sp* for Biodiesel Feedstock	Fahrian Andra Aditama
16.15	ST-11	Natural and Biodegradable Chitosan and Sago Based Membranes for Pervaporation of Liquid-Liquid Systems	Mohd Ghazali Mohd Nawawi
16.30	ST-10	Multi Component Gas Mixtures Permeation in ZSM-5 Zeolite Membranes	Sang Kompiang Wirawan

Room 4 (NAKULA ROOM, 1st Floor)

Moderator : Edy Saputra

Time	Code	Paper	Presenter
15.00	PCR-05	Acid-Catalysed Hydrolysis of Coconut Shells: Optimization of Furfural Production	Rodel D Guerrero
15.15	PCR-12	Study Using NiMo/Cengar-Clay Catalyst on Upgrading Pyrolysis Process of Nipa Frutican Stem Biomass to Produce Biooil	Syaiful Bahri
15.30	PCR-11	Isomerization of Crude Indonesian Turpentine Contains Alpha Pineneto Produce Camphene over Resin Catalyst	Retno Ringgani
15.45	PCR-10	Pyrolysis of Palm-Oil Shell to Bio-Oil	Naura Luthfia
16.00	PCR-02	Solid Acid Saccharification of Ionic Liquid Dissolved Sago Waste for The Production of Reducing Sugars	Kiat Moon, Lee
16.15	PCR-03	Synthesis and Characterization of Highly Ordered Solidacid Catalyst from Kaolin	Peter Adeniyi, Alaba
16.30	ST-13	Design of Absorption Tower on Nitric Acid Production to Increase Its Maximum Concentration	Renanto H

Room 5 (ARJUNA ROOM, 1st Floor)

Moderator : Andri Cahyo Kumolo

Time	Code	Paper	Presenter
15.00	OPP-03	Solid-Liquid Equilibrium of Saturated Fatty Acid and Urea in Urea Complexation	Setya Wardhani
15.15	OPP-04	The Electrochemical Hydrogenation of *Reutealis trisperma* Oil as Non-Edible Biodiesel Feedstock	Tedi, Hudaya
15.30	OPP-01	Rapid Screening and Charecterizations of Oligoglycerols from Etherification of Glycerol	Siwarutt Boonyarattanakalin
15.45	OPP-02	Conversion Extracted Oil of Spent Bleaching Earth to Biodiesel and Regenerating Spent Bleaching Earth	Yusnimar Sahan
16.00	WE-01	Multi - Criterion Decision Making for Selecting Municipal Wastewater Treatment Technology in Metro Manila Philippines	Aileen Huelgas – Obrecido
16.15	N-01	Application of Bimetallic Nanoparticles of Iron and Copper in The Degradation of Dichlorodiphenyltrichloroethane (DDT)	May Thant Zin
16.30	M-13	Preparation and Performance Study of Strain and Pin Types Porcelain Insulator	Thwe Linn Ko

Room 6 (BIMA ROOM, 1st Floor) is used field management meeting, consist of 10 personal

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The Electrochemical Hydrogenation of *Reutealis trisperma* Oil as Non-edible Biodiesel Feedstock

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Abstract

Nowadays various vegetable, especially non-edible, oils are considered as the most promising source of biofuel for future generations. Among these, oil obtained from a highly productive tree locally known as kemiri sunan (*Reutealis trisperma*) is now being developed as one of the non-edible oil feedstocks for biodiesel production. However, the oil possesses a relatively high Iodine value, typically about 120 g-I_2 / 100 g oil. Such oil will produce biodiesel with not only poor thermal as well as oxidative stability, but also insufficient cetane number.

In the present work, electrochemical hydrogenation was the chosen technique to lower the Iodine value of the oil, since it was not only simple and safe to operate, but also required very low capital cost. The system used stainless steel coil as the anode, whereas the cathode were nickel screen or copper raschig rings. An electrolyte solution of potassium formate or cuprous ammonium formate was utilized. The unsaturation level of the oil was measured by Wijs method (AOCS Cd 1-25).

The Iodine value of the original oil, which was initially around 115, could be significantly lowered to 55 – 95 at various KCOOH concentrations and reaction times. However, excessively low Iodine value would result in biodiesel with high cloud point (maximum 18 ^oC according to SNI standard). Thus, the process conditions had to be carefully chosen, and the use of 2.5 M KCOOH solution within 6 hours was sufficient to bring down the Iodine value to the desired (ideal from the cetane number and cloud point requirements) level of 85 g-I_2/100 g (equivalent to methyl oleate).

Even more promising results using cuprous ammonium formate were obtained, among which similar Iodine value decrease could be achieved using 0.6 M electrolyte solution within 6 hours. In addition, the use of cuprous ammonium formate could significantly save the electricity energy consumption. However, the benefit had to be compensated by the more tedious purification of the processed oil using EDTA solution.

Key Words: *Reutealis trisperma*; electrochemical hydrogenation; Iodine number; potassium formate; cuprous ammonium formate

1. INTRODUCTION

Lately, the use of non-renewable fossil fuels as the world primary energy source is slowly but certainly being replaced by more environmentally friendly, yet renewable, fuel sources. The awareness of the urgent need of renewable alternative fuel has triggered significant development of biomass-based fuels worldwide, including in Indonesia. Thus, the utilization of plant origin or derived oils come from local plantation is increasingly prominent. One of many potential oils as biodiesel feedstock is from the *Reutealis trisperma* (locally known as kemiri sunan) plantation, not only because its oil is non-edible but also the tree is more productive than oilpalm tree.

There are two, among many, important quality parameters for biodiesel, i.e. the cetane number and oxidative stability, which are closely related to the Iodine number (the measure of unsaturation) of the oil. The FAMEs of saturated fatty acids possess a high cetane number as well as oxidative stability. However, the more unsaturated (C=C, either mono- or poly-unsaturated) is the oil, the lower the cetane number and oxidative stability. Therefore, biodiesel with high Iodine number or greater than 115 g-I_2/100 g is considered as below the minimum requirements of cetane number and oxidative stability standards. Nevertheless, if the Iodine number of the biodiesel is too low, then the cloud point of the fuel will be too high / beyond the standard value (max 18 ^oC), and hence the ideal Iodine number of the biodiesel is considered at around the Iodine number of methyl oleate (85 g-I_2/100 g), at which the ester has a cetane number of 56,9 and cloud point at -20 ^oC (Soerawidjaja, 2009).

In kemiri sunan oil, a high content (typically around 50%) of α-eleostearic acid (Figure 1) is commonly found. The α-eleostearic acid, or 9(Z),11(E),13(E)-octadecatrienoic acid, has 3 conjugated double C=C bonds. Therefore, this oil has a relatively high I_2 number of around 120 g-I_2/100 g. Unsaturated fatty acids are much more easily oxidized than saturated ones. Moreover, the oxidation rate of saturated fatty acid depends strongly on the number of saturated bonds within the molecules. The ratio of oxidation rate of oleic acid (C18:1) : linoleic acid

(C18:2) : linolenic acid (C18:3) is 1 : 10 : 20 (White and Miller, 1988). Therefore, biodiesel synthesized from kemiri sunan oil will be extremely unstable to oxidation. In addition, the poly-unsaturated bonds are highly reactive, and hence, may result in fatty acid chain polymerization which in the end would cause fuel injection-nozzle blocking.

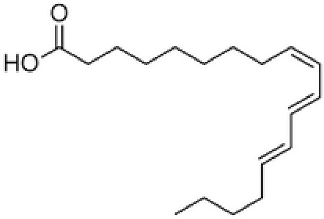

Figure 1 Molecular Structure of α-eleostearic Fatty Acid

Therefore, to improve both oxidative and thermal stability of kemiri sunan oil, before being processed as biodiesel, the unsaturated content (or I_2 number) of the oil should be reduced by hydrogenation. Hydrogenation process may be carried out via several ways, i.e. conventional catalytic hydrogenation using high pressure hydrogen gas, catalytic transfer hydrogenation with the help of hydrogen donor solution and solid catalyst (Arkad et al., 1987), and electrochemical hydrogenation. In this investigation, catalytic electrochemical (electrocatalytic) hydrogenation (Beck, 1979) is utilized for some reasons. This process not only can be operated at room temperature and pressure, but also over the advantage of not using a high pressure hydrogen gas so that it may eliminate the high risk as well as expensive capital cost, and therefore it is more suitable for small scale industry applications.

In general, the electrocatalytic hydrogenation process uses a cathode as an electrode as well as the catalyst for the chemisorption of reactants. At the cathode, adsorbed H is generated by the electrochemical reduction of water, which then reacts with the adsorbed unsaturated molecules (Yusem & Pintauro, 1992) as follows:

$$H_2O + e^- \rightarrow H_{ads} + OH^- \quad \text{(Eq. 1)}$$

$$2\,H_{ads} + R\text{-}CH{=}CH\text{-}R' \rightarrow R\text{-}CH_2\text{-}CH_2\text{-}R' \quad \text{(Eq. 2)}$$

Besides the reaction shown above, a side reaction (the hydrogen gas formation reaction from two adsorbed H atoms) which will ineffectively lead to a higher electricity consumption might also happen at the cathode.

$$2\,H_{ads} \rightarrow H_{2\,(gas)} \quad \text{(Eq. 3)}$$

This reaction needs to be avoided by using the optimum voltage, which can be experimentally determined. At the other electrode (anode), an oxidation reaction (if inert electrode is used) occurs:

$$\tfrac{1}{2}H_2O \rightarrow \tfrac{1}{4}O_2 + H^+ + e^- \quad \text{(Eq. 4)}$$

Mondal & Lalvani (2003 & 2008) studied the electrocatalytic hydrogenation of soybean and canola oils using Pt mesh as the hydrogenation catalyst as well as the cathode, and utilized formate ion (supplied as formic acid) as the mediator for transferring hydrogen attoms. The mechanism of the formate-assisted electrocatalytic hydrogenation cycle can be written as:

$$HCOO^{-} + oil + H_2O \rightarrow oil\text{-}H_2 + HCO_3^{-} \tag{Eq. 5}$$

$$HCO_3^{-} + 2H^{+} + 2e^{-} \rightarrow HCOO^{-} + H_2O \tag{Eq. 6}$$

In this investigation, the hydrogenation of kemiri sunan oil was carried out using potassium formate ion as H transfer mediator. In addition, the use of an electrolyte solution of cuprous ammonium formate was tested to hopefully accelerate and thus increase the extent of hydrogenation, since the Cu^{+} ions are capable of drawing the unsaturated (π) bonds of the unsaturated fatty acid chains into the aquatic phase, and thus reduced the mass transfer resistance of the liquid-liquid hydrogenation process.

2. METHODOLOGY

The electrocatalytic hydrogenation was carried out in an electrochemical cell filled with a circulated mixture of electrolyte and oil. The electrolyte was either potassium formate ion, or cuprous ammonium formate solution in water-methanol mixture Several different materials were tried as anode and cathode. The cathode was a bed of nickel (formate electrolyte) or copper (cuprous amonium formate electrolyte) raschig rings, while a stainless steel coil was used as the anode. Electricity was discharged into the cell through a DC power supply at an optimal constant voltage. Figure 2 presents the equipment set-up used for the electrocatalytic hydrogenation.

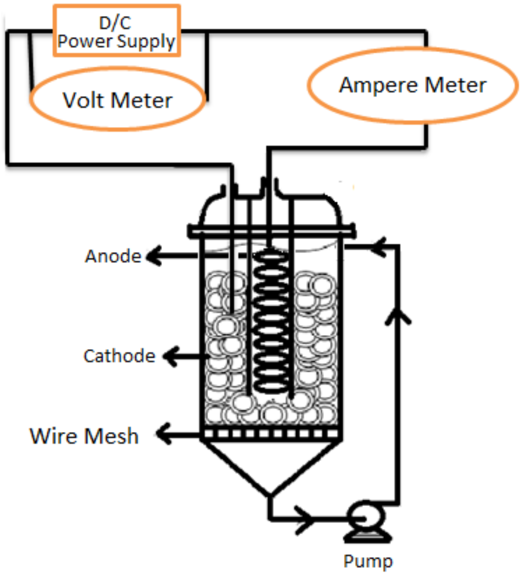

Figure 2 Electrocatalytic hydrogenation cell

The unsaturation level (I_2 number) of the oil was measured by Wijs method (AOCS Cd 1-25). Various potassium formate concentrations (between 2.5 – 10 M) were employed within 6 and 12 hours reaction period with KCOOH : unsaturated bond (calculated from Iodine value) mole ratio of 1 : 6. In the other experimental series, the reactions were carried out between 3 – 9 hours with several cuprous ammonium formate concentrations (0.1 – 0.6 M) at electrolyte : oil ratio of 3 : 4 v/v. Meanwhile, the kemiri sunan oil was supplied from local plantation and directly produced by mechanically pressing the kernel.

3. RESULTS AND DISCUSSION

In several preliminary tests, the optimum voltage for the electrocatalytic hydrogenation was determined from the current vs voltage profile at a certain operating condition. The current flowed through the cell was initially proportional to the given potential difference showing that the total transfer rate of electrons was slower than the ionic mass transfer between the electrodes and the solution. However, after a certain voltage, the current did not change significantly as now the process had been mass transfer limited. Just above this optimum / critical voltage, the formation of H_2 gas (bubbles) at the cathode surface became obvious. It was important to operate the electrocatalytic system under this optimum voltage in order not only to avoid the dangerous H_2 gas formation, but also to keep the electrical energy consumption minimum.

The optimum voltage for the Ni cathode and K-formate system was measured at 12 V with 56.5 mA current flowing through the system. Surprisingly, the Cu cathode and cuprous ammonium formate needed an extremely low optimum voltage of just only 80 mV and 13 mA. The cuprous ammonium formate created an almost homogeneous mixture of the oil and the electrolyte, and thus the mass transfer resistance within such system was much lower than the two-phase mixture in the other. In addition, the electrical conductivity of copper was almost 5 times higher than nickel.

3.1 Electrocatalytic hydrogenation with potassium formate ion electrolyte

The Iodine number of the unprocessed kemiri sunan oil was determined titrimetrically using Wijs method and the analysis showed that the initial Iodine number of the original (unprocessed) oil was 114.5 ± 1.5 g-I_2/100 g. In general, after being electrocatalytically hydrogenated there was a significant reduction in Iodine number of the processed oil, as shown in Table 1.

Table 1 The Iodine number of processed oil at various potassium formate concentrations and reaction times

	Reaction Times (hours)	**Formate Ion Concentration**			
		2.5 M	**5 M**	**7.5 M**	**10 M**
Iodine Number of the processed oil (g-I_2/100 g)	**6**	94.8	61.2	78.7	94.2
	12	61.5	55.0	54.0	73.7

The results above showed the significant effect of the formate ion concentration on the extent of hydrogenation of the unsaturated fatty acids in the oil. Initially, up to 5 M, the Iodine number decreased further as the formate concentration increased. Increasing concentration of electrolyte solution resulted in higher mass (ion) transfer capability between electrolyte solution and turpentine oil, so the hydrogenation rate might be increased. Among those conditions under investigation, the use of 2.5 M KCOOH solution within 6 hours reaction period was sufficient to bring down the original Iodine value to the desired level.

However, beyond 5 M there was a turning point at which excessive formate ion concentration caused the rate of hydrogenation was, surprisingly, inhibited. The inhibition might be due to less active site on the catalyst (Ni surface) was available for the bonding of the unsaturated group of the oil at higher mediator concentration (Mondal and Lalvani, 2008). Moreover, at a fixed KCOOH : unsaturated bond mole ratio of 1 : 6, higher formate concentration translated to less volume of electrolyte being circulated. As a result, the inter-phase contact area between the oil and the ion in the 2-phase reaction (Eq. 5) was considerably decreased so that the rate of hydrogenation diminished at high formate concentration. In addition, less water (needed in the formate regeneration reaction, i.e. Eq. 6) was available at higher formate concentration. Therefore, at the second stage of investigation we tried to not only improve the mediator formulae but also use a fixed oil : electrolyte volume ratio.

3.2 Electrocatalytic hydrogenation with cuprous ammonium formate electrolyte

As expected, the use of cuprous ammonium formate solution could also reduce the Iodine number of the oil (Table 2) to the desired level of around 85 g-I_2/100 g within 6 hours reaction period by using a much lower concentration of electrolyte, i.e. only 0.6 M, in comparison with the previous system.

Table 2 The Iodine number of processed oil at various cuprous ammonium formate concentrations and reaction times

	Reaction Times (hours)	**Concentration of electrolyte solution (M)**		
		0.1	**0.3**	**0.6**
Iodine Number of the processed oil (g-I_2/100 g)	3	115.7	110.5	108.4
	6	113.1	98.8	86.7
	9	110.5	84.5	67.6

The data above showed that the 0.6 M electrolyte was the most effective in reducing the Iodine number of the oil. On the other hand, the 0.1 M electrolyte practically brought no effect to the Iodine number of the oil even after 9 hours reaction. Higher concentration of the Cu^+ ions would lead to more double bonds were drawn (bonded) to the electrolyte phase, in which the formate ion could mediate the H transfer (Eq. 5). Meanwhile, a similar outcome could also be obtained by using lower concentration of electrolyte (0.3 M) but with a prolonged reaction time of 9 hours. However, it should be noted that using 0.6 M electrolyte for 9 hours would lead to processed oil with excessively too low Iodine number of 67.6, which in the end, producing biodiesel with too high cloud point.

The processed oil colour was dark green instead of originally brownish yellow colour. It was suspected that some of the copper metal ions were left behind due to liquid-liquid equilibrium had been established between the oil and the electrolyte phase. Several purification steps were therefore carried out to eliminate the impurities. Initially, the oil was separated from the electrolyte phase by centrifugation. Subsequently, the oil was contacted with 5% Na-EDTA solution to extract any remaining metal impurities responsible to the unusual colour of the oil. The EDTA acted as a complexing agent capable of making a strong coordinated bonding with the copper metal ions in the oil phase. The colourless EDTA solution slowly turned into blue after successfully capturing the metal impurities, and finally the processed oil itself was back to its original colour.

Moreover, as earlier described, a much lower voltage was required to electrocatalytically hydrogenated the unsaturated groups of the oil, and hence significant reduction in the electrical consumption would be acquired by adopting this new system. Table 3 compared the conditions under which the Iodine number of kemiri sunan oil could be dropped from initially 114.5 g-I_2/100 g to around the ideal value (85 g-I_2/100 g) within 6 hours reaction period.

Table 3 The energy usage comparison between potassium formate
and cuprous ammonium formate systems

	Potassium Formate (Ni cathode)	**Cuprous Ammonium Formate (Cu cathode)**
Electrolyte solution (M)	7.5	0.6
Reaction time (hours)	6	6
Iodine number of the processed oil (g-I_2/100 g)	78.7	86.7
Electrical energy consumption (W.s)	21,967	33

The usage of cuprous ammonium formate electrolyte clearly offered a significant advantage in reducing electrical energy consumption from 21,967 W.s (in potassium formate system) to just only 33 W.s, indicating the ability of the cuprous ion to form coordinate bonding with the unsaturated groups of the oil so that more homogeneous mixture was obtained. However, the advantage was balanced by the need of further purification of the processed oil with EDTA solution as previously explained.

4. CONCLUSION

In the present work, electrochemical hydrogenation was chosen and successfully applied to lower the Iodine number of the kemiri sunan oil, from originally about 115 g-I_2/100 g to the ideal value of 85 g-I_2/100 g (methyl oleate).

The Iodine value of the original oil could be significantly lowered to 55 – 95 at various KCOOH concentrations and reaction times. However, the process conditions had to be carefully chosen, so that the final Iodine value of the oil would not fall below the ideal value in order to meet both cetane number and cloud point requirements. Among those conditions under investigation, the use of 2.5 M KCOOH solution within 6 hours reaction period was sufficient to bring down the original Iodine value to the desired level.

Even more promising results using cuprous ammonium formate were obtained, among which similar Iodine value decrease could be achieved using 0.6 M electrolyte solution within 6 hours. In addition, the use of cuprous ammonium formate could significantly save the electricity consumption, indicating the ability of the cuprous ion to form coordinate bonding with the unsaturated groups of the oil so that more homogeneous mixture was obtained. However, the benefit had to be compensated by the more tedious purification of the processed oil using EDTA solution.

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