

A Preliminary study of deoxygenation of *Calophyllum inophyllum* L. oil for green diesel production

J Prasetyo^{1,3}, Adiarso¹, S D S Murti¹, S P Senda¹, S M RFDH², Y E Prada² and E Oktariani²

¹ Center of Energy Resources Development Technology and Chemical Industry, BPPT

² Polytechnic STMI Jakarta

E-mail: joni.prasetyo@bppt.go.id

Abstract. Biofuel is a solution to reduce the dependence of fossil fuels. Pure Plant Oil (PPO) of *Calophyllum inophyllum* L. is a potential raw material for green diesel through the processes of deoxygenation, hydrotreating, and isomerization. Deoxygenation of the PPO with NiMo / Al₂O₃ catalyst was carried out in a stirred autoclave reactor at a temperature of 300 - 400°C for 3 hours, and the water/PPO ratio was 1:2 and 1:4. The result showed that deoxygenation would work more effective at high temperature as indicated by higher CO and CO₂ resulting from carboxylation and carbonylation. In addition, raising the reaction temperature from 300 to 400°C succeeded in increasing the diesel fraction of C16 - C20 by 33.01% and decreased the fraction of C21-C25 by 2.41%. Increasing water/ppo ratio did not give any significant improvement on green diesel products.

1. Introduction

Energy crises especially fuel occurs in the world in last recent decades and has significant impact on the hiking fuel price, including in Indonesia. Indonesia which is not only in the list of crude fossil fuel exporting countries but also in the list of importing countries. Therefore, the price of the crude fuel currently affects further to domestic market.

Alternative fuel such as bio-fuel that treated from renewable resources is expected to reduce dependence on fossil fuel. Pure Plant Oil (PPO) that purified of crude plant oil is one of renewable bio-fuels [1]. PPO of *Calophyllum inophyllum* L.'s (PCO) derivative such as green diesel can replace fossil diesel. The green diesel can be achieved through a series processes of PCO through deoxygenating, hydrotreating and isomerization [2].

Indonesia as a tropical country is a heaven for plants for growing in. Almost all plants can grow in Indonesia. Biomass resources are scattered throughout the mainland of Indonesia but the utilization is not maximized yet. One potential plant that produces oil is *Calophyllum inophyllum* L. *Calophyllum inophyllum* L. oil is suitable as resource for green diesel because *Calophyllum inophyllum* L. oil is categorized as non-edible oil. Oil content in *Calophyllum inophyllum* L. seed is quite high at level 50%-73% [3]. In addition, *Calophyllum inophyllum* L. can grow in marginal areas. The extent of marginal area that can be utilized in Indonesia currently reaches 255,350 ha. The area is spread wide

³ To whom any correspondence should be addressed.



in West Sumatra, in Riau, in Jambi, in South Sumatra, in Lampung, in Java, in West Kalimantan, in Central Kalimantan, in Sulawesi, in Maluku and in Nusa Tenggara Timur [4].

In this study of deoxygenation of PCO as the first step of upgrading PCO process was done to produce green diesel. Green diesel is known as the second generation of bio-diesel that has very similar characteristic with diesel. Therefore, green diesel can replace fossil-diesel rather than partially blended like biodiesel (Fatty Acid Methyl Esther)[2]. Deoxygenation is an effective process in order to economization H_2 need to produce green diesel that usually through two processes HydroDeOxygenation (HDO) and isomerization of PCO. As is in HDO, deoxygenation is separation process of HDO with hydrotreating. Two reactions that expected to occur in deoxygenation as well as in HDO are decarboxylation and decarbonylation. This work studied the effect of temperatures and water-oil ratios in conversion of PCO to green diesel.

2. Materials and Methods

2.1 Materials

2.1.1 Crude of *Calophyllum inophyllum* L. oil, was gotten from Cilacap regency. This crude oil was purified so that the FFA content was less than 1%, namely PCO. The characteristic of Crude of *Calophyllum inophyllum* L. oil is shown on table 1.

Tabel 1. Characteristic of *Calophyllum inophyllum* LOil[5].

Characterization	Annotation
Color	Dark green
Viscosity	High viscosity
Iodinenumber(mg iod/g minyak)	100 – 115
Density at 20°C (g/cm ³)	0,920 - 0,940
Refraction Index	1,4750 - 1,4820
PeroxideNumber(meq/kg)	<20,0
Lipid fraction	98 – 99,5 %
Fatty Acid (%)	
• Palmitic Acid (C16 : 0)	15 – 17 %
• Palmitoleic Acid (C16 : 1)	0,5 – 1 %
• Stearic Acid (C18 : 0)	8 – 16 %
• Oleic Acid (C18 : 1)	30 – 50 %
• LinoleicAcid(C18 : 2)	25 – 40 %
• ArachidAcid(C20 : 0)	0,5 – 1 %
• GadoleicAcid(C20 : 1)	0,5 – 1 %

Unfortunately, the PCO still had high viscosity as its crude. Analyzing of PCO for total C, H, N, and S were 59.72, 8.65, 8.27% and 60 ppm, respectively. By this content, calorie content was 39,329 J/g.

2.1.2 A commercial catalyst, $NiMo/\gamma-Al_2O_3$, was used in this deoxygenation. In general, this $NiMo/\gamma-Al_2O_3$ catalyst has been analyzed and the composition is shown at tabel 2.

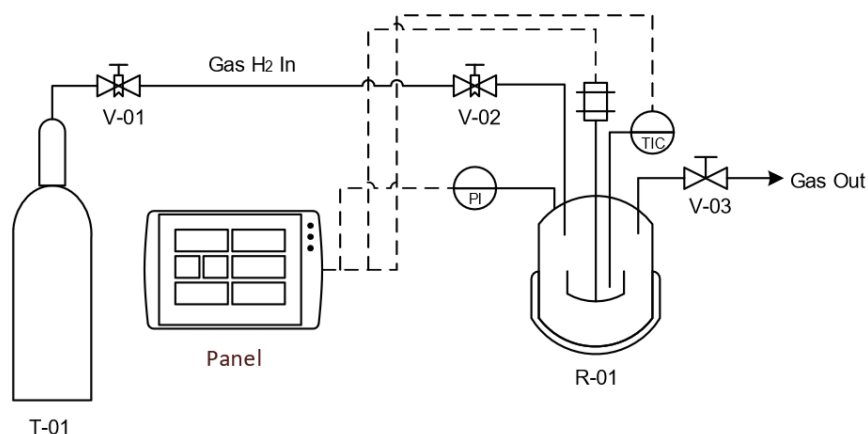
Tabel 2. Specification of commercial NiMo/ γ Al₂O₃ catalyst.

Compound	% weight
NiO	4,0 - 6,0
MoO ₃	2,0 - 24,0
γ Al ₂ O ₃	Balance

2.2 Methods

2.2.1 Catalyst Preparation. Catalyst preparation was carried out by putting the catalyst on the stirrer that covered by wire mesh in order to keep the catalyst from scattered and eroded. However, the catalyst was still able to have interaction with solution water-PCO. Next is the catalyst reduction to activate the NiMo/ γ Al₂O₃ catalyst with H₂ (T-01) in condition of 30 bar for 3 hours.

2.2.2 Deoxygenation. After catalyst reduction, reactor's cover is slightly opened to minimize contact with oxygen of air when the mixing of water-PCO was poured into reactor (R-01). The batch reactor was a stainless steel cylindrical shape with a volume of 500 ml. The stirrer was equipped to make the mixture homogeny. Figure 1. shows the batch reactor system. Water-oil ratio was adjusted according experimental design, at ratios 1:2 and 1:4. Deoxygenation was carried out by regulating temperatures at 300°C, 325°C, 350°C, 375°C and 400°C. Water would be evaporated and reach superheated steam. Prior to each experiment, to minimize oxygen content in the reactor, the rest air inside the reactor was purged using H₂ for 3 times before deoxygenation. The deoxygenation as prescribed in experimental planning was conducted within a 3-hour.

**Figure 1.** Schematic of Deoxygenation System.

2.2.3 Separation Process. During the deoxygenation process, agitation in the reactor would cause some of the catalyst to be crushed. Therefore, the catalyst particle in the water-PCO solution should be filtered gradually. The last filtering was using filter-vacuum system to remove the rest impurities.

2.2.4 Analysis. Viscosity was measured using the Lauda Viscotemp 18s Viscometer. 10 mL sample was inserted into the capillary tube using a pipette and suck the sample over the second limit (red ribbon mark). The time it took PCO dropped between the first marker and the second marker in the capillary was recorded. Each PCO was measured using different capillaries constants: 0.1199, 0.1198 or 0.1197 for various temperatures.

Gas chromatograph thermal conductivity detector (GC-TCD 8A) Shimadzu 2014 was used to analyze H₂, CO, CO₂ and CH₄. Injection temperature, cooling temperature and final temperature were set to 100°C, 50°C and 50°C, respectively. Gas in sample bag was inserted by pushing the sample bag smoothly for 30 seconds.

Gas Chromatograph Flame Ionization Detector (GC-FID) was used to analyze upgraded PCO with GC-FID SCION 456 appliance. The column was BR-1 with 100% dimethyl polysiloxane as stationary phase. The gases supply of He as mobile phase and H₂ and compressed air was used as make up to support the ignition. Vial that incorporated 0.05 gr sample was mixed with 1 mL hexane.

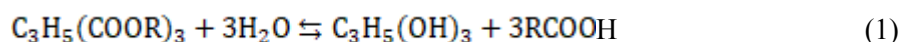
Flash Point, the point of flame of the upgraded PCO was measured using flash point AMETEK, Gabrer instruments mini flash FLP touch. Anisole was the standard at flash point 42-44°C and the setting of standard D6450 ASTM 930 was applied. The flash point apparatus has specification range of characteristic from 50°C to 200°C. Sample was analyzed by putting 1 ml sample in a cup and inserting into the apparatus.

3. RESULT AND DISCUSSION

Deoxygenation PCO with superheated steam was started with the hydrolysis of triglyceride. The hydrolysis would produce FFA [6]. Based on the product analyzing, the discussions will be explained by the gas analysis formed during the deoxygenation and the analysis of changes in structure or composition in PCO.

3.1 Observation at gas phase

Three moles superheated steam and one mole triglyceride would produce three moles of FFA and one mole of glycerol as described at equation 1[7]:



The presence of NiMo/ γ -Al₂O₃ catalyst would cause further the reaction of decarboxylation and decarbonylation. Once FFA was formed from triglycerides, the FFA would then break down catalytically to straight-chain alkenes and gases CO and CO₂, decarboxylation and carbonylation. At the first pathway was decarboxylation. The product formed was paraffinic hydrocarbon induced by carboxymethyl clumps and releasing carbon dioxide [8]:



The second pathway was decarbonylation. The product formed was olefinic hydrocarbon induced also by the removal of the carboxyl group and releasing carbon monoxide and H₂O [8].



Therefore, this work observed the deoxygenation of PCO in batch process over NiMo/ γ -Al₂O₃ through gases formation. The presence of unsaturated FFA like oleic acid and linoleic acid, they would also experience the same process, converted also to saturated diesel range hydrocarbons through hydrolysis, decarboxylation and carbonylation.

In the raising water amount as described by water-PCO ratio, for example from ratio = 1:4 and 1:2, the gases formation would shift to tend CO rather than CO₂, especially at high temperature as shown at figure 2. However, the magnitude of this process shift was not so significant. It can be seen in the amount of CO₂ that remains much higher than CO. Therefore, it should be more paraffinic hydrocarbon rather than olefinic hydrocarbon. The decrease of CO₂ caused by addition of water in decarboxylation was between 13.75% and 23.66%. The sharpest lowering was 7.36% at condition

375°C, from 31.09% to 23.73%. In addition, lowering CO₂ formed at 400°C was from 37.50% to 30.27% [9,10,11,12].

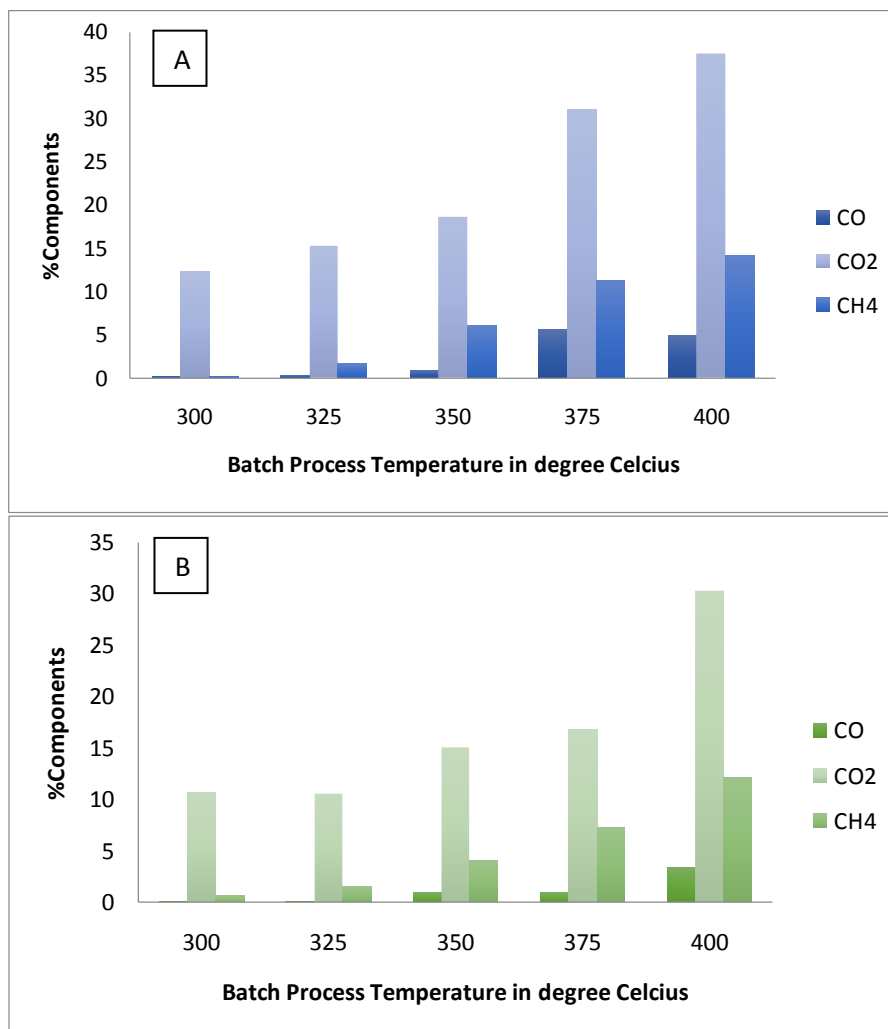


Figure 2. Deoxygenation of PCO with Superheated Steam (A) Water-PCO Ratio = 1:4, (B) Water-PCO Ratio = 1:2.

The composition of effluent gas was not only carbon dioxide and carbon monoxide but also methane [11,12]. Methanation occurred because of the presence of CO and CO₂ that react with steam, shift water reaction. Shift water gas reaction is an equilibrium reaction where H₂ would be produced with the existence of those components as described by equation 4.

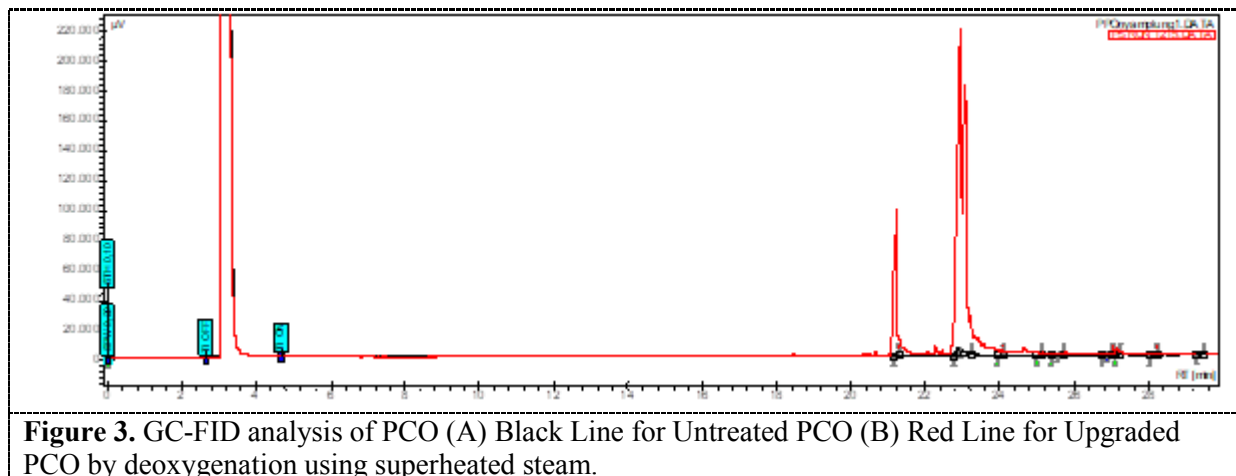


The subsequent process due to the formation of CO, CO₂, and H₂ was methanation as described at equation 5 and 6 [13,14,15]. CO and CO₂ would produce CH₄ and H₂O through hydrogenation.

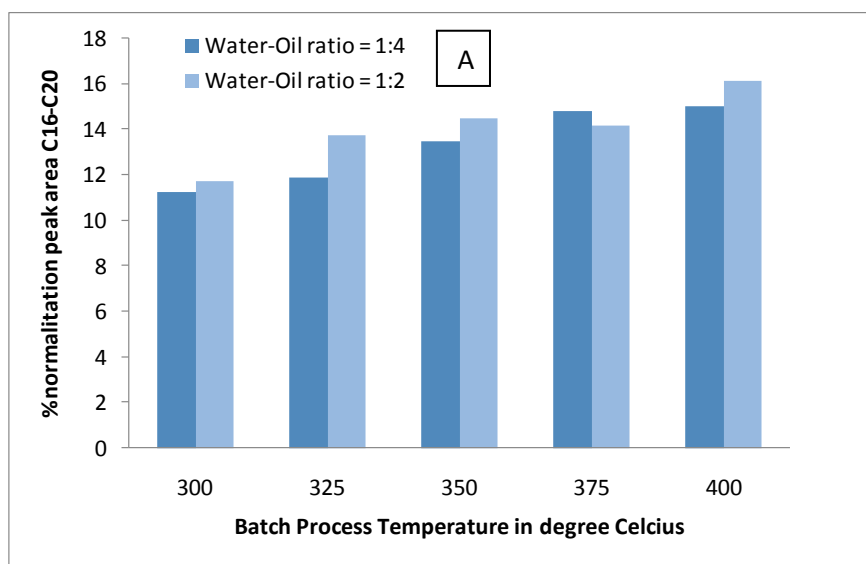


3.2 Observation at liquid phase

Discussion for the upgraded PCO is based on GC-FID analysis. As shown at figure 3, the column cannot detect triglyceride but only detect hydrocarbon. Therefore, there is no peak at original PCO analysis (black line). Upgraded PCO, red line, shows that paraffinic hydrocarbon and olefinic hydrocarbon was detected.



The presence of paraffinic hydrocarbon and olefinic hydrocarbon were is the evidence of the carbonylation and carboxylation occurrence in this deoxygenation. Estimation of the paraffinic hydrocarbon and olefinic hydrocarbon formation were calculated based on the peak area of GC FID analysis.



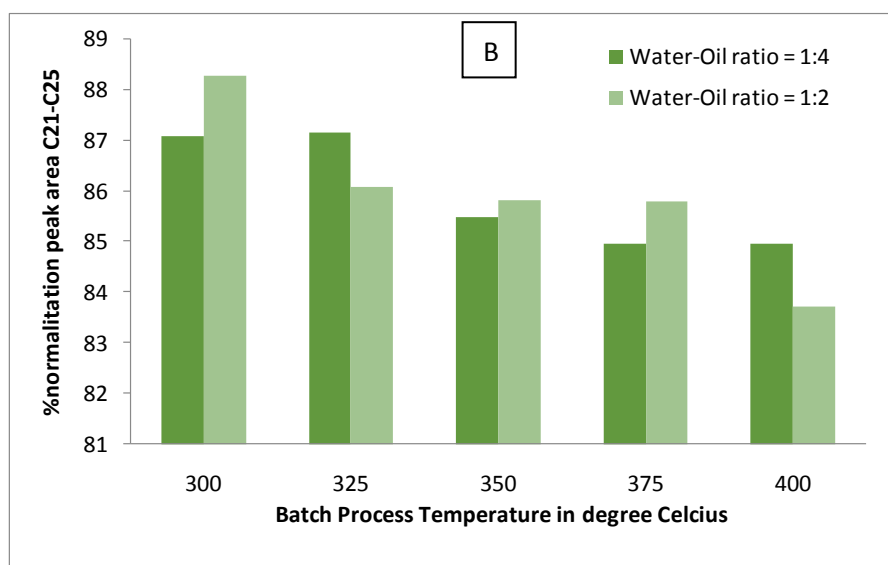


Figure 4. Estimation by Normalization of Conversion to Paraffinic Hydrocarbon and Olefinic Hydrocarbon in Upgraded PCO (A) C16-C20 (B) C21-C25.

As shown at figure 4, raising temperature would improve the conversion to longer hydrocarbon chain. However, water quantity was not significantly influence the hydrocarbon conversion, both C16-C20 yield and C21-C25 yield. C16-C20 yield increased only 3.74%, from 11.33% to 15.07% at operating conditions 300°C and 400°C, respectively. Meanwhile, C21-C25 yield decreased only 2.1%, from 87.08% to 84.98% at the same conditions.

However, deoxynated PCO analyzation was not improved significantly. The deoxynated PCO for total C, H, N, and S were 59.67, 8.71, 8.27, 7.91% and 50 ppm, respectively. Calorie content was 39,400 J/g. This calorie content was almost the same as untreated PCO. It might be some water trapped in upgraded PCO. Moreover, the properties of upgraded PCO have changed from its original PCO. Based on the regulation of fuel in Indonesia stated on Decree of Director General of Oil and Gas No. 978.K/10/DJM.S/2013: “Standard and Quality (specification) of fuel: Type Diesel 48 marketed in the country”, table 3 shows the comparison of the product deoxygenation with reference standards issued by the government.

Table 3. Properties of Upgraded PCO.

Characteristic	PCO	Upgraded PCO	Decree Oil and Gas No. 978.K/10/DJM.S/2013	
			Minimum	Maximum
Density, kg/m ³	912	892	815	860
Visosity, 40°C in mm ² /S	38.24	21.52	2	4.5
Sulphur content, ppm	<50	<50	-	50
Flash point, °C	>200	>200	52	-

4. Conclusion

Deoxygenation using superheated steam is complex and interconnected reactions. Starting from the hydrolysis of triglyceride to FFA formation, the catalytic reaction of carboxylation and carbonylation, shift water gas reaction and methanation. The properties of deoxygenation product and HDO product was similar. The effluent gases of both process was also almost the same. Therefore, deoxygenation offers efficiency process in H₂ usage.

Raising water-PCO ratio gave increasing C16-C20 yield 33.01% and decreasing C21-C25 yield 2.41% at temperature 400°C. The calorie content reached up to 39.400 Joule/gr because of Oxygen reduction in upgraded PCO. However, this work did not improve the calorie content in PCO yet. Further suggested process to achieve green diesel including improving calorie value is treated with hydrotreating and isomerization.

References

- [1] R. Prihandana dan R. Hendroko 2008 *Penebar Swadaya*, Jakarta.
- [2] E. Santillan-Jimenez and M. Crocker 2012 *Chemical Technology and Biotechnology* **87**(8) 1041-50.
- [3] A.C. Dweek and T. Meadows 2002 *International J. Cos. Sci.* **24** 1-8.
- [4] Balai penelitian dan pengembangan hutan 2008 *Forestry Department*.
- [5] V.J. Debaut, Y.B. Jean and S.A. Greentech 2005 *Greentech* St. France.
- [6] R. Brockmann, G. Demmering, U. Kreutzer, M. Lindemann, J. Plachenka, U. Steinberner 2005 *Fatty acids, Ullmann's encyclopedia of industrial chemistry* Weinheim Germany: Wiley-VCH Verlag GmbH & Co. 1-34.
- [7] P.H.L. Moquin and F. Temelli 2008 *Fluids* **45** 94-101.
- [8] M. Snåre, I. Kubickova, P. Mäki-Arvela, K. Eränen and D.Y. Murzin 2006 *Ind. Eng Chem Res* **45** 5708-15.
- [9] M. Snåre, I. Kubickova, P. Mäki-Arvela, D. Chichova, K. Eränen and D.Y. Murzin 2008 *Fuel* **87** 933-45.
- [10] S. Lestari, I. Simakova, A. Tokarev, P. Mäki-Arvela, K. Eränen and D.Y. Murzin 2008 *Catal Lett* **122** 247-51.
- [11] P. Mäki-Arvela, I. Kubickova, M. Snåre, K. Eränen and D.Y. Murzin 2007 *Energy Fuels* **21** 30-41.
- [12] W.C. Wang, et.al. 2012 *Fuel* **95** 622-29.
- [13] A. Srifa, et al. 2014 *Bioresource Technology* **158** 81-90.
- [14] W. Kiatkittipong, et al. 2013 *Fuel Processing Technology* **116** 16-26.
- [15] A. Guzman, et al. 2010 *Catalysis Today* **156**(1-2) 38-43.