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Procedia Engineering 148 (2016) 1369 – 1376

**Procedia
Engineering**www.elsevier.com/locate/procedia

4th International Conference on Process Engineering and Advanced Materials

Thermodynamic Equilibrium Analysis of Triolein Hydrodeoxygenation for Green Diesel Production

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Abstract

The recent trends in biofuel research outcome mainly focused on the conversion of vegetable oil to the value added hydrocarbon fuels. Hydrodeoxygenation is one of the promising route for clean energy production. In this study, triolein was selected as the model compound representing rubber seed and jatropha seed oil to produce straight chain hydrocarbon. The thermodynamic equilibrium analysis was carried out using Aspen HYSYS software to study the thermodynamic interaction between hydrogen to triolein molar ratio, reaction pressure and temperature. The study revealed that thermodynamically, the optimum feed molar ratio of H₂ to triolein is at 5:1 and pressure of 70 bar produced high amount of desired products, The selectivity for C₁₈ decreases with the increased of temperature, as well as the ratio of C₁₇/C₁₈. The by products such as methane and propane are resulted from several side reactions, namely methanation, thermal cracking and reverse water gas shift reaction. This can possibly be minimized by using efficient and effective catalyst design.

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Peer-review under responsibility of the organizing committee of ICPEAM 2016

Keywords: Thermodynamic modeling; Hydrodeoxygenation; Aspen HYSYS; Non-edible oil.

1. Introduction

The study of hydrodeoxygenation (HDO) reaction has opened up another pathway of providing alternative fuel other than the typical fossil fuel. Recent research works favored the conversion of non-edible oil to fossil fuels via HDO process. These oils may present many benefits including domestic usage, less greenhouse effect and increased national energy security [1-4]. However, there is a need to develop an efficient process of producing high quality biofuels. There are many types of oils and triglycerides are available for hydrocarbon conversion among which rubber seed oil and jatropha seed oil are the attractive options as feedstock. Rubber seed and jatropha seed contains high energy density, high oil production at reasonable price, easy conversion to liquid, and

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availability of land and maintenance of plantation of rubber seed [5]. Several technologies have been studied to convert the triglycerides into useable fuel such as transesterification, pyrolysis, micro-emulsifications and HDO [6, 7]. HDO however, possesses a greater opportunity to be studied in recent years due to selective product properties, lower environmental impact and economically viable [6, 8].

Several research works have been reported previously on experiments of HDO of vegetable oil and model compounds [9, 10]. There is a lack of studies on thermodynamic analysis of triglycerides to understand the HDO process. Smejkal *et al.* [11] has simulated the thermodynamic analysis of tristearate to represent vegetable oil using Aspen Plus software, and compared with the experimental data. However, many information and data are not specified and thus could not be retrieved from their work. The purpose of this work is to demonstrate the feasibility of conversion of triolein (represents the major component in rubber seed oil) into a diesel range hydrocarbon by HDO process [5]. With the use of rubber seed oil with different feed ratio, the change in pressure and temperature are further studied. The final product, long chain *n*-alkanes can be confirmed through the chemical equations given. The comparative studies of low and high hydrogen to feed ratio are also included.

In this study, a thermodynamic model for HDO of rubber seed oil was formulated using Gibbs free energy minimization method to predict the equilibrium composition of the product mixtures. The effects of reaction pressure, temperature and hydrogen-to-feed molar ratio on C_{17-18} yield and selectivity of C_{18} are determined using the proposed computational framework.

2. Methodology

Rubber seed and jatropha seed oil, like other vegetable oils, comprises of a mixture of triglycerides (fatty acid ester of glycerol). The unknown chemical composition and unavailability of physical and chemical properties of the triglycerides present in these oils pose a challenge in performing thermodynamic equilibrium analysis. As an example, linoleic acid is the major fatty acid constituent found in rubber seed oil, followed by oleic acid, palmitic and stearic acids as reported in the previous studies [5]. In this study, triolein was chosen as a model compound to represent rubber seed and jatropha seed oil as shown in Figure 1. The thermodynamic model proposed in this work is based on Gibbs free energy minimization method. There are four property packages (PR-TWU, SRK-TWU, Wilson and PRSV), in which Peng-Robinson as property package was found more compatible for this study due to combine equation state and Gibb's minimization energy method. The analysis performed using R-Gibbs reactor with Peng-Robinson as property package, the most general equation of state for the natural gas systems in the oil refineries.

The Gibbs reactor calculates the existing compositions such that the phase and chemical equilibria of the vapour and liquid streams are attained. The equilibrium calculations employing the method of Gibbs free energy minimization were carried out using Aspen HYSYS® V8.0, a simulation software developed by AspenTech™. Fig. 2. depicts the reactor scheme for the present investigation.

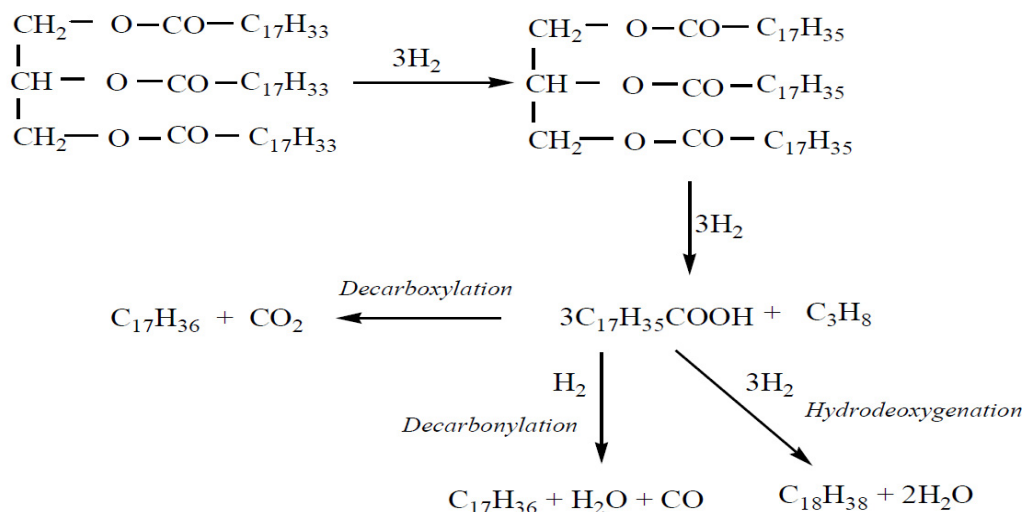


Fig. 1. Triolein reaction process routes for complete hydrodeoxygenation [11].

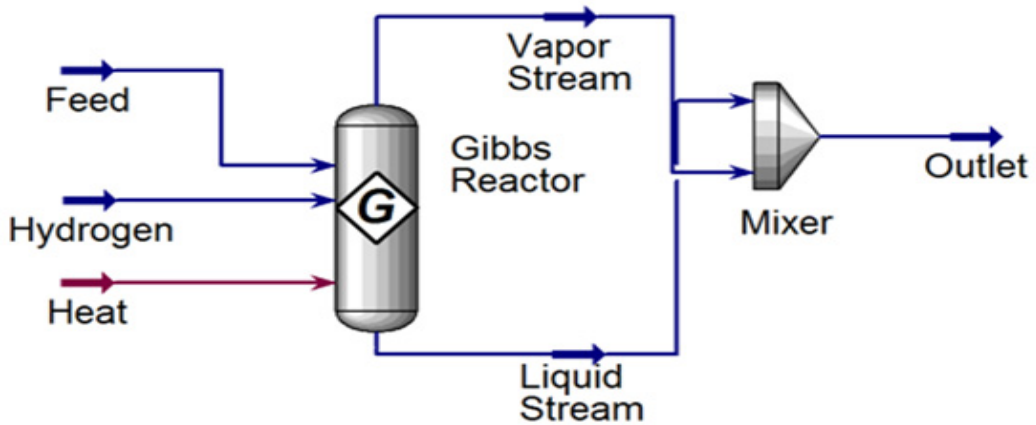


Fig.2. Simulation configuration of triolein using Aspen HYSYS software

2.1. Simulation layout by using Aspen Hysys V8.0

Feed and hydrogen inlet streams are composed of pure triolein (C₅₇H₁₀₄O₆) and H₂ gas respectively. Hydrogen-to-feed ratio mentioned refers to the ratio of the molar flow rate of the hydrogen stream to that of the feed stream. Feed of triolein is introduced with supply of pure hydrogen gas. Based on the hydrodeoxygenation process, breaking of triolein molecular bond requires hydrogen gas as the removal of oxygen gas from the system by using Gibbs reactor. Heat is supplied to ensure the reactor functioned isothermally and optimally. After the reaction, the products formed in vapour and liquid stream are further mixed gradually and finally completed at outlet line. The simulation result can be triggered based on outlet products. Previous studies suggested three possible reaction pathways for oxygen removal by H₂ from triolein (R1-R3), which produces *n*-alkanes of the full length of the fatty acid chains, *n*-alkane one C-atom shorter than the total length of the fatty acid, propane, water, carbon dioxide and carbon monoxide [12]. When carbon dioxide and carbon monoxide are formed, there are two additional reactions. These are water gas shift and methanation (R4-R5) [13, 14]. Therefore, the equilibrium calculations of the reacting system include *n*-octadecane, *n*-heptadecane, propane, methane, carbon dioxide, carbon monoxide, hydrogen and water as possible products.

2.2. Process Methodology (Thermodynamic balance (Oxygen removal) and Reaction mechanism of HDO of triolein)

Chemical equilibrium in the Gibbs reaction system is general can be classified by the minimisation of Gibbs free energy as represented in equation 1 [15].

$$\Delta G_r^T = -RT \ln K_E(T) \tag{1}$$

K_E represents a dimensionless equilibrium constant of the chosen reaction (mass/mass) and T is temperature (K). Besides that, change of energy can be achieved through a consideration of change of enthalpy and multiplication temperature and change of entropy as mentioned in equation 2 [15].

$$\Delta G_r^0 = \Delta H_r^0 - T \Delta S_r^0 \tag{2}$$

Gibbs free energy minimisation method is a non-stoichiometric method, which specify that if the total Gibbs free energy is minimised, then the system is favored thermodynamically. Subjected to a given temperature and pressure, to minimize the Gibbs free energy, both side of reactants and product side must have a zero difference [16]. The following equations are related to the derivation of Gibbs [17-21]. With the assumption of constant pressure and temperature, the equilibrium system can be expressed as follows:

$$dG = \sum_{i=1}^C \sum_{j=1}^P \mu_i dn_{ij} = 0 \tag{3}$$

In addition, the chemical potential of species *i*, μ_i can be calculated using the following equation:

$$\mu_i = RT \left[\ln \left(\frac{\phi_i P}{P_0} \right) + \ln(X_i) + G_i^0(T, P_0) \right] \tag{4}$$

2.3. Formulation (Selectivity)

In this work, selectivity is much concerned as it is to aim desired product from HDO reaction. Moles of C₁₈ and C₁₇ is divided by all carbon element present after the reaction.

$$\text{Selectivity } C_{18} = \left(\frac{\text{moles of } C_{18} \text{ formed} \times 18}{\text{moles of } C_{17} + C_{18} + CH_4 + C_3H_8 + CO + CO_2 + \text{Triolein}} \right) \times 100\% \quad (5)$$

$$\text{Selectivity } C_{17} = \left(\frac{\text{moles of } C_{17} \text{ formed} \times 17}{\text{moles of } C_{17} + C_{18} + CH_4 + C_3H_8 + CO + CO_2 + \text{Triolein}} \right) \times 100 \quad (6)$$

3. Results and Discussion

The operating conditions such as temperature pressure established the noticeable effects on the reaction products. The presence of hydrocarbon with other oxygenates in HDO process make it thermodynamically non-ideal systems. To deal with this type of system, there should be a suitable thermodynamic model that can reveal the reaction at high temperature and pressure, high liquid phase, non-ideality and natural gases such as CO₂, CO, H₂ and others[22]. Concerning HDO reaction, very fewer studies have reported on thermodynamic modeling and simulation of the reaction parameters.

In this work, the comparison between Aspen HYSYS v8 and Aspen Plus v8 at constant feed ratio H₂: Feed (5:1) and pressure of 70 bar are shown in Fig.3 and Fig.4. The results are significant by using Peng-Robinson as our property package, both processing simulator produced approximately same result based on the operating parameters and components included.

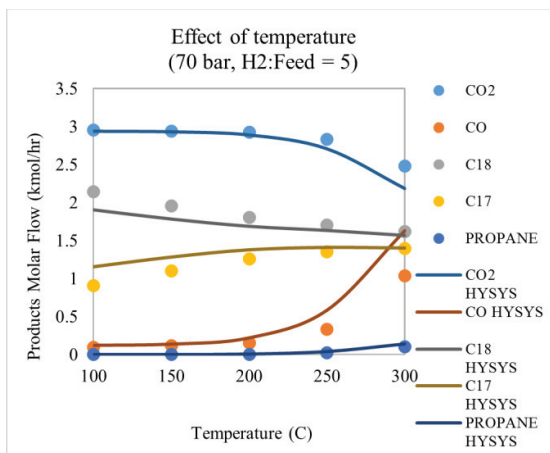


Fig.3. Product molar flow against temperature in Aspen HYSYS and Plus.

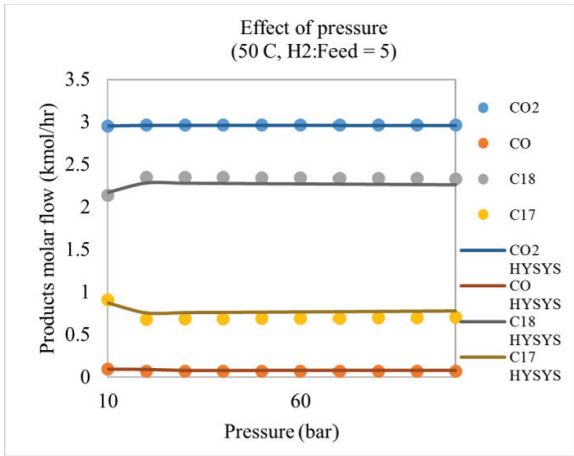


Fig. 4. Product of molar flow against pressure in Aspen Plus and HYSYS.

3.1 Effect of reaction pressure

The simulation study demonstrates that the effect of pressure increase at elevated pressures for C₁₇ and C₁₈ selectivity, as depicted in Fig.5. C₁₇ gives higher selectivity with a range of 25-30% with variable pressure applied. It indicates the effect of pressure is insignificant. A higher pressure applied onto this system makes fast reaction of triolein and hydrogen. Thus, the product of reaction favors to produce more carbon products. Besides, the selectivity of C₁₇ increase over range of pressure due to effect of higher decarbonylation/decarboxylation reaction over HDO of C₁₈ products. Other than that, C₁₈ would react also with excess H₂ thus producing C₁₇. The trends seem to be consistent as pressure is at 140 bars. The possible result of the trend due to excess hydrogen reacts with CO₂, which produces CO gas due to reverse water gas shift side reaction.

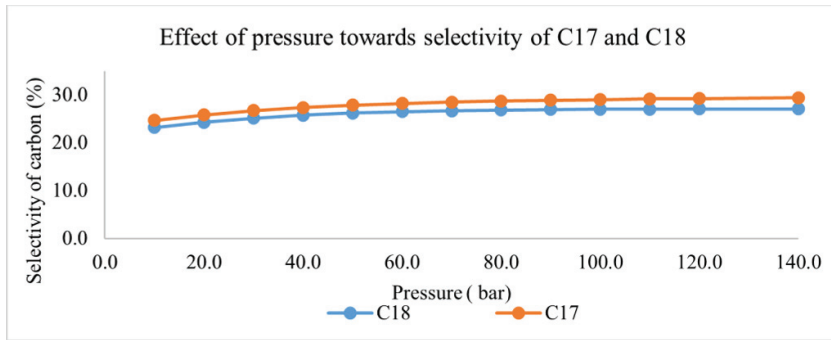


Fig. 5. C₁₈ selectivity against pressure at feed ratio of 20 and T=250 °C

3.2. Effect of Hydrogen to Feed Molar Ratio

The effect of the changing hydrogen flow rate at a constant total pressure was studied by varying hydrogen/feed molar ratio.

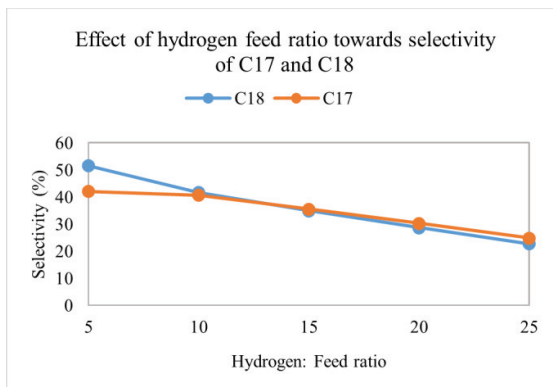


Fig. 6: C₁₈ & C₁₇ Selectivity against H₂: Feed ratio

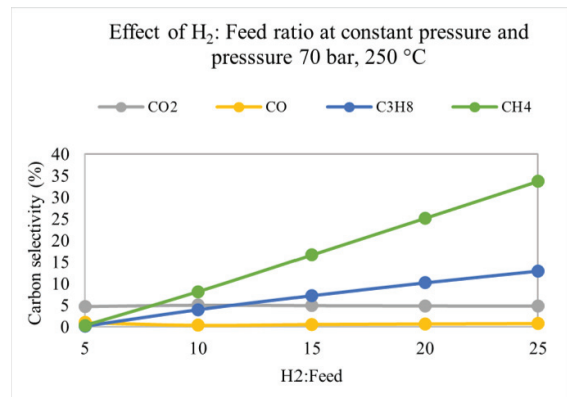


Fig. 7. Carbon Selectivity against H₂ to Feed ratio

An optimum hydrogen/feed ratio that produces highest desired products was identified. Fig. 6. shows hydrogen/feed ratio of 5:1 produced almost 100 % *n*-octadecane and *n*-heptadecane. With the increased of hydrogen flow rate (k mol/hr per mol) of triolein (feed) at constant total pressure, partial pressure of hydrogen increases. The extent of hydrodeoxygenation and decarboxylation reactions increases due to the increase in available hydrogen, producing more C₁₇ and C₁₈. However, further increase in hydrogen-to-feed ratio decreases selectivity to C₁₇ and C₁₈. As methane and propane are thermodynamically more stable than heptadecane and octadecane, the system tends to favor the formation of these species in the presence of excess hydrogen, as observed in Fig. 7. Long chain hydrocarbon cracked into lower alkanes such as propane. The availability of high hydrogen feed ratio promoted the formation of by-products due to high concentration of hydrogen. High hydrogen to feed ratio promoted formations of by-products.

3.3. Effect of reaction temperature

Figure 8. illustrates the effect of temperature on triolein hydrodeoxygenation. The hydrogen to feed ratio was fixed in 20:1 and a pressure of 70 bar while the reaction temperature varied from 50 to 450 °C. Based on the observation, hydrodeoxygenation was favored over decarboxylation and decarbonylation at low temperature. The selectivity to *n*-C₁₇ increased at the expense of *n*-C₁₈ with increasing reaction temperature. This concurs with Huber *et al.*[1], Kikhtyanin *et al.* [23] and Šimáčěk *et al.* [24] experimental observations on hydroprocessing of sunflower oil-high vacuum oil mixture, sunflower oil, and rapeseed oil respectively. Their studies verified that the selectivity to decarbonylation/decarboxylation products increases with temperature. It was observed that C₁₇-18 selectivity decreases gradually with temperature. As shown in Fig. 9, with the increase in temperature, a decrease in C₁₇-18 products is observed, which is expected as increasing temperature favors the undesirable hydrocracking reactions competing with the desirable reactions of Bezegegianni *et al.* [25]. This was proved the constant increment of C₁ and C₄ as high temperature is introduced in the simulation. In short, the temperature has actually provided high heat enables bond breaking of triolein, thus reduce the molecular weight of this triglyceride. As a result, desired products become less and cracking process promotes formation of by-products. It is a big challenge to ensure appropriate temperature and pressure used to produce less unwanted products as explained in Fig. 9.

The reversible water gas shift reaction makes it difficult to determine whether the observed CO and CO₂ are produced by a decarboxylation reaction or by decarbonylation route [26]. It can be observed that as the temperature increased, CO increases and CO₂ decreases, which could be attributed to the reverse water gas shift reaction (RWGS) [26]. The CO/CO₂ ratio of less than unity suggested that decarboxylation was preferred to decarbonylation route in producing *n*-C₁₇. Therefore, the reaction would favor to lower operating temperature thermodynamically but practically, this will only work at a temperature more than 200°C. Hydrogen gas used to react for main reaction and further react to the side reaction. From the graph, the methanation had taken place as CO/CO₂ concentration is higher at temperature above 300 °C. As the production of methane rapidly occurred, desired product of the C₁₇ and C₁₈ will slow down. Thus, it is important to control the temperature and feed ratio into to ensure RWGS and methanation process did not occur rapidly. The higher production of octadecane to rise in temperature, but less heptadecane produced. As a result, side reaction is less favored in low temperature. Main reactions maximize and potentially give out less by-products, which lead to less side reaction to take place. Therefore, increasing of operating temperature the reaction rate increases but the conversion of triolein to main products becomes less favorable. Due to its exothermic nature, the high CO conversion is thermodynamically favored at low temperatures. Despite the thermodynamic variability at low temperatures, the reaction is kinetically favored at high temperatures. Hence, RWGS reaction is sensitive to temperature, with the tendency to shift towards the reactants side as temperature increases due to Le Châtelier's principle [27].

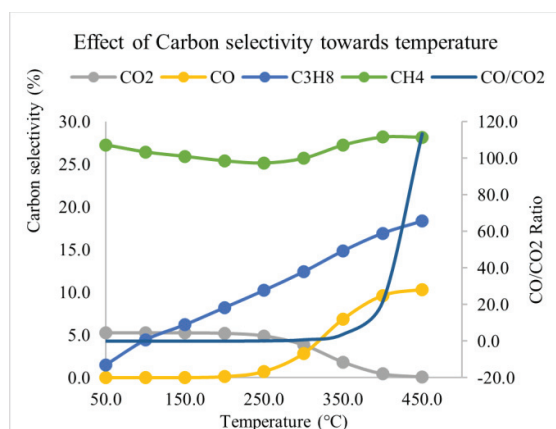


Fig. 8. Carbon selectivity against temperature.

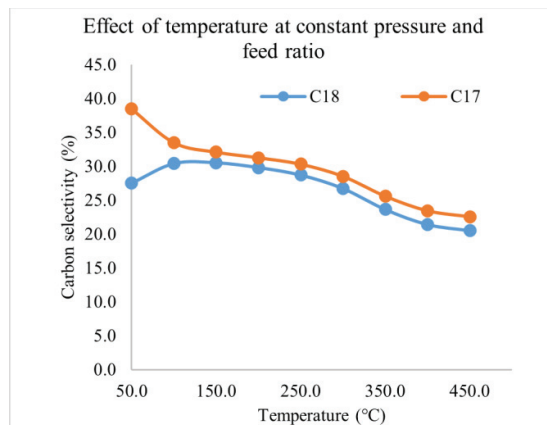


Fig. 9. Effect of temperature at constant pressure 70 bar and feed ratio 20 to 1.

4. Conclusion

Based on the results and discussion, we conclude that triolein would promote high selectivity of C18 and C17 by altering the feed ratio, temperature and pressure. The distribution of the desired products strongly depended on both reaction temperature and the hydrogen to feed molar ratio. The effects of the side reactions like methanation, thermal cracking and reverse water gas shift would be reduced if the reaction conditions are well controlled.

Acknowledgement

The authors would like to acknowledge the financial support provided by Yayasan Universiti Teknologi PETRONAS (YUTP) for this research project.

Reference

- [1] G.W. Huber, P. O'Connor, A. Corma, Processing biomass in conventional oil refineries: production of high quality diesel by hydrotreating vegetable oils in heavy vacuum oil mixtures, *Applied Catalysis A: General*, 329 (2007) 120-129.
- [2] M.A. Khan, S. Yusup, M.M. Ahmad, Acid esterification of a high free fatty acid crude palm oil and crude rubber seed oil blend: Optimization and parametric analysis, *Biomass Bioenergy*, 34 (2010) 1751-1756.
- [3] N.T. Tran, Y. Uemura, S. Chowdhury, A. Ramli, Vapor-phase hydrodeoxygenation of guaiacol on Al-MCM-41 supported Ni and Co catalysts, *Applied Catalysis A: General*, 512 (2016) 93-100.
- [4] N. Tran, Y. Uemura, S. Chowdhury, A. Ramli, A Review of Bio-Oil Upgrading by Catalytic Hydrodeoxygenation, in: *Applied Mechanics and Materials*, Trans Tech Publications, 2014, pp. 255-258.
- [5] J. Ahmad, S. Yusup, A. Bokhari, R.N.M. Kamil, Study of fuel properties of rubber seed oil based biodiesel, *Energy Convers. Manage.*, 78 (2014) 266-275.
- [6] S. Yusup, M. Khan, Basic properties of crude rubber seed oil and crude palm oil blend as a potential feedstock for biodiesel production with enhanced cold flow characteristics, *Biomass Bioenergy*, 34 (2010) 1523-1526.
- [7] M. Azizan, S. Yusup, F.M. Laziz, M. Ahmad, Production of bio-oil from oil palm's empty fruit bunch via pyrolysis, *Proceedings of the 3rd WSEAS International Conference on Energy Planning, Energy Saving, Environmental Education (EPES'09)*, (2009) 228-233.
- [8] M.M. Ahmad, M.F.R. Nordin, M.T. Azizan, Upgrading of bio-oil into high-value hydrocarbons via hydrodeoxygenation, *Ame. J. App. Sci.*, 7 (2010) 746.
- [9] M. Yasir, S. Chowdhury, N. Mansor, N.M. Mohamed, Y. Uemura, Upgrading of Pyrolysis Bio-Oil to Fuel over Supported Nanomaterials-A Review, in: *Appl. Mech. Materials.*, Trans Tech Publications, 2014, pp. 357-360.
- [10] N.T.T. Tran, Y. Uemura, S. Chowdhury, A. Ramli, Vapor-phase hydrodeoxygenation of guaiacol on Al-MCM-41 supported Ni and Co catalysts, *Applied Catalysis A: General*, 512 (2016) 93-100.
- [11] L. Hermida, A.Z. Abdullah, A.R. Mohamed, Deoxygenation of fatty acid to produce diesel-like hydrocarbons: A review of process conditions, reaction kinetics and mechanism, *Renewable Sustainable Energy Rev.*, 42 (2015) 1223-1233.
- [12] M. Jha, A.K. Sinha, P. Agnihotri, Hydroprocessing of Jatropha oil to produce green fuels, *Int J ChemTech Res.*, 5 (2013) 765-770.
- [13] R. Egeberg, N. Michaelsen, L. Skyum, Novel hydrotreating technology for production of green diesel, *ERTC*, Nov, (2009) 9-11.
- [14] M.T. Azizan, K. Hellgardt, D. Chadwick, Thermodynamic Analysis of Autothermal Reforming of Oxygenated Hydrocarbons At Thermoneutral Condition for Hydrogen Production, in: *Applied Mechanics and Materials*, Trans Tech Publications, 2014, pp. 730-733.
- [15] P.W. Atkins, *Physical chemistry*, Oxford University Press, 1978.
- [16] S. Aktas, M. Karakaya, A.K. Avci, Thermodynamic analysis of steam assisted conversions of bio-oil components to synthesis gas, *International Journal of Hydrogen Energy*, 34 (2009) 1752-1759.
- [17] S. Adhikari, S. Fernando, S.R. Gwaltney, S.D. Filip To, R. Mark Bricka, P.H. Steele, A. Haryanto, A thermodynamic analysis of hydrogen production by steam reforming of glycerol, *International Journal of Hydrogen Energy*, 32 (2007) 2875-2880.
- [18] Y.M. Alshammari, K. Hellgardt, Thermodynamic analysis of hydrogen production via hydrothermal gasification of hexadecane, *International Journal of Hydrogen Energy*, 37 (2012) 5656-5664.
- [19] C.C.R.S. Rossi, C.G. Alonso, O.A.C. Antunes, R. Guirardello, L. Cardozo, Thermodynamic analysis of steam reforming of ethanol and glycerine for hydrogen production, *International Journal of Hydrogen Energy*, 34 (2009) 323-332.
- [20] E.C. Vagia, A.A. Lemonidou, Thermodynamic analysis of hydrogen production via autothermal steam reforming of selected components of aqueous bio-oil fraction, *International Journal of Hydrogen Energy*, 33 (2008) 2489-2500.
- [21] W. Wang, Y. Wang, Thermodynamic analysis of hydrogen production via partial oxidation of ethanol, *International Journal of Hydrogen Energy*, 33 (2008) 5035-5044.

- [22] E.M. Turpeinen, E. Sapei, P. Uusi-Kyyny, K.I. Keskinen, O.A.I. Krause, Finding a suitable thermodynamic model and phase equilibria for hydrodeoxygenation reactions of methyl heptanoate, *Fuel*, 90 (2011) 3315-3322.
- [23] O.V. Kikhtyanin, A.E. Rubanov, A.B. Ayupov, G.V. Echevsky, Hydroconversion of sunflower oil on Pd/SAPO-31 catalyst, *Fuel*, 89 (2010) 3085-3092.
- [24] P. Šimáček, D. Kubička, G. Šebor, M. Pospíšil, Hydroprocessed rapeseed oil as a source of hydrocarbon-based biodiesel, *Fuel*, 88 (2009) 456-460.
- [25] S. Bezergianni, A. Dimitriadis, A. Kalogianni, P.A. Pilavachi, Hydrotreating of waste cooking oil for biodiesel production. Part I: Effect of temperature on product yields and heteroatom removal, *Bioresource technology*, 101 (2010) 6651-6656.
- [26] C. Ratnasamy, J.P. Wagner, Water gas shift catalysis, *Catal. Rev.*, 51 (2009) 325-440.
- [27] D.F.B. Lima, F.A. Zanella, M.K. Lenzi, P.M. Ndiaye, Modeling and Simulation of Water Gas Shift Reactor: An Industrial Case.