Biofuel Produced from Nyamplung Oil Using Catalytic Cracking Process with Zn-HZSM-5 Catalyst

Agus Budianto[1], Danawati Hari Parjitno[1], Kusno Budhikarjono[1], Achmad Roesyadi[1], and Ratna Ediati [2]

Abstract—***Indonesia Presidential Regulation No. 5/2006 on National Energy Policy suggests that the government should speed up the implementation of the use of alternative energy or fuel substitution. Biofuel synthesis is one way to overcome the shortage of energy and reduce global warming due to the use of fossil fuel. Biofuel can be produced from a variety of vegetable oil. Beside palm oil, nyamplung oil can be used to produce biofuel. The technically main obstacle in producing biofuel is the availability of the catalyst. The availability catalyst are only imported and expensive. Researchers have tried to engineer a new type of catalyst that complete the weakness of zeolite based catalyst. The study was conducted through experimental approaches, testing and observations and conducted the correlation of experiment variables with the quality of the resulted catalyst. The experiment was done by synthesizing catalyst and testing it to produce biofuel from nyamplung oil. The focus of the research is directed to the effect of operating variables on the composition of the resulted biofuel and obtain catalyst performance condition and optimum condition to produce biofuel in the fixed bed reactor. The resulted catalyst can change the nyamplung oil into biofuel. Biofuel from nyamplung oil cracking process showed that the composition is biogasoline, biokerosene and biodiesel. Biodiesel fraction is the highest fraction of the biofuel produced. The highest percentage of biodiesel at a temperature of 400°C was 60%, while the lowest percentage of biodiesel at a temperature of 300°C was 48%. Products density was in the range of 0.81 to 0.86 g/ml. The highest density occured at a reactor temperature of 300 °C was 0.86g/ml. The higher the nitrogen gas flow rate the more the biodiesel formed. At a temperature of 300°C and a nitrogen flow rate of 100 ml/min, the composition solar achieved was 60%.***

Keywords— Biofuel, Cracking, Catalyst, Nyamplung Oil, and Zeolites.

I. Introduction

In 2006, the Indonesian government has issued a policy that mandates a policy of national energy diversification. Presidential Decree No..5/2006 on National Energy Policy. This regulation states that the government should speed up the implementation of the use of alternative energy or fuel substitution in order to reduce fuel subsidy. Fuel used by the transport sector is the biggest consumption of the energy mix, so as to improve fuel security of supply in order to achieve a balance of energy mix by 2025. On the other hand depletion of world oil reserves and increasing environmental concerns pose a great demand to find a replacement for alternative sources of petroleum based fuel, including diesel and gasoline fuel (Leung et al, 2010).

Many scientists began researching to find a new kind of energy that is cheap, easy and environmentally friendly to replace energy sources that are available now, namely the use of vegetable oil. Vegetable oil which is converted into biodiesel by esterification and transesterification processes (Leung et al, 2010; Bhale, 2009, Demirbas, 2003; Budianto, et al, 2003, Kansedo et al, 2008) produces alkyl ester biodiesel. The completion of the characteristic of alkyl ester combustion was done by forming ozonida biodiesel (Bismo, 2005; Budianto, 2009). Vegetable oil can also be converted to biofuel by cracking to produce the broader product, i.e., biofuel (Dandik et al., 1980; Chang, 1983; Bhatia, et al., 1999; Farouq et al., 2004; Charusiri, & Vitidsant, 2005; Masuda et al., 2001; Thiam, 2009; Nurjannah et al, 2009a). Biofuel has advantages compared with alkyl ester biodiesel. The advantages of biofuel is that the product is liquid fuel with chemical components similar to those in conventional diesel oil (Dykstra. et al, 1988; Adjaye, et al, 1995).

Biofuel can be produced from a variety of plant and animal oil, but it is very interesting if the oil is an Indonesia's distinctive plant such as nyamplung. Nyamplung advantage as a raw material of biofuel is the seed has high yield, up to 74 %, and in the interests of its utilization, it does not compete with food. Several advantages in terms of the prospect of nyamplung development and other uses are nyamplung plant grows and spread naturally evenly in Indonesia; it easily regenerates and fruits throughout the year showed a highly survival power of the environment; a crop plant which is relatively easily cultivated either type (monoculture) or mixed forest (mixed-forest); it is suitable in drier climates; almost all parts of the the plant are useful and it produces a variety of products that has economic value; stand of nyamplung forest serves as a wind breaker for agricultural crops and conservation of coastal border, and the utilization of nyamplung biofuel reduces the use of forest trees for firewood; seed productivity is higher than that of other types of plant. Jatropha, palm and nyamplung produce seed of 5 tonnes/ha, 6 tonnes/ha and 20 tonnes/ha respectively. (PRESS RELEASE Number: S. 428/II/PIK-1/2008, Ministry of Forestry Republic of Indonesia)

Nyamplung oil is one of the alternatively potential raw materials to produce biofuel as a substitution of gasoline, kerosene and diesel because it is potential for the

[1]Agus Budianto, Danawati Hari Parjitno, Kusno Budhikarjono, and Achmad Roesyadi are with Departement of Chemical Engineering, Faculty of Industrial Technology, Institut Teknologi Sepuluh Nopember, Surabaya, 60111, Indonesia. E-mail: budi_2050@yahoo.com.

[2]Ratna Ediati is with Departement of Chemistry, Faculty of Mathematics and Science, Institut Teknologi Sepuluh Nopember, Surabaya, 60111, Indonesia.

development of nyamplung oil. This is supported by the fact that nyamplung cultivation does not require high investment. Potential availability of land for the development of nyamplung plants spread throughout Indonesia. When all of the needs of the biofuel were supplied by nyamplung, it will be needed 720,000 kilo liters of biodiesel, equivalent to 5.1 million tonnes of nyamplung seed, assuming that 2.5 kg of the seeds will produce 1 liter nyamplung oil. Thus it would need a minimum area of nyamplung crops of 254,000 acres in 2025. With the same pattern with the economic analysis study on the construction of Public Plantation Forest (HTR) which states that it takes 1 worker for 1 ha. Thus nyamplung cultivation area of 254 thousand hectares will be able to absorb 254 thousand workers. (ibid)

Production of biofuel from plant oil such as palm oil using zeolite as catalyst in the cracking process has been widely studied (Nurjannah, 2009a; Twaiq et al 1999; Twaiq et al., 2003; Twaiq et al., 2004; Ooi et al., 2003, Ooi et al.2004a; Ooi et al. 2004b; Nurjannah et al., 2009). HZSM-5 zeolite and its modification using a steering metal such as Cu, Ni, Zn, Pd, Au and Pt have properties and good performance in hydrocracking process (Budianto et al 2010, Budianto et al 2011, Budianto et al 2012, Nurjannah et al, 2009a). Zn-HZSM-5 is highly recommended for palm oil cracking because it has the highest yield for gasoline (Roesyadi et al, 2012). The modified catalysts are very good for palm oil cracking process, but the catalysts have not been tested for catalytic cracking of nyamplung oil to produce biofuel. The research team estimated that Zn-HZSM-5 catalyst is very interesting and it can be used for catalytic cracking process of nyamplung oil to produce biofuel, where the operating condition of the process still needs to be studied further. Although it is triglyceride oil but the composition of fatty acids is different, so it is interesting to be studied.

A. Research Objectives

The purpose of this research is to study the operating condition of catalyst preparation of Zn-HZSM-5 and to determine the characteristics of the resulted catalyst and cracking reaction operating condition of nyamplung oil converted into biofuel with the yield of biogasoline, biokerosene and biodiesel. Additionally, the purpose of this research is to study the effect of feed flow rate, temperature, catalyst composition of nyamplung oil cracking reaction on the selectivity of biofuel produced.

B. Literature Study

Biofuel is liquid or gaseous fuel that can be produced from biomass or substrate of bioresource (Stocker, 2008). Biofuel offers a number of advantages over fossil fuel in terms of (a) the availability of renewable resources, (b) represents the CO_2 cycle in the combustion, (c) green (d) biodegradable and sustainable (Puppan, 2002). In recent years, research on biofuel has been done a lot, such as the use of various types of catalyst for biofuel products (Farouq et al, 2004, Chewand Bhatia, 2008), studies of the optimization of the reactor used (Tamunaidu and Bhatia, 2007). Kinetics of cracking oleic acid to produce biofuel (Nurjannah et al, 2010), the use of composite catalyst and deactivation studies on palm oil cracking process to produce biofuel (Bhatia et al, 2009). Hydrocracking of used oil can also be processed into biofuel (Bezergianni and Kalogianni, 2009).

The increasing of interest in producing biofuel is caused by the depletion of fossil fuel. Environmental pollution is also a major factor to look for alternative energy sources. Today, 86% of world energy consumption and nearly100% of the energy needed in the transport sector is fulfilled by fossil fuel (Dorian et al, 2006). Since the world's oil reserve has begun gradually depleted, it is important to develop a suitable long-term strategy and based on the utilization of renewable fuel, it will replace fossil fuel gradually (Westermann et al, 2007). Palm oil has attracted the attention of researchers to develop environmentally friendly products and high-quality fuel, free of nitrogen and sulfur (Tamunaidu, 2006). Thus, nyamplung oil is expected to give higher quality than palm oil.

Nyamplung oil is vegetable oil. Oil is a general term for all organic liquid that are not soluble/mixed in water. Vegetable oil has long hydrocarbon chains that are similar to petroleum. Because of the similarity of the hydrocarbon chain, nyamplung oil can be used as biofuel. Therefore, petroleum cracking process can be applied to the manufacture of biofuel from vegetable oil (Nurjannah et al, 2010).

II. METHOD

Materials used for this study are divided into two groups. The first group is materials for making synthetic Zn-HZSM-5 catalyst: water glass, alum/$Al_2(SO_4)_3.18H_2O$, H_2SO_4, HCl, NaOH, NH_4Cl, Na SiO_4, H_2 gas and Zn Chloride. The second group is materials for cracking N_2 gas, nyamplung oil and seed.

The research equipments used to produce catalyst are autoclave and furnace equipped with thermocouple and temperature indicator, stainless steel hose, thermometer, hotplate, stirrer, micro bed reactor with high pressure, stative and clamp. While the characteristics of the catalyst test were conducted by Brunauer Emmett Teller (BET), Atomic Absorption Spectroscopy (AAS), and Scanning Electron Microscope (SEM). Equipment used in nyamplung oil cracking process establish biofuel is presented in Figure 1.

This study include:

The preparation stage of basic catalyst of synthetic Zn-HZSM-5 was the process of making synthetic zeolite catalyst which was done in two steps, i.e. synthesis and characterization of catalyst. In synthesis step, the process of making synthetic zeolite catalyst in an autoclave reactor and the results are expected to form NaZSM-5 and continued with the process of change into Zn-HZSM-5. In the second step, the catalyst was characterized to obtain the ratio of Si/Al, surface area and pore volume (porosity). Catalyst activation process was then conducted with impregnation of zinc metal.

The stage of nyamplung oil catalytic cracking process in the fixed bed micro-reactor gas phase was conducted at equilibrium temperature at a pressure of 1 atm. Cracking products were analyzed by gas chromatography FID column carbowax types of 20 meter. Analysis of the density was done by pycnometer.

III. Result and Discussion

A. Determination of the composition of biofuel

The resulted catalyst was tested in a fixed bed reactor at various temperatures to convert nyamplung oil into biofuel. The resulted products, biofuel, were analyzed using gas chromatography equipment (GC). By comparing the chromatogram of biofuel against the chromatogram of gasoline, diesel and kerosene, it will be obtained commercially produced biofuel composition. Figure 2, Figure 3 and Figure 4, are chromatograms using GC for commercially gasoline, kerosene and diesel fuel.

Figure 2, 3 and 4 were used to calculate the composition of biofuel based on its rentention time. Rentention time is between 0-17, 17-35 and 35-60 for gasoline, kerosene and diesel respectively. The chromatograms using GC for biofuels from nyamplung oil can be seen in Figure 5, 6 and 7.

By comparing the biofuel retention time data with the rentention time of commercial gasoline, kerosene and diesel, it was obtained biofuel product composition as shown in Figure 8. Figure 8 shows that the highest liquid biofuel composition is biodiesel and the lowest composition is biogasoline. In the temperature range of 300-400°C, it shows that the higher the temperature the higher the composition of biodiesel, but the higher the temperature the lower the composition of biokerosene.

B. Effect of nitrogen flowrate

Nitrogen gas is used to push the vapor of nyamplung oil feed to the reactor. The nitrogen flow rate affects the composition of the resulted product. In Figure 9, it can be seen that the higher the nitrogen gas flow rate the higher the composition of biodiesel, but the higher the nitrogen gas flow rate the lower the compositions of both biokerosene and biogasoline.

IV. Conclusion

From the research that has been done a few conclusions can be drawn: Biofuel from nyamplung oil cracking process showed that the composition was biogasoline, biokerosene and biodiesel. The Results of the chromatogram of biofuel from nyamplung oil using GC equipment showed that the highest percentage of biodiesel at a temperature of 400°C was 60%, while the lowest percentage of diesel fuel at a temperature of 300°C was 48%. Products density was 0.81 to 0.86 g/ml. The highest density occured at a reactor temperature of 300 °C was 0.86 g/ml. The higher the nitrogen gas flow rate the more the biodiesel formed. At a temperature of 300°C and a nitrogen flow rate of 100 ml/min, the composition biodiesel achieved was 60%.

Acknowledgement

Thanks to the Higher Education through DP2M and DIPA ITS in 2013 that financed this research.

References

[1]. Bhatia S, Zabidi, N. Twaiq, A, and Farouq, A., (1999), "Catalytic Conversion of Minyak sawit to Hydrocarbons: Performance of Various Zeolite Catalyst ", Ind. Eng. Chem. Res., 38(9), hal. 3230-3237.

[2]. Bhatia S, Mohamed, A.R., Noor A.A.S., (2009), "Composites As Perengkahan Catalyst In The Production Of Biofuel From Palm Oil: Deactivation Studies", Chemical Engineering Journal 155, hal. 347–354.

[3]. Bezergianni, S., and Kalogianni, (2009), Hydrocracking of used cooking oil for biofuel Production, Bioresource Technology 100, hal. 3927–3932.

[4]. Budianto, A., Widianto A., dan Maghfiroh A., (2003), "Pembuatan Biodiesel dari Crude Palm Oil (CPO) degan Proses Esterifikasi dengan Kondisi Basa", Prosiding Seminar Nasional Rekayasa Kimia Dan Proses 2003 ISSN:1411-4216, Hal. F.3.1 - F.3.7

[5]. Budianto, A., Purwanti E., Marta M., dan Retta D.M., (2005), "Pengaruh Suhu Konversi Terhadap Proses Konversi Metana Dengan Katalis Zeolit Termodifikasi", Jurnal IPTEK, Media Komunikasi Teknologi, Volume 8 no 3 Mei 2005, ISSN No 1411-7010, hal. 111 – 122.

[6]. Budianto, A. (2009), "Ozonasi Minyak Super Olein dalam Catalized Bed Reaktor menjadi Ozonida Criegee sebagai Bahan Bakar Diesel Alternatif Bermutu tinggi", Laporan PHB, ITATS.

[7]. Bhale P. V., Nishikant V. Deshpande, Shashikant B. Thombre, (2009), "Improving the low temperature properties of biodiesel fuel", Renewable Energy 34 (2009) 794–800

[8]. Bismo, S., (2005), "Sintesis Biodiesel Dengan Teknik Ozonasi: Ozonolisis Etil Ester Minyak Sawit Sebagai Suatu Bahan Baker Mesin Diesel Alternative", Jurnal Teknik Kimia Indonesia vol 4 no 1. april 2005, hal 175- 182.

[9]. Charusiri, W. dan Vitidsant, T., (2005), "Kinetic Study of Used Vegetable Oil to Liquid Fuel over Sulfated Zirconia", J. Energy & Fuel, 19, 1783-1789.

[10]. Chang, C.D. (1983), "Hydrocarbon from Methanol".Catalyst Science Engineering, hal. 25.

[11]. Chew, T.L dan Bhatia S. (2008), "Catalytic Processes Towards The Production Of Biofuel In A Palm Oil And Oil Palm Biomass-Based Biorefinery". Bioresource Technology 99, hal.7911–7922

[12]. Dandik L, Askoy HA, Erdem-Senatalar A. (1980), "Catalityc Conversion of Used Oil to Hydrokarbon Fuel In Fractionating Pyrolisis Reactor", Energy Fuel 12, hal. 1148-1152.

[13]. Demirbas A. (2003), "Biodiesel fuel from vegetable oil via catalytic andnon-catalytic supercritical alcohol transesterifications and other methods: a survey", Energy Conversion and Management 44 (2003) 2093–2109

[14]. Farouq A., Twaiq A., Mohamad R., Bhatia S., (2004). Performance of Composite In Minyak Sawit For The Production of Liquid Fuel And Chemicals. Fuel Processing Technology, 85, 1283-1300.

[15]. Gerpen V.J., B.Shanks, D. Clements, G. Knothe, and R. Pruszko (2004), Biodiesel Production Technology, National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, Colorado 80401-3393 303-275-3000

[16]. Gosselink, J.A.R. van Veen, in: B. Delmon, G.F. Froment (Eds.),(1999)," Catalyst Deactivation", Elsevier, Amsterdam, 1999, hal.. 3–16.

[17]. Holum J. (1990), "Fundamentals of General Organic and Biological Chemistry", 4th ed., John Wiley & Sons. New York.

[18]. Hui,Y. H. (1996), "Bailey's Industrial Oil and Fat Products": Industrial and ConsumerNon edible products from Oil and Fats", vol 5, 5th ed, John Wiley & Sons, New York

[19]. Kansedo J, Lee, K.T., and Bhatia, S., (2008).Biodiesel Production From Palm Oil Via Heterogeneous Transesterification, Biomass And Bioenergy 33,hal. 271 – 276.

[20]. Ketaren, S. (1986), Pengantar Teknologi Minyak dan Lemak Pangan, UI Press Jakarta

[21]. Leung D.Y.C, Xuan Wu, M.K.H. Leung, (2010, "A review on biodiesel production using catalyzed transesterification", Applied Energy 87 (2010) 1083–1095

[22]. Liu H, H. Zao, X. Gao, J. Ma, (2007), "A Novel FCC Catalyst Synthesized Via In Situ Overgrowthof NaY Zeolite on Kaolin Microspheres For Maximizing Propylene Yield", Catal. Today 125, hal 163–168.

[23]. Masuda,T., Kondo, Y., Miwa, M., Shimotori, T., Mukai, SR., Hashimoto, K., Takano, M., Kawasaki, S. and Yoshida, S., (2001, "Recovery of useful hydrocarbons from palm oil waste using ZrO Suppor-ting FeOOH catalys, Chemical Engineering Science, 56, hal. 897-904

[24]. Nurjannah, Irmawati, Roesyadi, A, Danawati (2009a) "Perengkahan Katalitik Minyak Sawit untuk Menghasilkan Biofuel" Prosiding Seminar Nasional Waste Based Energy And Chemicals, Department of Chemical Engineering, Industrial Technologi Faculty UPN "VETERAN" EAST JAVA.

[25]. Nurjannah, Irmawati, Roesyadi, A, Danawati,(2009b) "Perengkahan Katalitik Minyak Sawit Menjadi Biofuel

Menggunakan Katalis HZSM-5 dengan Impregnasi Logam" Prosiding Seminar nasional Thermofluid, Universitas Gajah Mada Yogyakarta, 2009

[26]. Nurjannah, Roesyadi, A, Danawati, "Perengkahan Minyak Sawit dan Metil Ester Menggunakan Katalis HZSM-5 nntuk Menghasilkan Biofuel" Prosiding Seminar Teknologi Industri FTI ITS, 2009c.

[27]. Ooi, Twaiq,A., Zakaria, R., Mohamed, A.R., Bhatia, S., Biofuel Production From Catalytic Cracking Of Minyak Sawit, Energy Sources 25 (2003) 859–869.

[28]. Ooi, Zakaria, R., Mohamed, A.R., Bhatia, S., Catalytic Conversion Of Palm Oi Based Fatty Acid Mixture To Liquid Fuel, Biomass and Bioenergy 27 (2004) 477-484.

[29]. Ooi, Zakaria, R., Mohamed, A.R., Bhatia, S., (2004), "Hydrothermal Stability And Catalytic Activity Of Mesoporous Aluminum-Containing SBA-15", Catal.Commun.5, hal.441–445.

[30]. Rautiainen,E, Pimental R, Ludvig M, and Pouwels C, (2009), Deactivation of ZSM-5 Additives In Laboratory For Realistic Testing, Catalysis Today 140, hal. 179–186

[31]. Stocker, M., 2008. Biofuel and Biomass-to-Liquid Fuel In The Biorefinery: CatalyticConversion of Lignocellulosic Biomass Using Porous Materials. Angew. Chem. Int.Ed. 47, 9200–9211.

[32]. Tamunaidu, P., 2006. Biofuel Production From Crude Palm Oil and Used Palm OilUsing a Transport Riser Catalytic Reactor, Master thesis, Universiti SainsMalaysia, Malaysia.

[33]. Tamunaidu P., and S Bhatia et al., 2007, Catalytic Cracking Of Palm Oil For The Production Of Biofuel: Optimization Studies, Bioresource Technology 98 (2007) 3593–3601

[34]. Twaiq, A., Zabidi, N.A.M., Bhatia, S., Catalytic Conversion of Palm Oil To Hydrocarbons: Performance of Various Zeolite Catalyst, Ind. Eng. Chem. Res. 38 (1999) 3230–3237.

[35]. Twaiq, A. Mohamed, R. Bhatia, S. " Liquid Hydrocarbon Fuel From Palm Oil By Catalytic Cracking Over Aluminosilicate Mesoporous Catalyst With Various Si/Al Ratios, Micropor. Mesopor.Mater. 64 (2003) 95–107.

[36]. Twaiq, Mohamed, A.R., Bhatia, S., "Performance of Composite Catalyst In Palm Oil Cracking For The Production of Liquid Fuel And Chemicals", Fuel Process Technol. 85 (2004) 1283–1300.

[37]. Zhu H, Liu, Z. Kong, D., Wang, Y. Yuan, X., dan Xie, Z., (2009), "Synthesis of ZSM-5 With Intracrystal Mesopores By Polyvinyl Butyral Templating Method", Journal of Colloid and Interface Science, Volume 331, Issue 2, 15 March 2009, Hal.s 432-438.

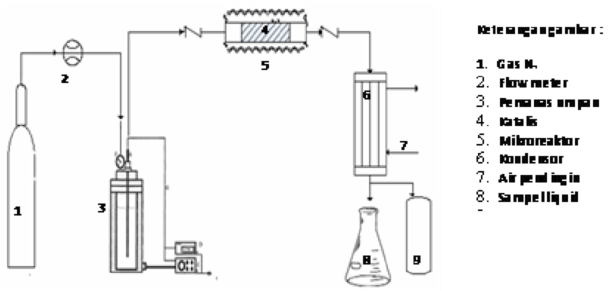

Figure 1. Equipment of vegetable oil cracking process

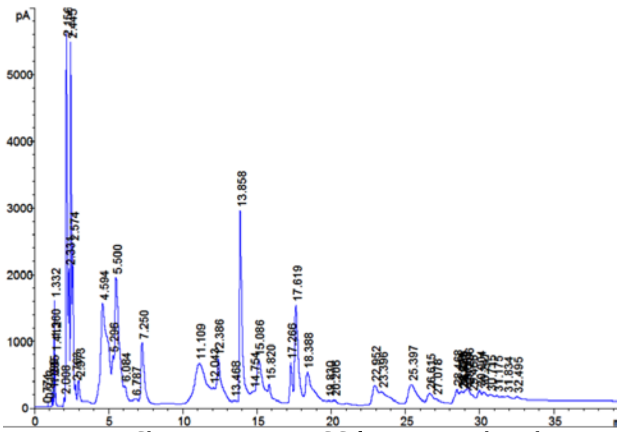

Figure 2. Chromatogram using GC for commercial gasoline

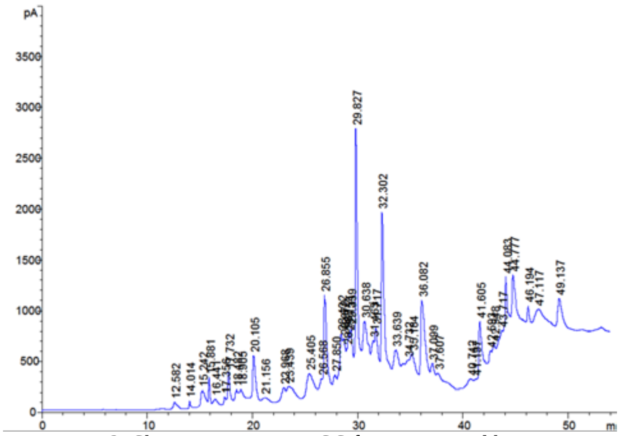

Figure 3. Chromatogram using GC for commercial kerosene

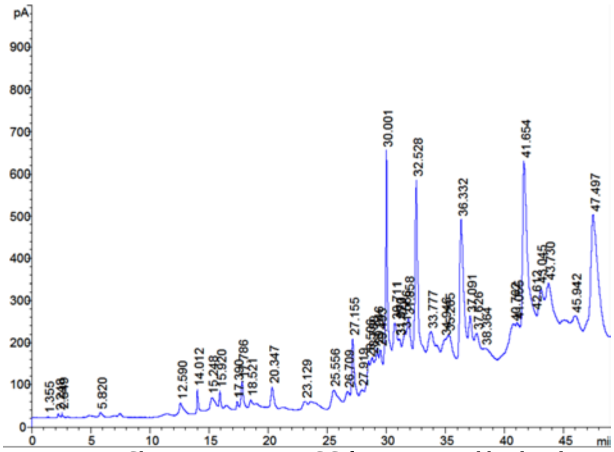

Figure 4. Chromatogram using GC for commercial biodiesel

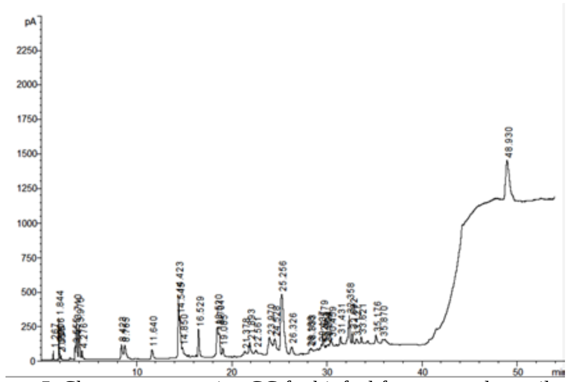

Figure 5. Chromatogram using GC for biofuel from nyamplung oil at a temperature of 300°C

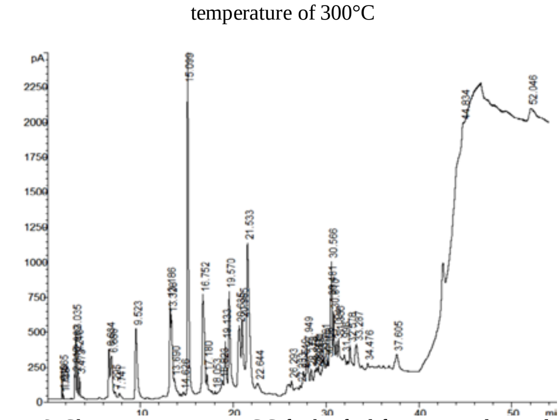

Figure 6. Chromatogram using GC for biofuel from nyamplung oil at a temperature of 350°C

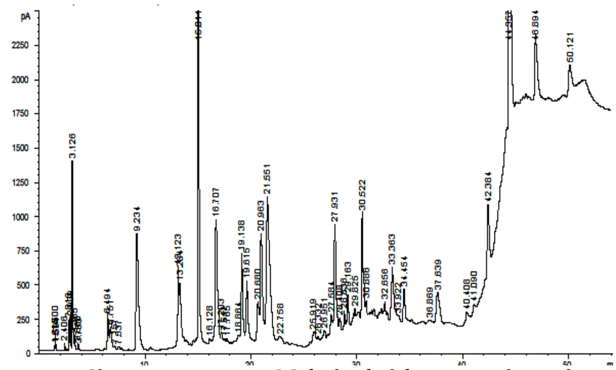

Figure 7. Chromatogram using GC for biofuel from nyamplung oil at a temperature of 400°C

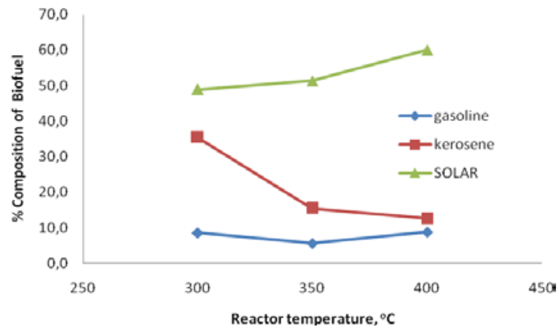

Figure 8. The effect of reactor temperature on the composition of the resulted biofuel

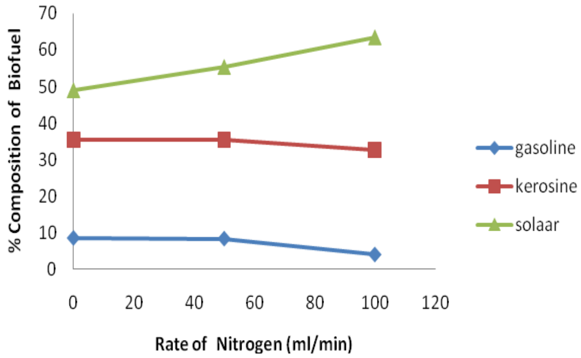

Figure 9. The effect of nitrogen gas flow rate on the composition of biofuel at 300°C