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Preface

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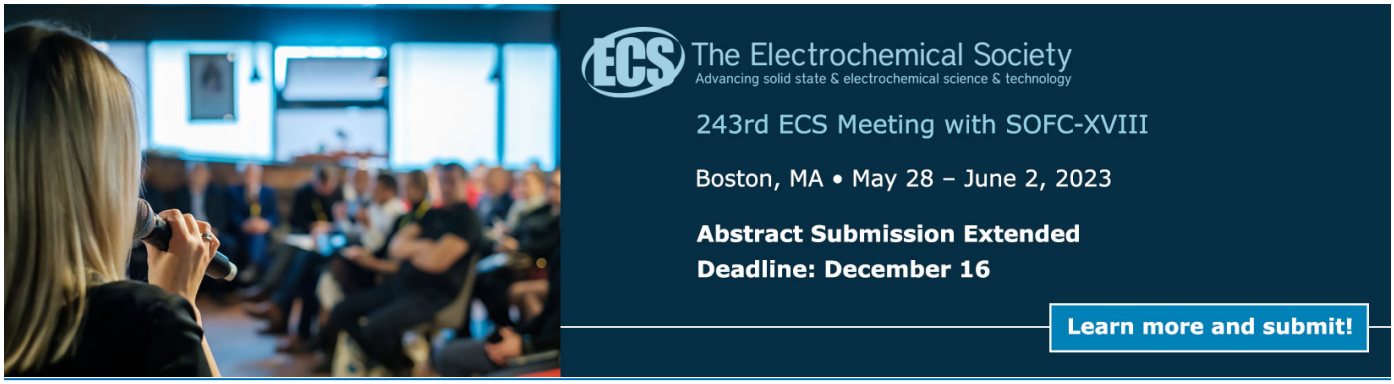

IOP Conf. Series: Materials Science and Engineering **823** (2020) 011001 doi:10.1088/1757-899X/823/1/011001

International Seminar on Chemical Engineering Soehadi Reksowardojo (STKSR) 2019

"Bioenergy and Bio-based Chemical Product for National Sovereignty and Self-Reliance"

7th-9th October 2019
Swiss-Belinn Kristal Kupang Hotel
Kupang, Nusa Tenggara Timur
Indonesia

Editor:

Dr. Antonius Indarto
Dr. Graecia Lugito
Dr. Khoirudin

Preface

The first higher education in Indonesian Chemical Engineering was established at ITB in 1941. International Seminar on Chemical Engineering Soehadi Reksowardojo (STKSR) is an annual seminar held by the Chemical Engineering Study Program of ITB, in collaboration with other institutions, and usually takes place in Bandung. The International Seminar on Chemical Engineering Soehadi Reksowardojo (STKSR) 2019, however, was held in Kupang, the Province of East Nusa Tenggara (NTT) for three days, starting from October 7th to October 9th. Brought forward the theme of "Bioenergy and Bio-based Chemical Products for National Sovereignty and Self-Reliance", the STKSR 2019 was inviting scholars, practitioners and experts to contribute to this event. The aim of STKSR 2019 is to promote the implementation of EBT (Energi Baru Terbarukan/Renewable Energy) in Timor Island, NTT supporting the government program of national sovereignty and self-reliance. Throughout the procession of this seminar, there have been collaborations between the Department of Chemical Engineering of ITB, Faculty of Agricultural Technology of Universitas Kristen Artha Wacana (UKAW) Kupang, the City Government of NTT, and Directorate General of Renewable and Conservation Energy (EBTKE), Ministry of Energy and Mineral Resources of the Republic of Indonesia (ESDM).

Message from Chairman of STKSR 2019

On behalf of the Organizing Committee of International Seminar on Chemical Engineering Soehadi Reksowardojo, I would like to show my gratitude to all stockholders of STKSR 2019. The Seminar raises the topic of "Bioenergy and Bio-based Chemical Products for National Sovereignty and Self-Reliance", expanding the scopes into a multidisciplinary platform.

As we all aware of the global issues of climate change and energy crisis, STKSR 2019 was intended to be the first step toward the frontier of petroleum-to-bio-based movement, especially for our society in the Eastern part of Indonesia. Being blessed with great varieties of natural resources, Indonesia should be able to achieve it's national independence and self-reliance in terms of bioenergy and bio-based materials.

STKSR 2019 was enriched by plenary lectures and parallel oral presentations from scholars and industrial practitioners coming from 5 countries as well as Indonesian government agencies representatives. We have received more than a hundred abstracts, among which one fourth comes from the Eastern part of Indonesia; we are sincerely grateful for your great enthusiasm and contributions. Also, for those of you who return to STKSR again and again, thank you for your continued friendship, scientific sharing, and kind support.

Taking place in Kupang, STKSR 2019 could not be made possible without the great support from our counterparts in Universitas Kristen Artha Wacana. They have arranged several social functions (welcoming dinner, gala dinner, and excursions) so that all of you may leverage your community outreach and collaborative partnerships as well as experience the Kupang exotic beauty and warm hospitality.

Finally, the committee is most grateful to all sponsors for providing funds. And I thank all the committee members, all the plenary and invited speakers, as well as all oral presenters for their kind efforts and contributions in making this conference a grand success.

Warm regards,

Chairman of STKSR 2019,

Dr. Antonius Indarto

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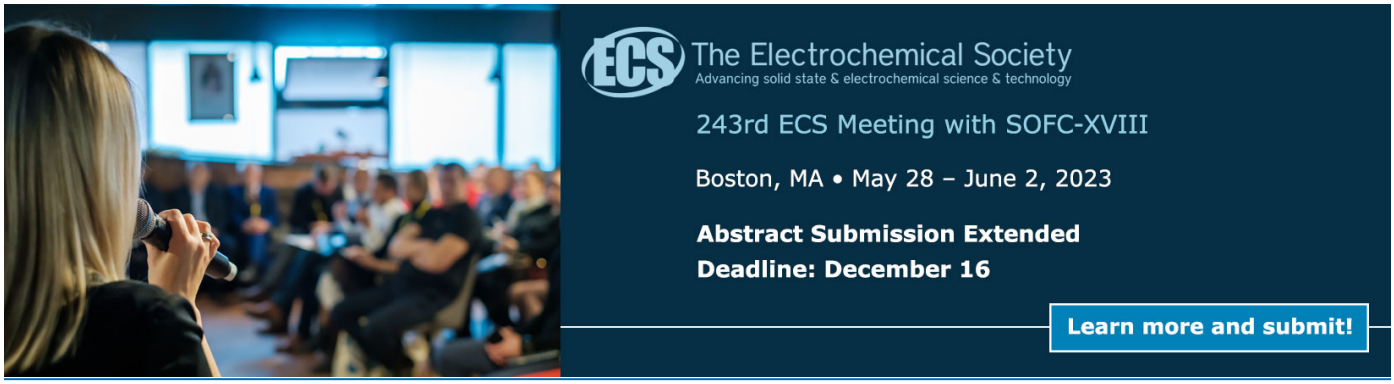

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Green diesel production from Crude Palm Oil (CPO) using catalytic hydrogenation method

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Green diesel production from Crude Palm Oil (CPO) using catalytic hydrogenation method

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Abstract. Green diesel is an alternative solution for solving problems using biomass energy as a fuel source. The advantages of this second-generation green diesel or biodiesel (Gen-2nd) are capable of reaching cetane numbers 70-90, far higher than the Gen-1st biodiesel performance of cetane numbers 50-65, respectively. The production process is through hydrogenation reactions with hydrogen injection of 4-9 MPa, the use of heterogeneous NiMo/Al_2O_3 catalysts, and takes place in temperatures of 280 - 380^{o}C. The need to design this catalytic hydrogenation reactor to convert crude palm oil (CPO) into green diesel fuel is good and safe when operating at high pressures and temperatures. The optimum operation was obtained by varying the amount of CPO oil raw material and NiMo/Al_2O_3 catalyst used in producing the best percent yield and green diesel characterization. At a temperature of 315^{o}C, the highest yield was 68.2%, where the number of products began to decline above these temperature conditions. The green diesel specifications obtained have met diesel oil standards (Directorate General of Oil and Gas, 2016) by testing density, kinematic viscosity, water content, flash point, calorific value, and cetane numbers.

1. Introduction

Technological products are needed in a continuous search for improved sources of energy, and green diesel is an alternative solution for solving problems using biomass energy as a fuel source. This renewable green diesel fuel has efficiently, the same energy densities as petroleum, derived fuels due to the removal of oxygen contents and equal carbon-carbon percentage [1]. The advantages of this second-generation biodiesel or green diesel (Gen-2nd) are capable of reaching cetane numbers 70-90, far higher than the Gen-1st biodiesel performance of cetane numbers 50-65, respectively.

Green diesel is produced with hydrodeoxygenation vegetable oil (triglycerides) or animal fats through catalytic processing with hydrogen, produced a mixture of straight-chain and branched saturated hydrocarbons which typically contain 15 to 18 carbon atoms per molecule (C15 to C18) [2]. Hydrodeoxygenation can be a very expensive process due to hydrogen injection of 4-9 MPa, the use of heterogeneous NiMo/Al_2O_3 catalysts, and takes place in temperatures of 280–380^{o}C. In hydrogenation process, the C-O bond will be cut using H_2 gas, the carboxylic functional group is disconnected into the form of CO_2 compound by decarboxylation process, and CO and H_2O compounds were released through decarbonylation process [3].

Compared to the transesterification of triglyceride reactions to the Gen-1st biodiesel, methyl or ethyl esters compounds, catalytic cracking and hydrogenation have several advantages such as low

processing costs, and energy consumption for the process separation. In addition to producing diesel fuel types, this reaction (fig.1) also produces light hydrocarbon such as propane, gasoline, and kerosene. However, this cracking process usually requires high operating conditions (temperature and pressure), and it becomes a major consideration on its process safety [4].

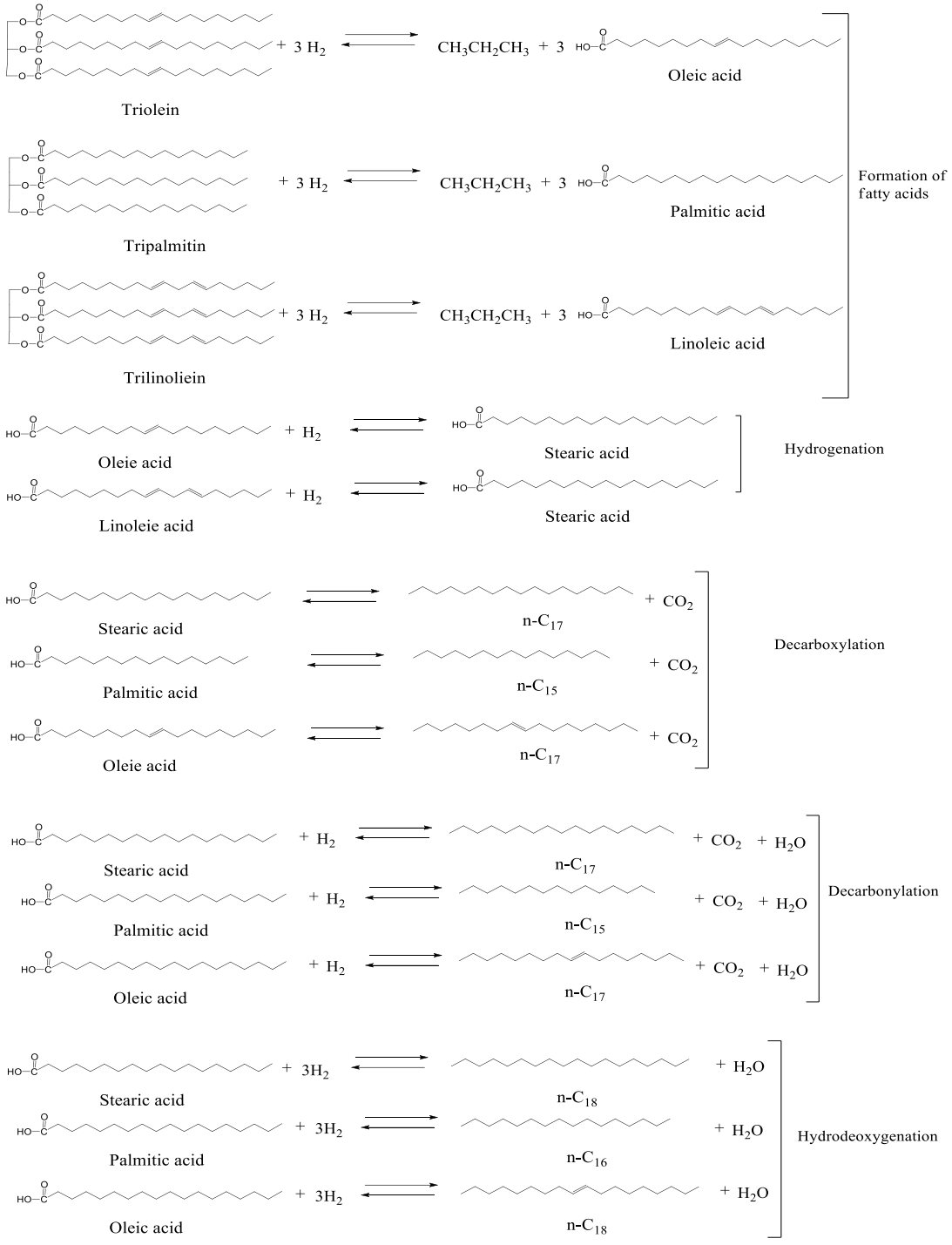

Figure 1. The synthesis of triglycerides into green diesel [5]

Future biorefineries are expected to be projected to enhance sustainable and integrated bioenergy products. Therefore, research continues to be conducted, and catalysts play an important role in increasing the conversion of vegetable oil in producing the desired product. The selection of the catalysts for the hydrodeoxygenation process depend upon the activity, stability, and importantly the selectivity of metal and support catalyst as well as its high surface area and extensive range of high porosity. The new catalysts to process vegetable oils may be synthesized taking into account the following considerations: a) high activity toward deoxygenation, b) minimization of coke formation, c) water resistance, d)capability to regenerate in single processes, e) high tolerance to chemical poisons, f)scalability in any commercial process [6].

The activity of monometallic Ni/Al_2O_3, Mo/Al_2O_3, and $NiMo/Al_2O_3$ sulphided catalysts were studied for comparative hydroprocessing activity of sunflower oil. Harnos et al. [7] compared the activity of sulphided catalysts with the non-sulphided catalysts. They tested both sulphided and non-sulphided Pd/activated C, Pd/Al_2O_3, Ni/Al_2O_3, and bimetallic solid acid catalysts $NiMo/Al_2O_3$. The reaction conditions were set at 613.15 K under the pressure of 21 bars of H_2 gas. The major products distribution were found to be C17, C18 and small alkanes with different catalyst.

The content of $NiMo/\gamma\text{-}Al_2O_3$ in each catalyst was about waste cooking oil 5 wt%. A maximum of 77.97% green diesel yield was achieved at nearly complete conversion of WCO using $NiMo/\gamma\text{-}Al_2O_3$ at a temperature of 400°C, a pressure 60 bar, and 4 hours of reaction time. The oxygen content was decreased from 14.25 wt% to 13.35 wt%, at a temperature of 400°C, a pressure of 30 bar and 1 hour of reaction time [8].

2. Methodology

2.1. Material

The materials used in this research are Crude Palm Oil (CPO), hydrogen gas, Ammonium Heptamolibdat Tetrahidrat, Nickel (II) Nitrate Heksahidrat, Aluminium Oxide. CPO produced from PT Perkebunan Mitra Ogan which is circulating in the area of Palembang, South Sumatera.

2.2. Experimental procedure

This study began with the process of making catalysts, nickel molybdenum with support of alumina ($NiMo/Al_2O_3$). The raw materials used are Nickel (II) Nitrate Hexahydrate ($Ni\ (NO_3)_2.6\ H_2O$) as for Ni, Ammonium Heptamolybdate Tetrahydrate ($(NH_4)\ 6Mo_7O_{24}.4\ H_2O$) as for Mo, and alumina commercial Al_2O_3. The process of making this catalyst consists of impregnation, drying, and calcining.

The Aluminium Oxide (Al_2O_3) commercial is heated at 120°C for 2 hours and then cooled in the desiccator. Ammonium heptamolybdate tetrahydrate (NH_4) $6Mo_7O_{24}.4\ H_2O$) 0.87 M as much as 10 ml and Nickel (II) Nitrate Hexahydrate ($Ni\ (NO_3)_2.6\ H_2O$) 2M as much as 10 ml is impregnation with 12 gr of Al_2O_3 which has been activated. The mixture is stirring and heated at a temperature of 80°C to dry, then more drained in the oven with a temperature of 120°C for ± 4 hours. The mixture is calcined in a furnace with a temperature of 600°C for 5 hours. After that, the mixture can be used in hydrodeoxygenation reaction as a $NiMo/Al_2O_3$ catalyst.

Hydrodeoxygenation reaction of 300 ml CPO uses 0.15 gr $NiMo/Al_2O_3$, and 25 psia hydrogen, the process is performed during 1 hour of operation in the temperature in the range 270 – 330°C. Analysis condensate of green diesel products through the analysis of physical (qualitative and quantitative) and chemical properties.

3. Results and Discussion

The cracking product consists of organic liquid products, water, gas, and coke. The organic liquid product contains a large number of components of liquid hydrocarbons [9]. This hydrodeoxygenation reaction occurs at constant pressure in 55 bars, Figure 2 shows the percent yields of green diesel products that continue to rise with the higher operating temperature, the temperature of 315 °C is the

optimum condition of the result at 68.2%. Yield is the ratio of the weight of condensate products obtained by the amount of crude palm oil used as raw material.

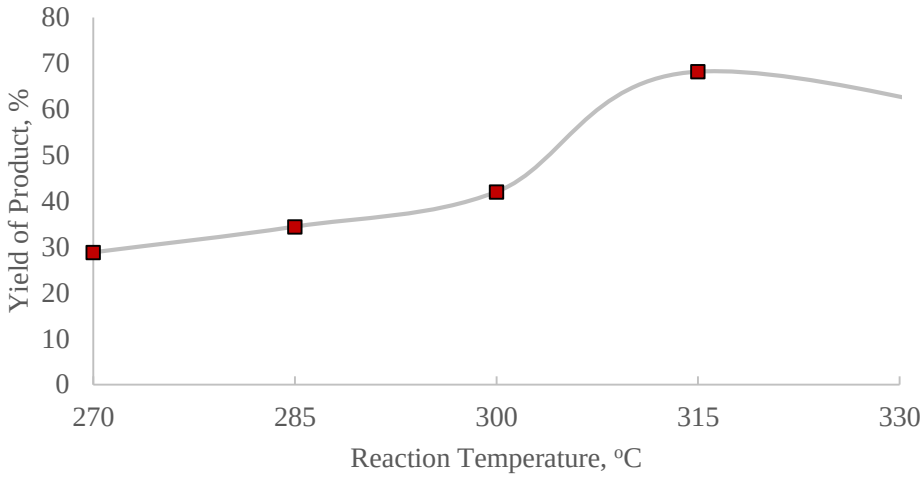

Figure 2. Effect of reaction temperature on the percent yield of green diesel

Under optimum temperature, CPO has not been fully converted into green diesel products, so that while the condensation product is excreted many of the vapor is detached. However, at a temperature of 330 °C there is a decrease in the quantity of products produced, this is because the temperature is too high resulting in the occurrence of hydrocarbons that have formed carbon deposits (coke) and aromatic compounds, this is shown from the more blackish colors and odors of products. Coke formation was observed for all catalytic cracking of used palm oil [10] and will affect the density (Fig.3-a) and viscosity (Fig.3-b) of the product.

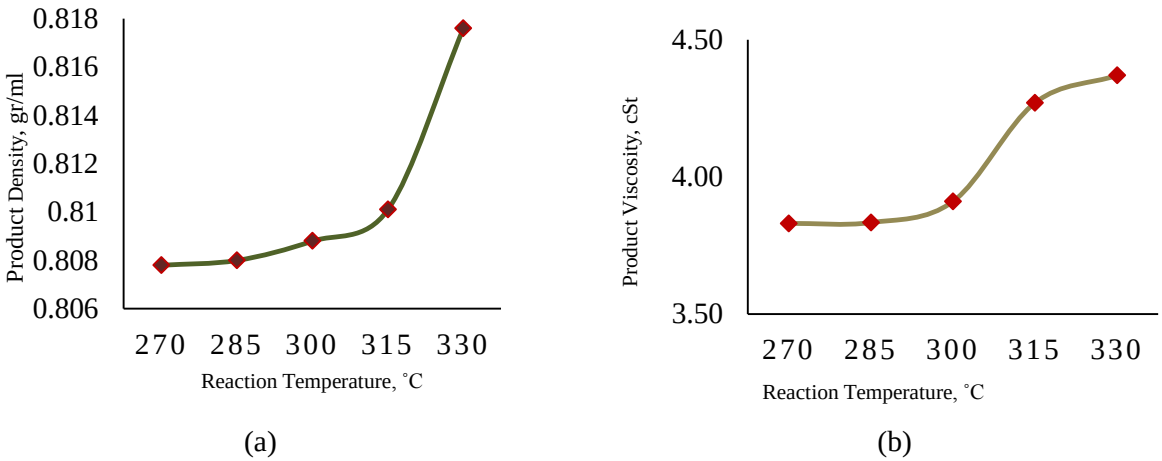

Figure 3. Effect of reaction temperature on the product density (a) and viscosity (b) of green diesel

Table 1. Green diesel product specifications

Characteristics	Unit	Standard*	Research	Test Method
Density @15 ^oC	gr/ml	0.8150 – 0.8600	0.8101	ASTM D 1298
Kinematic Viscosity @ 40 ^oC	cSt	2.0 – 4.5	4.27	ASTM D 445
Flash Point	^oC	52	58	ASTM D 93
Cetane Number		48	75	ASTM D 613

* The standard and quality of diesel fuel from the Directorate General of Oil and Gas RI 2016 [11]

The density and viscosity of the product are strongly influenced by the number of paraffin hydrocarbons that are formed, the shorter the chain then the more the value. Figures 3 are shown, at the optimum temperature of the density is 0.8101 gr/ml and the viscosity is 4.27 cSt, and this is still in the specification of the diesel fuel (Table 1). The amount of value is increased with the high operating temperature, coke has started to form. Increased density of thermal cracking product fluid followed by increased viscosity of the fluid. The test of the flashpoint product (ASTM D-93) is still above standard, which is 58^{o}C, but still in the limit of 52–96^{o}C from diesel fuel. The ignition delay is caused by still not pure diesel product that is analyzed and the content of oxygen. The presence of oxygen, in water molecules and acid, reduces the stability and quality of the fuel. Deoxygenation process does not last perfectly, can be caused by the amount of hydrogen injected is still limited. At the test of the heating value, obtained the value of 10693 cal/gr. The heating value product is close to the standard of green diesel fuel, 44 MJ/kg [8] or equivalent to 10516 cal/gr, the resulting fuel products has approached its standard value.

In chemical composition testing with GC-MS analysis (Fig.4), it was obtained that the resulting product was dominated by the paraffin chain C15-C18 39.63%, range of diesel fuel. While other compositions are gasoline, kerosene, and naphtha (17.55%), lubricating oils (6.28%), paraffin (3.82%), and other compounds (33.44%).

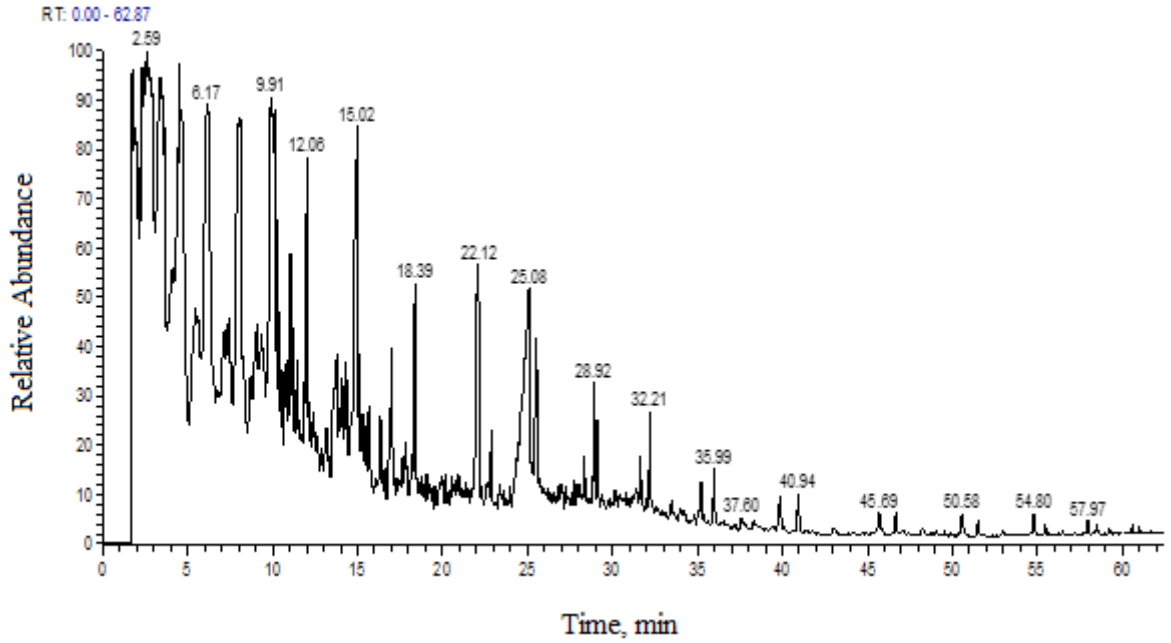

Figure 4. GC-MS analysis of green diesel product

Compounds from the C5-C14 chain contained in the product due to the continuous thermal cracking reaction to convert the compound into a lighter fraction, and also formed a myristic acid which has a chemical formula $C_{14}H_{28}O_2$. Meanwhile, the hydrocarbon > C18 is due to the large molecular fatty acids in the feed such as oleic acid (fig.1) not yet fully crack by the process. Da Mota, et al. (2014) in their research on the scale pilot plant produces green diesel by using CPO, through GC-MC analysis product obtained including 91.38% (w/w) of hydrocarbons such as normal paraffin, naphthenic, Olefin and 8.62% (w/w) oxygenation compounds [12].

4. Conclusion

The optimum temperature of the hydrogenation of crude palm oil using $NiMo/Al_2O_3$ catalyst to produce the green diesel fuel is 315 °C, with a product yield of 68.2%. The physical and chemical properties have fulfilled the specification of diesel fuel, which is density 0.8101 gr/ml, kinematic viscosity 4.27 cSt, flash point 58 ^oC, cetane number 75, and calorific value is10693 cal/gr.

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