

Two-Stage Thermal Conversion of Indonesian Nyamplung Oil (*Calophyllum inophyllum*) to Improve the Selectivity of Light Organic Liquid Product

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Abstract. Catalytic cracking processing has a potential to become an important process for conversion of vegetable oils into renewable bio-based fuel. This process has advantages in the feedstock flexibility without considering the level of free fatty acid and gum contents, compared to trans-esterification process for biodiesel production. This work aims to improve the selectivity of organic liquid product cracking of Indonesian nyamplung oil with two stages thermal conversion namely thermal and catalytic process using fixed bed reactor with zeolite-based catalyst. The thermal cracking process was carried out in the pre heater where the oil would turn into vapor phase. This is to ensure that the non-volatile matter of crude nyamplung oil can be separated in the pre heater so the oil vapor which flowed into the reactor has the homogeneous and fixed composition. The previous process was done with single stage thermal conversion of semi batch reactor. The liquid hydrocarbon products obtained from this process were analyzed using Gas-Chromatograph and GC-MS and grouped into 3 lumps, i.e., C₅-C₁₁, C₁₂-C₁₅ and C₁₆-C₂₂ that having similarity to gasoline, kerosene and diesel fraction. The experimental results show that the process with two stage of thermal conversion can improve the selectivity of fraction C₅-C₁₁ from 33.3% up to 74.03%.

Keywords: Catalytic cracking, Nyamplung Oil, zeolite

1. Introduction

The increasing energy demand will lead to more fuels based on bio-renewable resources. Vegetables oils are the best alternative source from which an environmentally friendly biofuel can be derived. The main problems associated with the use of these vegetable oils as liquid fuels directly are their instability, high viscosity and formation of carbon deposits in parts of automobile engines [1]. Biofuel present many benefits including domestic production, less greenhouse gas emissions, less dependence on fossil fuels, improvement of rural economies, and increased national energy security [2]. There are many biofuel production technologies that are capable of producing liquid transportation fuels, e.g., fermentation, transesterification, pyrolysis, thermal and catalytic conversion. Even though biodiesel from transesterification processing has shown a potential of reducing the net carbon dioxide emission, there are still many inevitable disadvantages such as high viscosity, pour point, acid number, low heat value and stability because of its high oxygen content [3]. In recent years, there has been increasing interest in producing biofuels by catalytic cracking methods.

The cracking process has usually been accomplished by using solid catalysts with good shape selectivity and appropriate pore size, such as HZSM-5 and zeolite [4]. This process has an advantage over transesterification, including lower processing costs, compatibility with engines and fuel standard, and

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feedstock flexibility without considering the level of free fatty acid [5]. Pyrolysis or thermal cracking which is a direct thermal decomposition method, operates at very high temperature (600-850 °C) and yields mostly gaseous products containing straight chain hydrocarbon fuels with high carboxylic acid content (acid number 116-142 mg KOH/g) [5]. These undesirable products have a large effect on the corrosion value, cold filter plugging point and freezing point of the biofuels. The catalytic cracking can convert vegetable oils into hydrocarbons in the absence of oxygen at atmospheric pressure and at relatively low temperature (400-600 °C).

As a tropical country, Indonesia has great potential for renewable natural resources to produce alternative energy in the form of plants. One of this potential is nyamplung oil (*Calophyllum inophyllum*). The aim of this paper is to increase the selectivity of light organic liquid product from conversion of the crude non-edible Indonesian Nyamplung oil with two stage thermal conversion. This process was done by combine the thermal and catalytic cracking process and is expected can improve the properties of light organic liquid product approaching the properties of biofuel.

2. Materials and Methods

2.1. Materials

Crude nyamplung oils a raw material used in this study was obtained from Mirit, Kutoarjo, Central Java of Indonesia without further purification. Nyamplung oil is non-edible oil, containing high kernel oil (40-60%), tolerant to marginal environmental conditions (acidity, salinity, drought and temperature) and requires little maintenance. The composition of nyamplung oil is 17.56% of palmitic acid ($C_{16}H_{32}O_2$), 57.61% of oleic acid ($C_{18}H_{34}O_2$), 18.90% of stearic acid ($C_{18}H_{36}O_2$) and free fatty acid (FFA) 29%. This long chain hydrocarbon of nyamplung oil (C_{16-18}) making it possible to crack into shorter hydrocarbon

2.2. Catalysts

Catalysts used in this experiment was DHC-8 zeolite-based obtained from Pertamina, Indonesia and composed of Alumina Silicate 85-95%, Tungsten Oxide 5-15%, Nickel oxide 0-2%. The physical properties of catalysts are surface area 50.375 m²/g, pore volume 0,51 cc/g, pore diameter 45.54 Å. This catalyst should be activated before used by heating at temperature of 500 °C for 4 hours by flowing N₂ gas with flow rate of 1 ml/min.

2.3. Single Stage Thermal Conversion by Semi Batch Reactor

This stage was done in a semi-batch reactor. Prior to the experiment, inside the reactor was flowed on nitrogen gas to remove oxygen. Subsequently, the reactor which filled with the oils was heated at the specified temperature reaction. The vapor which formed due to the heating process flowed upward through the bed of catalyst on the top of reactor and cracked into the shorter chains of hydrocarbon. The vapor left the reactor and entered into the condenser. The liquid product obtained from the condenser was analyzed using GC (Gas Chromatography). The experiment was repeated with various mass of catalyst (3 – 5 g) and temperature reaction (350-450 °C). The scheme of the experiment equipment is presented on Fig. 1.

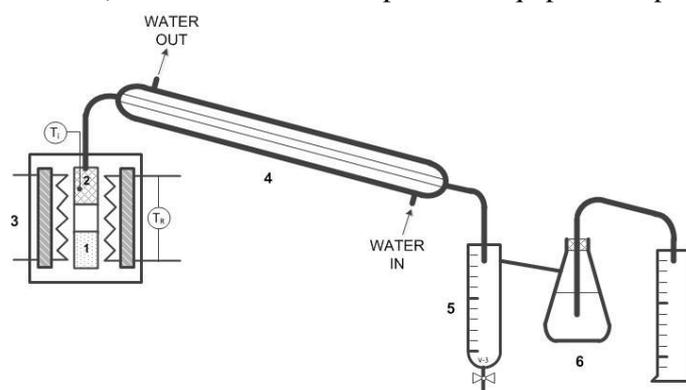


Fig. 1: Schematic diagram of the experimental for single stage cracking reaction. 1. nyamplung oil as feedstock; 2. bed of catalysts; 3. reactor with electrical heater element; 4. condenser; 5. liquid product; 6. water displacement for gas product

2.4. Two Stage Thermal Conversion by Fixed Bed Reactor

The two thermal stages were developed from the single stage thermal conversion. In this process, the reactor was equipped with 2 stages pre heater which operates at 275-325 °C. This pre heaters were expected can increase the quality of liquid product because the oil which entered the reactor was on homogenous vapor phase and the non-volatile matter of the oil like impurities and gum were separated on this pre heater. Detail and the scheme of the equipment was described on the paper that will be presented on Regional Symposium on Chemical Engineering (RSCE) 2014.

3. Results and Discussion

The two stage thermal cracking of nyamplung oil on fixed bed reactor was studied over zeolite-based catalyst. During the cracking reaction vegetable oil has occurred a wide variety of reaction. In the starting of reaction, the triglycerides of the vegetable oil are breaking down into three carboxylic acids and propane, thereafter these acids undergo decarboxylation and decarbonylation reactions to produce CO, CO₂ and H₂O and alkanes ranging from C₆ to C₁₈ [6].

Fig. 2 and 3 show the relationship between the selectivity of organic liquid as a function of mass of catalyst and temperature reaction from single and two stage thermal conversion at the steady condition. From Fig. 2, it can be seen that selectivity of light organic liquid product from the single stage thermal conversion was relatively low which below the value of 35%. The low selectivity of light product at this stage due to non homogeneous composition of feed. By heating the reactor, the volatile components of the oil will evaporate first. The analysis of the first output showed that the product contain light fractions with relatively high selectivity (85%), but then decreased to below 35% at steady condition. Since vegetable oils are thermally unstable, triglycerides are decomposed and undergo deoxygenation reaction, releasing CO, CO₂ and H₂O to yield heavy hydrocarbon [5]. The highest selectivity of 33% was obtained at a temperature of 400-450 °C with the addition of 3 g catalyst. From GCMS analysis, the components from this fraction were consist of oxygenated compounds like C₃H₆O and C₃H₆O₂ which undesirable component of biofuel

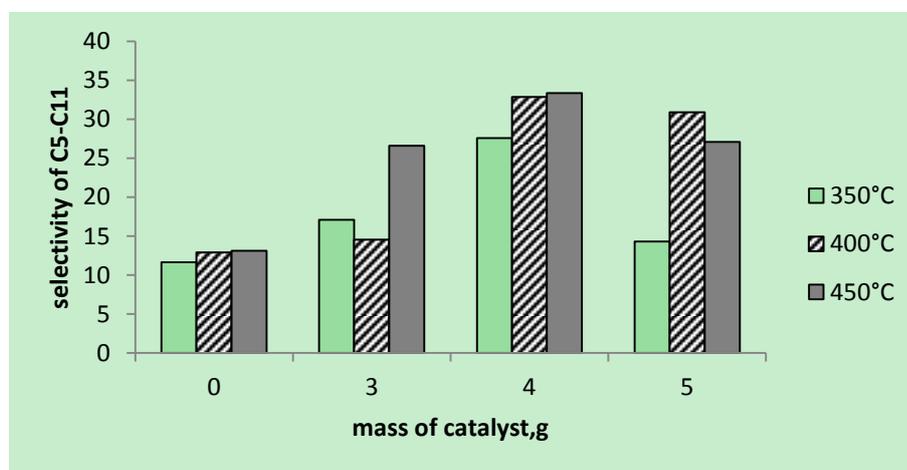


Fig. 2: Selectivity of liquid product with fraction C₅-C₁₁ in various mass of catalysts and temperature in single stage thermal conversion

The presence of double bonds of fatty acid of the triglycerides would influence the length of hydrocarbon chains of product which less than ten or more than sixteen [7]. The presence of double bonds also determine which of the two routes is favoured. Whereas in saturated fatty acids deoxygenation precedes C-C bond breaking, in the case of unsaturated fatty acids C-C bond breaking is favored due to the lower bond dissociation energy of the allylic C-C bond compared to C-C bond next to the carboxyl group [7], [8].

From Fig. 3, the selectivity of fraction C₅-C₁₁ in addition of 3 g catalysts shows a significant increase compared with the thermal process. The presence of acid sites in a solid catalyst promoted fragmentation of the compounds derived from primary thermal cracking. However, at the higher temperature 450 and 500 °C, there was no increasing of selectivity of fraction C₅-C₁₁ from the addition 3 g of catalyst. This is due to

increasing acid sites of catalyst which generating from the impregnation of Nickel in zeolite would enhance further cracking reaction into lighter hydrocarbon C₁-C₄ in the gas phase [7], [9].

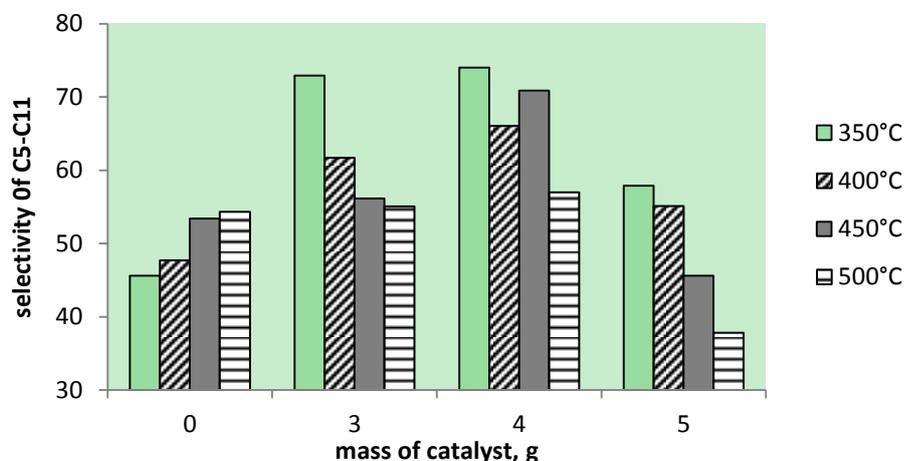


Fig. 3: Selectivity of liquid product with fraction C₅-C₁₁ in various mass of catalysts and temperature with two stage of thermal conversion

From the GC analysis showed that products come out from pre heater had fragmented into shorter hydrocarbon and grouped as fraction of C₅-C₁₁: 30.55%, C₁₂-C₁₅: 22.53% and C₁₆-C₂₀: 46.92%. This behavior can be associated with fatty acid which compose nyamplung oils, have a high contents of oleic acid (C18:1) up to 57.61%. From oleic acid chains, it is possible to obtain C₅, C₇ and C₉-C₁₄ hydrocarbons through β -scission to the double bond, before fatty acid deoxygenation and followed by radical reactions [5]. The hydrocarbon products result from the pre heater showed that there was a thermal cracking of the triglyceride chains into fatty acid, light hydrocarbon and acrolein inside the pre heater. The product of thermal cracking from pre heater was an oxygenate component. These undesirable components have deleterious effect of biofuel on the corrosion value [8]. However to minimize the oxygenate component, product cracking from pre heater was passed through the bed of catalyst on the reactor for the further cracking reaction.

The addition of catalyst at temperature of 500 °C shows no increasing in selectivity of light fraction. Furthermore, if the catalyst added up to 5 g for all temperature range 350 - 500 °C show the decreasing in selectivity. The explanation from this phenomena was due to the incorporation of Ni to the catalyst will promote the formation of gaseous hydrocarbons likely associated to the occurrence of hydrogen transfer, which increase the formation of light olefin [10], [11]. According to Botas et.al. (2014) incorporation of metal active phases to zeolites provides them bi-functional properties showing both acid and metal sites. The presence of some metals, such as nickel, is expected to promote hydrogenation/dehydrogenation reactions, enhancing the production of high quality hydrocarbons without additional hydrogen consumption [9]. This point is suitable with the result from the GC analysis, the hydrogen present in the gases is up to 13%. The highest selectivity of fraction C₅-C₁₁ up to 74% was reached at temperature reaction 350 °C and 4 g of catalyst. Besides liquid organic product, the two stage thermal conversion also produces much gas which composed of CO, CO₂, CH₄ and H₂. It was generally assumed that they are produced by deoxygenation reactions of heavy oxygenated compound coming from thermal decomposition of the feedstock triglycerides [8].

4. Conclusion

In this work, the two stage thermal conversion of nyamplung oil over zeolite-based catalyst can improve the selectivity of light liquid product (C₅-C₁₁) compared with the single thermal conversion from 33.4% up to 74%. The highest selectivity obtained at temperature reaction of 350 °C with addition of 3 g of catalyst. The

zeolite-based catalyst which impregnated by Nickel and Tungsten have a high reactivity to convert triglyceride of crude nyamplung oil with free fatty acid up to 29% into the light organic product C₅-C₁₁ by catalytic cracking process.

5. References

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