**Effect of Polyethylene Terephthalate (PET) Addition to Crude Palm Oil (CPO) Catalytic Pyrolisis**

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Abstract. The growth of global population has also raised global energy need, but the availability of fossil fuel as the primary energy source has also been decreasing and it is predicted to be run out in the near future. Additionally, the problem of plastic waste has also been a global issue because of its nonbiodegradability. Crude palm oil and polyethylene terephthalate (PET) can be used as raw materials for catalytic co-cracking, as the method has been studied intensively and been proved to be able to produce bio-gasoline with optimum quality and quantity. Nevertheless, the optimum CPO and PET ratio for the co-cracking process has not been studied. This research was conducted to identify the optimum ratio of CPO:PET with Ni/Al-MCM-41 catalyst to produce liquid bio-gasoline. The CPO:PET ratio were 1:0, 2:1, 1:1, 1:2, and 0:1. The Ni/Al-MCM-41 catalyst was characterized using XRD, N2 adsorption-desorption (BET), and TPD-NH3. From GC-MS analysis, it is concluded that the optimum ratio for biogasoline production was 1:1, which yielded the highhest aliphatic C7-12 fraction at 25,529%. The produced biogasoline from this research cannot be used for the internal combustion per se, since the physical parameter of density do not meet the SNI 3506:2007 standards. However, the produced biogasoline can be used as an additive to the fossil gasoline for its high average octane number (RON) of 101,9.

**INTRODUCTION**

As the global population grows, the global energy need grows as well. Fossil fuels (oil, gas, and coal) were the main supply with more than 80 % of total energy usage globally [13]. On the other hand, the fossil fuel supply is increasing because of its non-renewable properties. One study predicts that oil and gas will be unavailable in 50 years, while coal will be scarce in 100 years [12].

Renewable and sustainable alternative fuels are needed to overcome the upcoming energy crisis, as well as to decrease our dependence with fossil fuels. Crude palm oil (CPO) is one potential raw material for the purpose. CPO contains many kinds of triglyceride with fatty acid composition ranging from C12 and C20 [6]. CPO can be cracked at 400-500°C to obtain gasoline-like biofuel fraction of C6-C12 [1,2].

In addition to energy crisis, environmental problems pose the same threat. Plastic waste is a very crucial problem because of its non-biodegradability. According to data from the Ministry of Environment and Forestry, the citizens of Indonesia dispose 38.4 tons of plastic waste per day [17]. One type of common plastic is polyethylene terephthalate (PET), which is mainly used for polyester production and beverage bottle [Li-Na 2013]. One way of reducing the plastic waste is by incineration, but it will pose another environmental problem as well as health problems [16]. Thus, another effort is necessary.

The PET waste can be used as a raw material for fuel production, as many studies suggested. Catalytic cracking on phenol dissolved PET with Ni-Pt/Al-Ti catalyst produced many kinds of light hydrocarbons such as styrene, acetic acid, benzene, and other compounds [9]. Cracking of PET with Carbon supported Pd catalyst at 400 – 700°C induced ring cleavage of the cyclic hydrocarbons and reducing many hazardous compounds as a result [11].

In this study, mixture of CPO and PET were pyrolyzed with Ni/Al-MCM-41 catalyst to produce biogasoline. In this study, the CPO:PET mass ratio was varied and investigated to get the optimal mass ratio for biogasoline production. The obtained fuels were then analyzed their chemical and physical parameters, and then compared to the gasoline standard SNI 3506:2017 which includes the parameters of density, viscosity, calorific value, and octane number.

**METHODS**

**Catalyst Preparation**

The Ni/Al-MCM-41 catalyst was prepared by wet impregnation method [10]. The Al-MCM-41 support was impregnated with Ni solution 5 % w/v, which was prepared by mixing 61 grams of NiCl2.6H2O to 300 mL of water. As the solution was formed, 30 grams of Al-MCM-41 support was added to the solution and stirred at 250 rpm, while being heated to 120°C. The obtained paste was then dried over night at 80°C. The solid was then heated at 120°C for 2 hours and calcinated at 550°C for 4 hours.

**Catalytic Pyrolysis**

The obtained Ni/Al-MCM-41 was activated before use. Three grams of catalyst was heated at 80°C for 15 minutes then was pressed to form pellets. The pellets of catalyst were then assembled in the fixed bed column as seen on Fig 1. On the other hand, 200 grams of CPO was filled to the reactor tank (for CPO:PET = 1:0 ratio). Then, 2 kg/cm2 of nitrogen was injected to the tank to *flush* the air content. The valve was opened to purge the nitrogen out of the tank and 2 kg/cm2 of hydrogen was injected. The co-pyrolysis reaction was held in a semi-continuous system. The reaction system is illustrated on Figure 1.

Diagram

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**Figure 1** Experiment set-up and apparatus

After purging air and injection of hydrogen to the reaction chamber, the chamber was heated to the reaction temperature (400°C) with a heating rate of 10°C/min. When gas was formed inside the reactor chamber (indicated by an increase in the pressure gauge), the valve to the tubular reactor was opened so that the gas flowed through the catalyst bed. Table 1 presents the composition of each CPO:PET variation.

**Table 1** CPO : PET mass ratio variations

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| No. | Sample Code | CPO:PET Mass ratio | CPO mass (gram) | PET mass (gram) |
| 1 | A | 1 : 0 | 200 | 0 |
| 2 | B | 2 : 1 | 200 | 100 |
| 3 | C | 1 : 1 | 100 | 100 |
| 4 | D | 1 : 2 | 100 | 200 |
| 5 | E | 0 : 1 | 0 | 200 |

**Liquid Fuel Characterization**

The obtained fuels were characterized chemically as well as physically. The fuel samples were analysed chemically using GC-MS. The physical analysis were density, viscosity, calorific value, and average octane number (RON).

**RESULTS AND DISCUSSION**

**Catalyst Characterization**

The diffractograms of the catalyst and the Al-MCM-41 support can be seen on Figure 2. The diffractogram of the support shows a broad peak at 20-35°. The broad peak shows the amorphous phase of the Al-MCM-41 material [10]. On the other hand, the XRD spectrum for Ni/Al-MCM-41 catalyst shows additional sharper peaks at 37.26°, 43.29°, and 62.86° which corresponds to the (111), (200), and (220) index of the NiO face-centered cubic structure. The Ni composition of the catalyst was also indicated on the XRF analysis as presented on Table 2. This shows a successful impregnation process on the surface of the support.

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**Figure 2** Diffractogram of the Al-MCM-41 support and the catalyst

**Table 2** CPO : PET mass ratio variations

|  |  |
| --- | --- |
| **Compound** | **Concentration (% w/w)** |
| Al2O3 | 1 |
| SiO2 | 23 |
| Cl | 17.8 |
| CaO | 0.33 |
| Fe2O3 | 0.11 |
| NiO | 57.21 |
| SrO | 0.14 |
| Y2O3 | 0.1 |

The acidity of the catalyst was characterized using TPD-NH3. Figure 3 shows (a) the calibration curve of the instrument; and (b) desorption curve of the catalyst sample. The ammonia desorption curve shows an average area of 0.14062 with the calibration curve having a linear relation y = 0.3538x where y is the mmol of the ammonia on the surface of the sample and x is the area. Calculation gives the result of 0.04975 mmol of NH3, divided by sample weight of 0.0525 grams, giving the acidity of the catalyst 0.9476 mmol NH3/g.

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**Figure 3** (a) Callibration curve of the instrument; (b) Desorption curve of the catalyst sample

Surface area of the catalyst was analyzed using N2 adsorption-desorption method (BET method). Figure 4 shows the N2 adsorption-desorption profiles on the sample of (a) Al-MCM-41 support; and (b) Ni/Al-MCM-41 catalyst. The isotherm curves are identical to that of type IV isotherm from IUPAC classification, which is identical to mesoporous material. The spike on the curve at P/P0 = 0.2 indicates monolayer adsorption on the sample materials [15].

A graph of support adsorption

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**Figure 4** BET Isotherms of (a) support material; (b) catalyst

The BET isotherms indicate that the surface area of the catalyst decreases compared to the support material. This is due to the NiO particles scattered on the Al-MCM-41 support surface [7]. The more detailed BET analysis results is presented on Table 3.

**Table 3** CPO : PET mass ratio variations

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **No.** | **Material** | **Surface area (m2/g)** | **Pore volume (cm3/g)** | **Pore diameter (nm)** |
| 1. | Al-MCM-41 | 774,2563 | 0,624912 | 3,22845 |
| 2. | Ni/Al-MCM-41 | 259,4898 | 0.209405 | 3.22796 |

**Catalytic Pyrolysis of CPO and PET**

Nitrogen was injected to the reactor prior to the reaction to purge the remaining oxygen inside the chamber so that oxygen free condition could be met. After that, hydrogen was injected. Hydrogenation was conducted to reduce the unsaturated products while the reaction took place, so that a gasoline-like fuel can be directly obtained by the end of the reaction [8].

The pyrolisis was done at 400°C to make sure that the mixture inside the reaction chamber was completely evaporated into gaseous phase and flowed through the catalyst bed. This is due to the boiling point of CPO at 300°C [18], and the degradation of PET which begins to take place at 320°C [14]. Beside, high temperature also increased the kinetics energy of the gas molecules in the reaction system so that the reaction was easier to take place. The reaction product was initially weighed, as well as the coke which was formed inside the reactor chamber, to calculate the yield of the reaction.

Composition of the raw material (CPO:PET) ratio affects the yield of the liquid fuel product. Figure 5 shows yield percentage of each mass ratio of the feed. Generally, decrease in CPO ratio also decreases the yield percentage of the product. Inversely, the by-product (coke) did not show significant change. The most produced coke was observed on the CPO:PET = 1:1 ratio and the lowest on 100 % PET feed. This is due to the property of PET which is not completely degraded at temperature below 450°C [5]. In addition, the yield of the liquid fuel for the PET 100% feed was also the lowest. This is due to the incomplete condensation of the product so that much of the gas escaped without being condensed. This inline with a study conducted by Gutta et al. (2019) which stated that the pyrolysis of PET produced more gas (76.9 %w/w) than liquid hydrocarbon (23.1 % w/w) [4].

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**Figure 5** Yield percentage of each feedstock mass ratio

Moreover, the GC-MS analysis showed the chemical composition of each product. The composition is divided into 3 categories: hydrocarbon fraction lighter than C7, hydrocarbon fraction C7 – C12 (which is the gasoline fraction), and fraction heavier than C12. The compositions were calculated based on the area percentage (% area) on the chromatogram of each liquid fuel product. Figure 7 presents a graphic of the relation between hydrocarbon fraction content of the co-pyrolysis product to the CPO:PET mass ratio of the feed. It can be seen from the graph that the light fraction hydrocarbon (C < 7) was mostly not formed during reactions. The pyrolysis of CPO 100% produced the lowest hydrocarbon fraction of C7 – C12 which was 19.20 %. Addition of PET to the CPO feed increased the C7 – C12 fraction up to the maximum value of 44.72 % which was obtained on the 1:1 mass ratio. Further PET addition decreased the gasoline fraction on the co-pyrolysis product. This shows that there is a positive (synergistic) effect on the co-pyrolysis instead of pyrolysis of only one kind of biomass, as suggested by Caroko et, al. (2021) that on the pyrolysis reaction of palm shell, addition of PET could increase the yield of the reaction, and even lowered the reaction temperature.

The GC-MS analysis also shows the hydrocarbon compounds of each cracking product. The hydrocarbons can be classified into alkanes, alkenes, aromatics, and esters. Figure 8 shows the relation between the composition of each compound to the feedstock mass ratio. Generally, all variations of feedstock shows the same trend, i.e. the highest concentration of alkanes and the lowest on esters. Furthermore, the addition of PET into the CPO feed could also increase the amount of aromatics in the reaction products.

Table

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**Figure 6** Relation between hydrocarbon fraction content to CPO:PET ratio

The highest concentration of aromatics was observed on the CPO:PET = 2:1. Further addition of PET decreased the concentration of aromatics in the products. The high concentration of alkanes and on the other hand the low concentration of ester shows that the Ni/Al-MCM-41 catalyst was effective in cracking the big molecules of the CPO and PET reactants. In addition, study by Castro, et al (2020) shows that the use of Ni/Al-MCM-41 catalyst could decrease the concentration of oxygenate on the product, because of Ni acid sites on the impregnated Al-MCM-41.

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**Figure 7** Hydrocarbon concentration of each pyrolysis product

In addition to chemical analysis, physical properties of the produced fuels were also characterized. Density, viscosity, calorific value, and RON of the products were analysed and compared to SNI 3506:2017. The physical parameters are presented on Table 4.

**Table 4. Physical paarameters**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Physical parameter** | **Gasoline standard (SNI 3506:2017)** | **CPO : PET mass ratio** | | | | |
| **1:0** | **2:1** | **1:1** | **1:2** | **0:1** |
| Density at 15°C (g/mL) | 0.71 – 0.77 | 0.820 | 0.873 | 0.872 | 0.878 | 0.853 |
| Kinematic viscosity at 40°C (mm2/s) | < 1.17 | 0.876 | 0.963 | 0.999 | 1.333 | 0.983 |
| Calorific value (kcal/kg) | 10150 | 10375 | 10057 | 9369 | 9785 | 8968 |
| RON | Min. 88 | 101,9 | | | | |

Density is an important parameter which correlates with the volatility of the fuel, hence the fuel performance in the machine [19]. Generally, the densities of the produced fuels did not suit the Standard which is 0.71 – 0.77 g/cm3. Then, the kinematic viscosities of the fuels generally fulfils the standard, except for the 1:2 CPO : PET ratio, which is 1.333 g/cm3. For the calorific values of the fuels, the highest value was obtained for the CPO 100% variation which is 10375 kcal/kg. Decline in the calorific values due to PET addition was because the pyrolysis of CPO relatively still contained the longer chains of hydrocarbon, hence having higher calorific value. In addition, the composition of the hydrocarbons also causes the different calorific values. Generally, alkanes and alkenes have lower heat of combustion compared to aromatics and esters. For the RON value, the obtained mean value of the RON is 101.9. The high RON value is due to aromatics content in the obtained fuel, especially benzene and its derivatives, which enriched the RON value [3]. Nevertheless, the physical characterizations showed that the obtained fuel did not fulfil the standard, hence cannot be directly applied to the machine, but it can be used as an additive or composite with the petroleum gasoline.

**CONCLUSIONS**

Crude palm oil was proved good for producing biogasoline by catalytic pyrolysis. The use of Polyethylene terephthalate (PET) for co-reactant also proved to improve the obtained biogasoline from the process. The co-pyrolysis of CPO:PET with 1:1 mass ratio showed the highest yield in the biogasoline product on C7 – C12, which was 44.72 % w/w. That mass ratio also showed the highest selectivity for the C7 – C12 fraction, which was 25.33 % w/w. Further addition of PET into the feedstock proved to decreased the yield as well as the selectivity of the reaction. However, physical characterizations showed that the obtained fuels did not fulfil the Standard SNI 3506:2017 for gasoline. It means that the obtained biogasoline from this reaction cannot be used in the gasoline engine, but must be combined with the petroleum gasoline.

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