New generation biofuel from polypropylene plastic waste with co-reactant waste cooking oil and its characteristic performance

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Abstract. Liquid fuels from polypropylene plastic waste and co-reactants biodiesel from Waste Cooking Oil have been successfully performed by catalytic cracking method. The catalyst used is Al-MCM-41: Ceramics with ratio 7:3. The catalyst was characterized by XRD, SEM, Pyridine-FTIR, N2-Adsorption-Desorption, and the product of catalytic cracking were investigated by GC-MS. The Liquid fuels obtained was mixed with commercial fuels and MTBE with ratio (10:87.5:2.5). The results showed liquid fuels have the largest percentage of gasoline (C7-C12) are 93.92 fraction produced. The performance of liquid fuels is enhanced with the additive MTBE investigated by generator set engine with gasoline-based fuel. The liquid fuel blends on the CB50 feedstock variation has the highest percentage of thermal efficiency of 27.42%, with a density value of 722.55 Kg/m³, a flash point of -5.9 °C, a viscosity of 0.238 cst, and a heating value of 15,465 , 94 Kcal/Kg. Characteristics of liquid fuel blends (CB) manufactured in accordance with SNI 06-3506-1994. Addition of the MTBE additive enhances the performance of CB100 mixture by 0.74% to the variation of TCB100 and 4.66% to Premium RON 88 at maximum loading of 2090 Watt. Characteristic of liquid fuels produced were also suitable with commercial gasoline standard.

1. Introduction
Waste plastics are still a material that widely used by industry and home. The use of very high plastic causes the building up of plastic waste. The process of polypropylene (PP) cracking is one way to handle plastic waste. Cracking is a termination reaction of long chain hydrocarbons with large molecular weights into short chain hydrocarbons of small molecular weights. Two kinds of cracking process are thermal cracking and catalytic cracking [1-2]. Based on a previous study , the catalytic cracking of polypropylene use a catalyst of Zeolite β (BEA) of 5% w/w produces 85% gasoline with Si / Al ratio of 30 at 300-350 °C [3].

In the research that has been done by Bintarasari [4], pyrolysis of polypropylene plastic waste with Al-modified MCM-41 catalyst and ceramic obtained liquid fuel product at gasoline fraction with yield of 71.89%. The resulting liquid fuels have characteristics approaching the characteristics of fuel oil of gasoline type according to the quality standard of SNI 06-3506-1994. Liquid fuels from high-calorie plastic pyrolysis results into an additional source of hydrogen and other carbon rich sources in order to obtain high aromatic yields and are on the kerosene fraction to increase the calorific value of the resulting liquid fuels [5].
One of the main important route to make renewable fuel is producing a biogasoline. Biogasoline is made from vegetables sources consisting C₄–C₁₁ hydrocarbon. The next stage of this process is converting the FAMEs to bio-gasoline by a cracking reaction. Catalytic hydrocracking is one type of cracking process that converting FAMEs compounds into hydrocarbon fractions using active acid sites available in the chemical structure of a catalyst [6]. To improve the quality of bio-oil, catalytic cracking methods of biomass or co-catalytic cracking with plastics have been recommended [7-8]. Catalytic cracking of biomass and plastics is also referred to as one method to produce aromatic hydrocarbons in the final product of oil. The synergistic effect for the formation of aromatic hydrocarbons by co-pyrolysis with plastics in the biomass cracking system has found [2][9-10].

This study the hydrocarbon fuel (C₈–C₁₂) synthesis was carried out through catalytic conversion process from waste plastic with Al-MCM-41 catalyst [11]. Furthermore, the characterizations of resulting product, such as density, viscosity, flash point, boiling point, calorific value, and analysis using Gas Chromatography-Mass Spectrometer (GC-MS) were tested. The results compared with SNI 06-3506-1994 gasoline fuel oil quality and international standard HIBER11Z Hibernia Petroleum Canada 2016.

2. Experimental

2.1 Materials
Sodium aluminate (PA), tetra ethyl ortho silicate (PA), and ethyl trimonium bromide (PA) have been supplied by Sigma Aldrich. Phosphoric acid (PA), methyl tertbutyl ether (MTBE), methanol (99.8%), n-pentana (95%), and pyridin (99.9%) received as it were from Merck. A sampel of waste cooking oil.

2.2 Procedures

2.2.1 Synthesis of Al-MCM-41. Catalyst Al-MCM-41 was synthesized by hydrothermal technique according to the procedure of previous studies [12], using a wet impregnation method.

2.2.2 Characterization of catalysts. Samples for acidity have saturated steam of pyridine absorption and measured by FTIR, morphologies by SEM. The N2 adsorption measurements of the calcined samples were performed using a Tristar II 3020. Surface area calculations were carried out using the Brunauer-Emmett-Teller (BET) methods.

2.2.3 Catalytic activity. The samples were dried until the moisture content below 5% and were squeezed using hydraulic press to obtain raw oil of the nyamplung. The transesterification reaction was carried out by the addition of methanol. FAMEs compounds obtained by 98.15%. All products were analyzed using GC-MS Shimadzu.

2.2.4 Synthesis of biodiesel waste cooking oil. The synthesis of liquid fuels was carried out in reflkus reactor at 60 °C 800 rpm by adding NaOH(s) and methanol PA. The result of biodiesel was accommodated on erlenmeyer.

2.2.5 Synthesis of liquid fuels. The synthesis of liquid fuels was carried out in a continous reactor. The result of hydrocarbon fuel was accommodated on erlenmeyer. Repeated use of catalysts to obtain samples PM100, PM80, PM60, PM50, and PM40. Hydrocarbon fuel was mixed with Premium RON 88 and MTBE to obtain the optimum performance in gasolin engine.
Table 1. Composition of Liquid Fuels Blend

| Sample  | Liquid Fuel (v/v) | Premium (88) %(v/v) | MTBE % (v/v) | Liquid Fuel Blend (CB) |
|---------|-------------------|---------------------|--------------|------------------------|
| PM100   | 10%               | 90%                 | 2.45%        | CB100                  |
| PM80    | 10%               | 90%                 | 2.45%        | CB80                   |
| PM60    | 10%               | 90%                 | 2.45%        | CB60                   |
| PM50    | 10%               | 90%                 | 2.45%        | CB50                   |
| PM40    | 10%               | 90%                 | 2.45%        | CB40                   |
| PM100   | 10%               | 90%                 | 0%           | TCB100                 |

2.2.6 Preparation of catalyst
Unused spark plugs were rinsed clean, crushed and sorted into ceramic parts. The Al-MCM-41 catalyst was mixed with a ceramic powder with a mass ratio of 7:3. A total of 9 grams of the pelleted catalyst blend were inserted into a catalyst tube filled with glass wool [13].

2.2.7 Characterization of hydrocarbon liquid fuels and performance test in gasolin engine
Characterization of hydrocarbon fuels includes test of density, viscosity and heating value [5]. The test methods were shown in table 2. Components of chemical compounds were analyzed using Gas Chromatograph-Mass Spectrophotometry (GC-MS). Performance of liquid fuels Blend was characterized in Gasolin Engine at Motor Fuel Laboratory Mechanical Engineering Industry Department.

Table 2. Method of Physical Properties

| Parameter | Testing Method |
|-----------|----------------|
| Density   | ASTM D.4052    |
| Viscosity | ASTM D.445     |

3. Result and Discussion

3.1 Synthesis of Hydrocarbon Fuels
Hydrocarbon fuels produced from different variation volume by catalytic conversion process took place for 2 hours refer to [14-15]. The measurement of hydrocarbon fuels volume as a cracking result of each variation shown on table 3.

Table 3. Synthesis of Hydrocarbon Fuels

| Feedstock Variation | Liquid Fuel (mL) | Waste (mL) | Type Liquid Fuel |
|---------------------|------------------|------------|------------------|
| 100% (P):0% (J)     | 45               | 162        | PM100            |
| 80% (P):20% (J)     | 100              | 235        | PM80             |
| 60% (P):40% (J)     | 72               | 220        | PM60             |
| 50% (P):50% (J)     | 30               | 217        | PM50             |
| 40% (P):60% (J)     | 38               | 230        | PM40             |

3.2 Characterization

3.2.1 FT-IR. The acidity of catalyst was measured by pyridin adsorption and FTIR was presented in figure 1 [16]. The spectra shown in figure 1 shows the interaction between pyridine compound and the active site of Al-MCM-41 catalyst at wave number 1537-1554 cm⁻¹ showing the active side of
Bronsted Acid with an amount of 0.0670 mmol / g. While the wave number 1437-1454 cm\(^{-1}\) with the amount of 0.0386 mmol / g shows the interaction between pyridine compound with Al-MCM-41 active side Lewis acid \([17]\).

![Figure 1. Spectra FTIR of pyridine adsorption](image)

Table 4. The Result of FTIR

| Type of Acid | Wavenumber (cm\(^{-1}\)) | Amount Of Acid (mmol / g) |
|--------------|--------------------------|---------------------------|
| Lewis        | 1437-1454                | 0.0386                    |
| Bronsted     | 1537-1554                | 0.0670                    |

3.2.2 Gas Chromatography-Mass Spectroscopy. The chromatogram of the product (FAMEs compounds) of the transesterification reaction can be seen in figure 2.

![Figure 2. GC-MS chromatograms of FAMEs compounds](image)

The chromatogram showed that the FAMEs compounds were 98.15% consisting of peak (1) 20.86% methyl palmitate, (2) methyl oleate 59.25% and (3) 18.04% methyl stearate. The GC-MS analysis showed that the catalytic conversion process produced not only a gasoline fraction (C\(_8\)-C\(_{12}\)), but also short chain hydrocarbon fractions (C\(_1\)-C\(_7\)) and long chain hydrocarbon fractions (C\(_{12}\)-C\(_{16}\)). The composition of each fraction could be seen in figure 3.
3.2.3 Surface Morphology of Catalyst. The morphology SEM of the catalysts was shown in figure 4. In the SEM results, Al-MCM-41 is visually attached to the ceramic surface. The appearance of Al-MCM-41 is shown in A at figure 4 (a) and ceramic sightings are shown in B at figure 4 (b). In pure Al-MCM-41, fine surfaces are seen to agglomerate from solids with hexagonal structures, whereas in the Al-MCM-41: ceramic (7: 3) variation, there are fine particles with hexagonal structures attached to the ceramic surfaces that act as solids supporters [18].

3.2.4 Adsorption-Desorption of N₂ Gas. The result of The N₂ adsorption–desorption was shown in figure 5. This graph indicates isotherm type IV which corresponds to a typical Al-MCM-41 catalyst graph [19]. This result proves the addition of ceramic with the mass ratio of Al-MCM-41: ceramic (7: 3) does not change the isotherm graph type of Al-MCM-41. The surface area of the catalyst is increased from the previously synthesized Al-MCM-41 catalyst by [17]. This suggests that the presence of ceramics adds to the surface area of Al-MCM-41.
3.2.5 Determination of Density. Fig. 6 showed the recurrence use of catalyst affect to density of hydrocarbon fuels which were decreasing density of the sample. The decrease of density in liquid fuel blends (CB) is caused by density possessed by premium fuel which is lower than liquid fuel (PM) that is equal to 736 Kg/m$^3$. CB0 type liquid fuel density of 740 Kg/m$^3$. The additive of methyl tertiary butyl ether has a density value of 744 Kg/m$^3$ with fully dissolvable properties in premium fuel so that the addition in the liquid fuel blends tends to reduce the premium fuel density value [19-21]. All liquid fuels blend of this research product compared with the criteria which based on SNI 06-3506-1994 on petroleum gasoline which states that minimum density of fuel oil is 715 kg/m$^3$ and maximum 770 kg/m$^3$ at temperature measurement 40˚C.

3.2.6 Determination of Viscosity. Figure 7 showed that the viscosity of liquid fuel blends (CB) in the research tends to increase. This is due to the addition of co-reactant of Waste Oil biodiesel. The entire liquid fuel blends (CB) has a viscosity below 0.3 cSt. This is due to the viscosity of the main components of the mixture i.e. premium fuel measured having a viscosity of only 0.275 cSt and TCB100 fuel of 0.274 cSt. International standards issued by Hibernia Petroleum Canada 2016 HIBER11Z on crude oil specification testing have limits on measured kinematic viscosity values at 40°C at a maximum of 0.620 cSt [3]. All samples has lower viscosity than the standard.
3.2.7 Calorific value. The result of the calorific value of liquid fuels blends was shown in figure 8. The result shows MTBE has increased sample calorific value. It was shown that CB100 has higher calorific value than TCB100 (without addition of MTBE). CB40 has higher calorific value than the other samples. The value was 19.456 Kcal/Kg. All samples have fulfilled with the HIBER11Z standard of Hibernia Petroleum which has a minimum of 10.347 Kcal/kg [19].

3.2.8 Thermal Efficiency. The result of thermal efficiency of liquid fuels were shown in figure 9. Percentage of thermal efficiency of liquid fuel blend increases with the increase of loading (watt) on gasoline engine. The greatest efficiency value was shown in liquid fuel blend CB50 ((10% (PM50): 90% (Premium), 2.45% MTBE)) obtained by 27.42% thermal efficiency at 2090 Watt. While the other variation and Premium RON 88 has lower thermal efficiency than CB50 at the same power. MTBE also increase the percent thermal efficiency of the samples. It was shown that CB100 has higher percent thermal efficiency than TCB100 (without addition of MTBE). Addition of 10% MTBE additive can increase the percent of thermal efficiency of gasoline [22].
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Figure 9. Thermal Efficiency of Liquid Fuels

The product of liquid fuel from catalytic cracking have probability to use as an alternative fuel, based on data result, regarding its possible as new generation fuel.

4. Conclusion

The following conclusion can be drawn from the synthesis of Al-MCM-41 catalysts and the catalytic hydrocracking of FAMEs. Hydrocarbon fuels (C\textsubscript{7}-C\textsubscript{12}) from propylene plastic waste (PP) have been synthesized through catalytic conversion method using Al-MCM-41 catalyst of 11.18 gram and also repeated use of catalyst three times. The Liquid fuels obtained was mixed with commercial fuels (Premium RON 88) and methyl tertiary butyl ether (MTBE) with ratio (10:87.5:2.5). The results showed liquid fuels have the largest percentage of gasoline (C\textsubscript{7}-C\textsubscript{12}) are 93.92 fraction produced. The performance of liquid fuels is enhanced with the additive MTBE investigated by generator set engine with gasoline-based fuel. The liquid fuel mixture on the CB50 feedstock variation has the highest percentage of thermal efficiency of 27.42\%, with a density value of 722.55 Kg / m\textsuperscript{3}, a flash point of -5.9 °C, a viscosity of 0.238 cst, and a heating value of 15,465, 94 Kcal / Kg. The addition of MTBE additive improves the performance (percent thermal efficiency) of CB100 by 0.74\% to the variation of TCB100 and 4.66\% to Premium RON 88 at maximum loading of 2090 Watt.

5. References

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