Catalytic Conversion of Oil and Gas Residue to Liquid Fuel Using Heterogeneous Catalysts

Pusparatu\textsuperscript{1,*} R.Y. Perry Burhan\textsuperscript{1,2} Sylvia Yusnica\textsuperscript{1} Oksil Venriza\textsuperscript{1}

\textsuperscript{1}Politeknik Energi dan Mineral AKAMIGAS, 58315, Indonesia
\textsuperscript{2}Institute Teknologi Sepuluh November, 60111, Indonesia
*Corresponding author. Email: pusparatu2000@yahoo.com

ABSTRACT
Petroleum residue is a by-product of oil refineries that has not been utilized optimally so that it accumulates in the stockpile tank causing disruption of the processing of petroleum into motor vehicle fuel. The catalytic conversion of oil and gas residue into liquid fuel has been carried out using a heterogeneous acid catalyst using a bath reactor which has resulted in a conversion of 40\% with a temperature of 350° C for 60 minutes with a pressure of 1 atm. The resulting product was analysed using Gas Chromatography Mass Spectroscopy (GCMS) with components C\textsubscript{1} to C\textsubscript{17} hydrocarbon.

The effect of temperature on the catalytic cracking of petroleum residue has also been studied with the result that increase in temperature will increase the catalytic conversion of crude oil residue.

Keywords: Catalytic, Residue, Heterogeneous, Fuel.

1. INTRODUCTION

Petroleum residue is the lowest fraction in the processing of petroleum with the highest boiling point. Therefore, at room temperature (20 - 30° C) the residue is generally in solid form. In the problem, the residue always accumulates in the storage tank, this is due to the very cheap selling price so that crude oil processing will be disrupted by the full storage tank, in addition to the results of processing crude oil into fractions with very low quality so that it does not meet as motorized fuel. However, it is only used as a solvent of poor quality. Another thing if processing the residue requires a complex and expensive reactor unit, alumina, silica, zeolite catalysts are used or a mixture of alumina and silica which is acidic, where using a catalyst does not get the desired product selectivity, such as a good quality gasoline fraction.

The residue of the PPSDM Migas refinery processing has not been utilized optimally so that the residue from the processing results has accumulated in the tank. So that the residue of the PPSDM Migas refinery can be utilized or can be sold at a high price, further processing is necessary. Residue processing can be carried out in several ways, including a blending process with additive components that reduce the pour point so that it can be sold as ship fuel (MFO) and the residual catalytic hydro-conversion to Crude Oil [1], or a reprocessing process using catalysts such as: Heavy reaction catalytic processing with Zeolite ZSM-5 [2-4], catalytic cracking residues with Zirconia- Supporting Iron Oxide [5] and Fluid Catalytic Cracking [6]. RFCC nano zeolite-based catalist preparation and evaluation of the Catalytic Performance Process at the RFCC [7], Zeolite HZSM-5 as an additive for catalytic cracking residue [8-12]

In addition, Indonesia is experiencing a fuel oil (BBM) crisis which can be predicted by three data, namely: (1) Indonesia's oil production has continued to decline after reaching its peak in the 1980s; of nearly 1.6 million barrels/day, currently only 1.2 million barrels / day (2) Growth in domestic energy consumption which reached 10% per year, and (3) The trend of world oil prices that continued to increase after the monetary crisis that hit Asia in 1998 [13]. To avoid the oil energy crisis in the future, efforts to meet energy needs must be focused on finding and utilizing alternative energy sources of oil that are efficient, economical and environmentally friendly, thereby reducing the role of petroleum, by creating clean technology and efforts to protect the global environment. One of the steps that can be taken is to improve the quality (upgrading) of the residue from petroleum fractionation. In general, the purpose of the up-grading process of petroleum residues is to convert large molecular weight hydrocarbons into smaller molecular weight oils (cracking) which have small molecular weights, with boiling points below
525°C. This conversion requires breaking the carbon-carbon and carbon-sulphur bonds and increasing the H/C atomic ratio in the product, making it suitable for transportation fuels such as diesel or gasoline. This research is focused on finding a catalyst and operating conditions for the processing of PPSDM Migas residue into Light Naphtha. So, in this paper we present a solid acid catalyst with 0.5 x 0.5 μm with various catalyst pores so that it is expected to get gasoline fractions with high octane numbers.

2. METHOD

Synthesis of ZSM-5 by DGC method [14]. A typical procedure (100 mmol of SiO₂) was as follows: 100SiO₂:1Al₂O₃:58TPAOH:15NaOH:3000H₂O. The initial solution was stirred to give a homogeneous gel. Despite the hydrothermal method, here, the initial gel was dried at 80°C temperatures. The resultant dried gel was put into an autoclave with a small amount of distilled water. This cup was placed in a Teftlon-lined autoclave (125 ml) with the support of a Teflon holder. Small amounts of external bulk water (ca. 0.2 g per 1 g of dry gel), was placed at the bottom of the autoclave. The crystallization was carried out at 175°C for 30 h. After the crystallization was completed, the autoclave was cooled to room temperature. The zeolite was removed from the cup, washed thoroughly with distillate water and dried at room temperature over night. To remove the organic SDA occluded inside the pores, the as-synthesized zeolite sample was kept in a muffle furnace, and heated in a flow of air (50 ml/min). The temperature was increased from room temperature to 550°C for 4 h (2°C/min), and maintained at this temperature for 7 h. Finally the sample was cooled to room temperature under ambient conditions. Ion Exchange is carried out to replace the neutral sodium atom with a hydrogen atom which will make the catalyst an acid catalyst.

Residue cracking catalytic is carried out to change the residue into smaller components (light naphtha) at a temperature of 300 - 450°C with a pressure of 1 atm in a batch reactor. The residual cracking catalytic test was carried out at PEM Akamigas using the batch type 100 ml batch reactor facility.

3. RESULT AND DISCUSSION

SEM observations on the PR-02-2020 sample showed more varied grain characteristics, with a grain size range of 5 μm to 200 μm or equivalent to the size of silt to fine sand. Morphologically, the grain shape in the PR-02-2020 sample is spherical with a rounded surface to some which is slightly tapered, and at some points the spherical grains are found to coalesce to form lumps or coagulation. The level of uniformity of the size of the sample compiler grains is classified as poor to moderate (Figure 1). The SEM appearance generally shows grains with a grain size range of 5 - 200 μm, which is equivalent to the size of silt to fine sand. Morphologically, all the constituent grains in the sample show a generally rounded surface area, but some grains have a slightly tapered part, and poor to moderate uniformity. The main compositions that make up the granules in this sample are Silica (SiO₂) and Alumina (Al₂O₃). The SEM detail image shows the results of SEM-EDX observations on several representative grains, with the general chemical composition dominated by Silica (SiO₂) with a mass percentage (mass%) between 39.32% - 67.25% and Alumina (Al₂O₃) between 32.75% - 60.68%.

EDX analysis of the constituent components of the sample shows that all the granules have component-forming compounds with relatively the same composition, namely composed by Silica (SiO₂) and Alumina (Al₂O₃) with the percentage of mass (mass%) Silica ranging from 39.32 % - 67.25% and Alumina (Al₂O₃) between 32.75% - 60.68% (Figure 2).

Figure 1 SEM of catalyst

![Figure 1 SEM of catalyst](image)

Figure 2 Composition of catalyst

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The element content in the PR-02-2020 sample was dominated by La (48.5%), Fe (14.2%), Al (11.9%), Ti (11.6%) associated with minor elements such as Ba (5.91%) and Si (5.6%). The content of other comorbidities is present with a proportion of <1%, such as Ni, Zr, Ga, Sr, Zn, Cu, and P.
XRD test results showed the dominance of zeolite content, namely Faujasite (65.00%) and Zeolite ZSM-5 (2%). Several other minerals that were also detected included lepidocrocite (19.00%) and kaolinite (14.00%). The XRD test graph on this sample can be seen in Figure 3; sample PR-02-2020.

The catalytic conversion of the PPSDM oil and gas residue into liquid fuel has been carried out using a heterogeneous acid catalyst using a bath reactor which has resulted in a conversion of 40% with a temperature of 350°C for 60 minutes. The resulting product was analyzed using Gas Chromatography Mass Spectroscopy (GCMS) with components C1 to C17 hydrocarbon molecules (see Figure 4).

The effect of temperature was also studied where there was an increase in the conversion of the residue with an increase in operating temperature up to 95% conversion at a temperature of 450°C this was due to more energy being given to the process so that large molecules could be cracked into larger hydrocarbon molecules. Where in the research will be continued by determining the optimum conditions of the process by studying the effect of pressure, the amount of catalyst and the time of the residual conversion process into light hydrocarbon fractions Figure 5.
4. CONCLUSION

From the results of the research, it can be concluded that the residue from the processing of crude oil into a light fraction that a good catalyst for the conversion process of residue into liquid fuel is a heterogeneous acid catalyst with promising results because it is produced from 20% to 95% wt. with operating temperatures from 250 to 450°C with the product being C$_4$ to C$_{17}$ hydrocarbons molecules.

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