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# Pyrolysis of Vacuum Residue By Thermal and Catalytic Cracking Using Active Alumina Catalyst

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## Abstract

Vacuum Residue as feedstock derived from Pertamina Refinery Unit III was cracked in a fixed batch reactor under thermal and catalytic with single stage pyrolysis process using active alumina oxide ($Al_2O_3$) as a catalyst. The catalytic pyrolysis process carried out at a temperature 450°C in the presence of a varied catalyst to feed ratio 0.5-2.5% (w/w) and varied of reaction times 5-30 minutes. While the thermal process performed under same operating conditions without presence the catalyst. The effect of alumina catalyst ratio on quantity and quality of yield product, the effect of operating conditions (reaction times) on yield distribution has been investigated. As a result, the cracked products are liquid, gas and coke residue. The yield of liquid products was dominant, the highest catalyst ratio showed the highest yield of the liquid product reached 63.1 wt% and the lowest yield of coke residue by 24.75 wt%. The highest yield of gas by 23.9 wt% was found at minimum catalyst used by 0.5 wt%.

*Keywords: Alumina Catalyst, Metal Catalyst, Vacuum Residue, Catalytic Cracking, Pyrolysis*

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## INTRODUCTION

In recent years, the world demand of fuels oil and petrochemicals product has been increased rapidly and predicted will continue to grow up in the near future, while the fuels oil supply is decreasing in every year because of the limited of crude oil. Heavy oils and vacuum residue as a side product of refinery have low quality and low price [1]. Vacuum residue as cheaply available feedstocks has shown an alternate source for the production of useful oil because it normally constitutes 30-60% of crude oil by weight [2]. These material are poor in quality due to the presence of asphaltene, heavy metals and heteroatoms [3]. Therefore, upgrading of heavy residue has a renewed interest to convert these feedstocks into valuable fuels oil by using the advanced technologies today; thermal and catalytic cracking. The goals for upgrading of vacuum residue are to decrease viscosity, density and boiling point, convert into lighter fuels with high H/C ratio [3-4]

Many studies have been performed to obtain lighter oils by using thermal and catalytic cracking with pyrolysis of heavy oil or vacuum residue. Vafi, *et al* applied atomization of feed to minimize coke in thermal cracking of vacuum residue at 700-800 °C, that result of liquid yield by 18-36 wt%, 10-39 wt% of gas yield and 6.3-9 wt% of coke yield [5]. Meng *et al* investigated secondary cracking from heavy oil catalytic pyrolysis at 600-700 °C on catalyst CEP-1 ($Al_2O_3$ content by 46.3 wt%), produce liquid yield by 58-67 wt%, 21-24 wt% of gas yield, and 11-16 wt% of coke yield [6]. Wang *et al* studied catalytic cracking of heavy residue for maximizing liquid products at 600-700 °C on commercial Y-zeolite, the cracked product of liquid yield by 68-71 wt%, gas yield by 8-10 wt%, 2-5 wt% of coke yield [7]. Eshraghian & Husein investigated Athabasca vacuum residue and bitumen in a closed autoclave reactor system at 400-420 °C and produce gas yield below 10 wt% [8]. Most of the studies reported that in cracking process performed

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under high temperature [5-7] and produce low gas yield [6-8].

Here, we reported thermal and catalytic cracking of vacuum residue with pyrolysis process over alumina oxide ($Al_2O_3$) catalyst, the reaction temperature would be reduced in mild operating conditions (450 °C) to saves the cost. Some of researchers used commercial zeolite catalyst with a varied ratio of Si/Al [7]. In this works, we selected alumina as main catalyst with high thermal stability to avoid coke formation in catalyst surface. In addition, alumina also included as a low-cost catalyst. Therefore, we selected alumina as a single catalyst for upgrading vacuum residue.

The main objective of this research was to investigate the effect of alumina on quantity and quality of yield product compared with the thermal cracking process. The presence of alumina catalyst is expected to increase yield of liquid and gas product and installed double heating elements in reactor has a purpose to reduce the reaction times in the cracking process.

## MATERIALS AND METHODS

### Materials

The vacuum residue obtained from Pertamina Refinery Unit III Plaju, South Sumatera was used as a feedstock. Active Alumina Oxide ($Al_2O_3$) as a catalyst was purchased from MERCK without any preparation. The properties of catalyst presented in Table 1.

### Methods

The experiments were conducted in a stainless steel fixed batch reactor with single stage pyrolysis process. The reactor tube was placed horizontally with double heating elements separate in outer of the reactor and coated with silica wool. The electrical component was connected to control panel unit. The schematic diagram of the apparatus is shown in Figure 1. The vacuum residue was preheated at 100 °C before injecting into the reactor to reduce the viscosity. The pyrolysis runs in a two-step process: thermally without catalyst and catalytic in the presence of various amount of alumina catalyst ratio.

**Table 1.** Properties of Alumina Catalyst

| Characteristic | Value |
|---|---|
| Molar mass (g/mol) | 101.96 |
| Boiling point (°C) | 2980 |
| Particle density at 20 °C (g/cm$^3$) | 3.94 |
| Particle size (mm) | 0.063-0.2 |
| Surface area (m$^2$/g) | 100 |
| Activity (kcat mol/s) | II-III |
| Chemical content (by weight %) | |
| Alumina ($Al_2O_3$) | > 90 |
| Chloride (Cl) | ≤ 0.1 |
| Sulphate ($SO_4$) | ≤ 0.1 |

For each experiment, 2000 g of feedstock was loaded into a fixed batch reactor and the varied ratio of alumina catalyst (20-100 g) placed into a catalyst chamber in the middle of the reactor. The experiments carried out at a temperature 450 °C and varied of reaction times 5-30 minutes. Before starting the heating, the system was sealed by turn on the vacuum pump to remove the inert gas ($O_2$) content inside the reactor (vacuum condition) for 2-3 minutes. During the heating process, the vacuum residue turned into a gaseous phase and then sent to flash tank to reduce the pressure and separated the non-condensable gas and condensable gas.

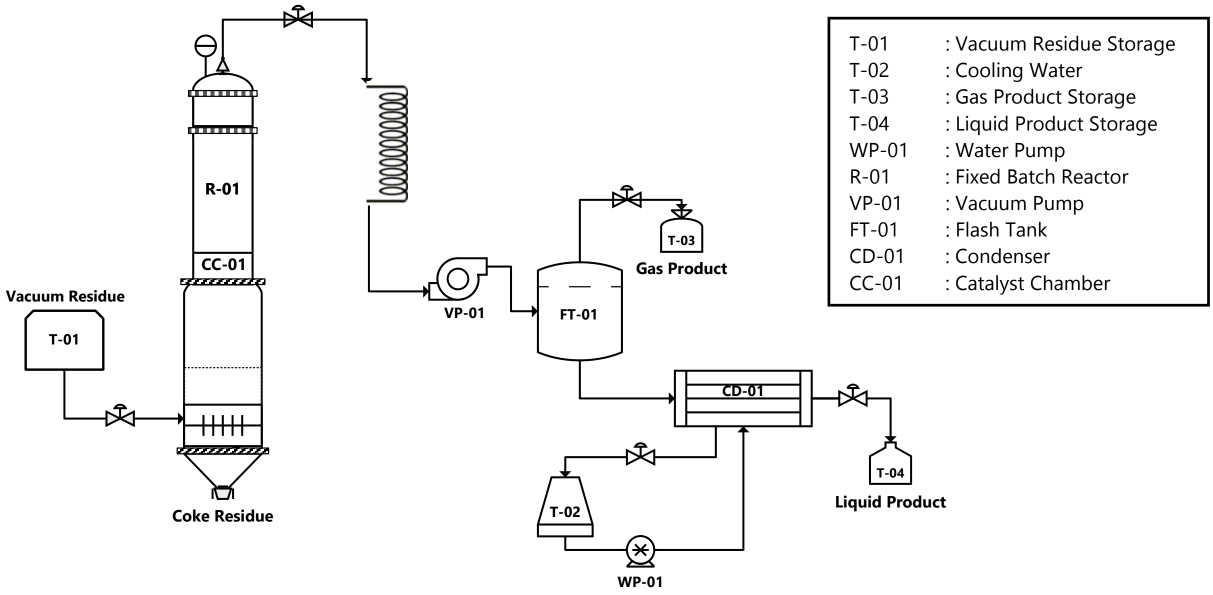

**Figure 1**. Experimental Set Up for Single Stage Pyrolysis

The non-condensable gas was collected into gas storage tank as a gas product and the condensable gas sent to the condenser for cooling down purpose after the condensable gas is condensed and form the liquid phase, it collected into liquid storage tank as a liquid product. The cracked products included gas, liquid and coke residue. The conversion of feed was defined as the sum yields of liquid, gas and coke residue. For each 100 ml sample of the liquid product was distilled by using Atmospheric Distillation D-86 to obtained the lighter oil products with a lower boiling point. The liquid products from distillation were analyzed qualitatively in Laboratory Section Research and Development PT. Pertamina RU III Plaju by using Instrument Aromate FIA ASTM D-1319 to observed the aromatic and olefin content. The density of the liquid product was determined by ASTM D-1298.

## RESULT AND DISCUSSION

The effect of reaction time on yield distribution and the effect of catalyst to oil feed ratio on total yield product and its component was studied for thermal and catalytic cracking with pyrolysis process on active alumina catalyst. Qualitative analysis of the liquid product was discussed to determined the quality of the product and compared them with standard fuels of the refinery.

### *Effect of Reaction Time on Liquid Yield Distribution*

Experiments were carried out at temperature 450°C and conducted at varied reaction times (5, 10, 15, 20, 25 and 30) minutes, respectively. In this research, the conversion was defined as the sum yields of liquid and gas. The reaction times depend on the variation of catalyst ratio as illustrated in figure 2.

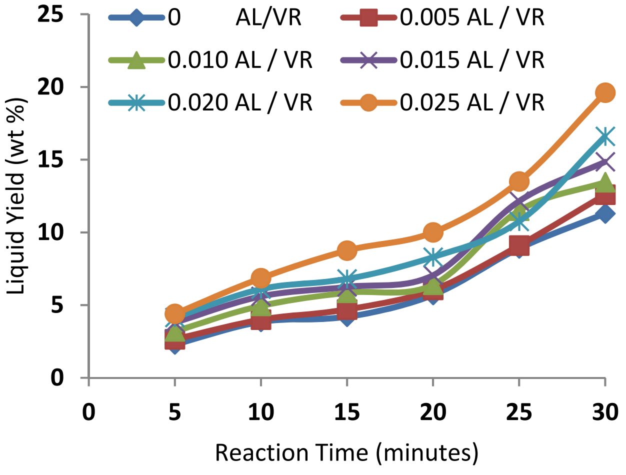

**Figure 2**. Effect of reaction times on liquid yield distribution

As can be seen in the figure above, the liquid yield at different catalyst ratio and thermal process without catalyst increases as reaction times increases. The largest amount of catalyst ratio shows the highest conversion of liquid yield by 19.6 wt% in 30 minutes. While the thermal process without using the catalyst shows the least conversion of liquid yield by 11.3 wt% in 30 minutes. But, in shortest reaction times (5 minutes) they show the lower liquid yield by 4.4 wt% at highest catalyst ratio (0.025 % w/w) and slowest reaction times in noncatalytic process by 2.3 wt%. It can be assumed that in longer reaction times can produce more liquid yield.

From the figure, it found that by using the highest ratio of alumina catalyst shows the maximum yield compared to the thermal process in the absence of a catalyst. Alumina as a catalyst can improve the number of liquid yields in cracking process. The complex molecules of hydrocarbons in vacuum residue can be broke faster by catalytic cracking than thermal cracking process [2,4]. It means that in this experiment the alumina as catalyst shows the good cracking reaction. Besides that, as seen in the figure, the liquid product can be produced in shorter reaction times (5 minutes) after reaching the set temperature (450°C) by using double heating elements in the reactor. Double heating elements in this experiment have a function to increase the heating rate in cracking process, so the liquid product can be produced in shorter times. It concluded that by using double heating elements in the process has reduced the reaction times and presence of alumina as a catalyst has improved the quantity of liquid yield in the cracking process.

### *Effect of Alumina Catalyst Ratio on Total Yields Product*

In this experiment, the effect of catalyst ratio on total yield of each product was investigated in 105 minutes of reaction times at 450°C. Zero value "0" in catalyst ratio means the cracking process was conducted in thermally without presence the catalyst. Figure 3. represents the effect of varied catalyst used on the quantity of total yield. As the catalyst ratio increases, the yields of liquid is also increased and the gas yields increase from thermally to minimum catalyst ratio used then decrease to maximum catalyst ratio. The unconverted feed was defined as coke residue yields that decrease as the catalyst ratio increases.

The highest catalyst ratio used (2.5 wt %) shows the maximum yields of liquid product by 63.10wt % and less of the gaseous product by 12.15 wt %. It can be assumed, by using much higher of catalyst to feed mass ratio, the yields of liquid product can increase more than 63.10 wt %.

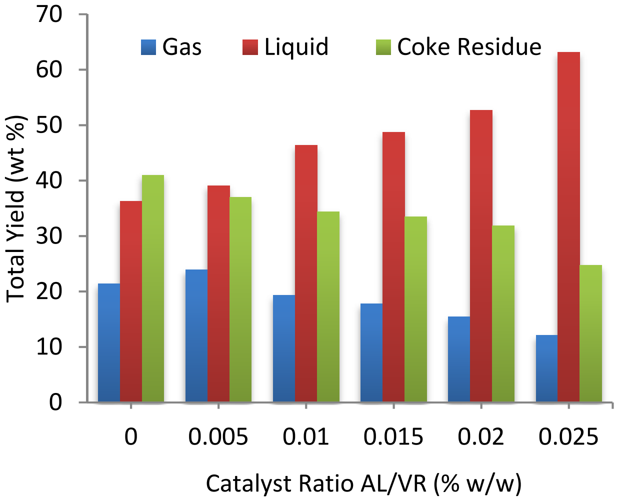

**Figure 3**. Effect of catalyst to feed ratio on total product yields

The reason why the yields of the gas product are lowest in this experiments because it was performed in mild operating conditions (450°C), so the yields of the gas product are lower than a liquid product. In theoretically, the liquid products as a medium fraction of hydrocarbons can further crack into a lighter fraction (gaseous product) with increasing the temperatures [4,10]. Therefore, to produce a high amount of gaseous product, the experiments should be conducted at high temperatures. From the figure above, in the thermal process shows the largest amount of coke residue yields by 42.35 wt %, it means that the conversion is lower than catalytic process.

Conversion of feed was defined as sum yields of liquid and gas. The higher conversion is achieved by applying the alumina catalyst in the catalytic process. Figure 4. illustrated the feed conversion and products selectivity versus catalyst to feed ratio, respectively. Conversion of vacuum residue was increased as the catalyst to feed ratio increased. Selectivity of the liquid product is much higher than the gas product. The selectivity of the liquid product also increased as the catalyst to feed ratio increased, the highest liquid selectivity by 171% then the lowest liquid selectivity by 56.86% on thermal process . While in gas selectivity it was decreased as the catalyst to feed ratio increased. The lowest gas selectivity by 13.83% on highest catalyst used.

In this results, it can be concluded that by presenting the alumina oxide as catalyst the heavy fraction of molecular weight in vacuum residue can be converted into medium – lighter fraction by breaking down the long chain hydrocarbons molecules into shorter molecules.

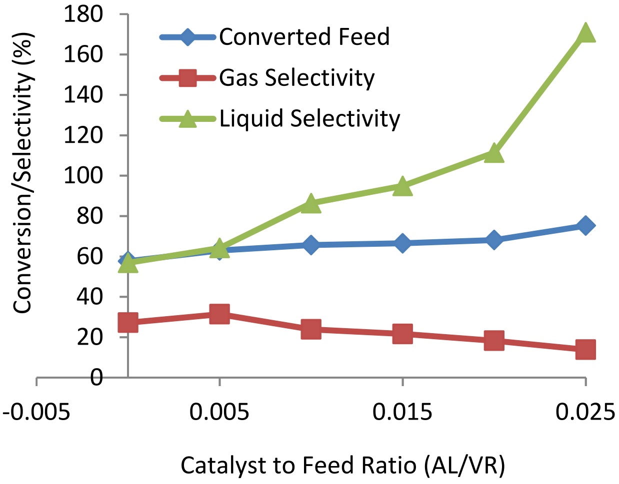

**Figure 4**. Effect of catalyst to feed ratio on feed conversion and selectivity of products

Alumina catalyst can weaken the energy bonds [11] in vacuum residue molecule, so it can be cracked easier at lower temperatures. The larger amounts of alumina catalyst used in this process indicate the high activity of catalysts because more active sites in catalyst surface [11-12], so it can increase the yields of liquid product and also minimize the coke residue.

### *Analysis of Liquid Product by Aromate FIA ASTM D-1319*

Liquid product in 100 ml of sample was distilled by ASTM D-86 before further analysis and then a small quantity of liquid sample (0.75 ml) was analyzed by Aromate FIA (Fluorescent Indicator Aromatic) ASTM D-1319 to measure the components, mainly in aromatics and olefins contents. According to the analysis data, the saturates content was assumed as the rest amount of total % volume with 100 percent.

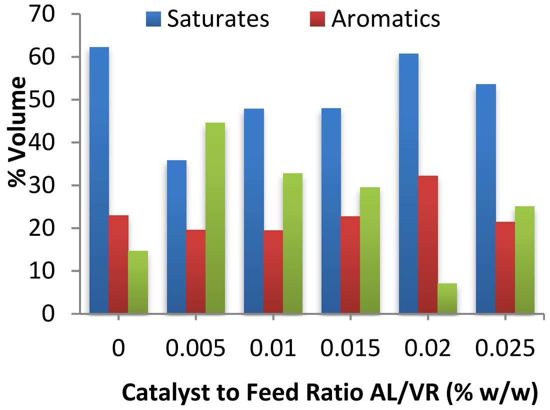

**Figure 5**. Analysis Components of Liquid Product

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Based on the theory, the saturates component (paraffin and naphthene) are the lighter fraction than aromatics and olefins [2,9,10]. But in liquid products like gasoline, the aromatics and olefins components is most important, because liquid products with high aromatic and olefin contents have higher octane number.

With increased the catalyst to feed mass ratio, the aromatics, olefins and saturates contents are fluctuating as shown in figure 5. The largest amount of saturates content by 62.3 % vol was found in the thermal process without presence the catalyst and the largest amount of aromatics by 32.2 % vol was found at the catalytic process with 2 % wt of catalyst to feed mass ratio. While, for olefins content, the largest amount by 44.59 % vol was found at lowest catalyst ratio (0.5 % wt).

So, it can be seen from the figure, the saturates is most dominantly component in this product. Because in theoretically the saturates compound is easier to crack than aromatics. Paraffins with straight-chain or branched-chain single bond is easier to broken, while the aromatic compound with unsaturated cyclic multiple bond structure is difficult to crack [2,9], because they need more energy, typically in high temperature.

The liquid product with higher octane number means the better quality of the product [10]. But the gasoline product from the refinery (Pertamina) called Premium and Pertamax has a maximum content of aromatic by 50 % vol and 25 % vol for Avtur product. Although the saturates has a lower octane number than aromatic and olefin, the products with high saturates compound (mainly paraffin) has higher calorific value [2]. However, the lower aromatic and olefin contents in the liquid product can be used as solvents in petrochemical [9].

### *Specific Gravity and API Gravity of Liquid Products*

Specific gravity can be defined as the relative density of liquid oils per density of water at a same standard temperature (15°C) and pressure conditions (1 atm) [10]. The density is important properties of petroleum products as they are a part of product specifications. Relative density at 20°C (65°F) of liquid product from cracking vacuum residue was analyzed by ASTM D-1298 method in Laboratory of Pertamina RU III. The relative density at standard reference temperatures 15°C (60°F) was determined by calculation with SG correction. As shown in figure 6. the density of experimental products in varied catalyst ratio was compared with the standard density of refinery products.

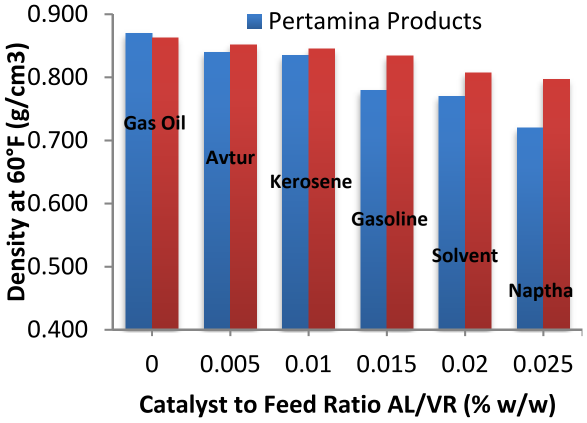

**Figure 6**. Density of Liquid Product Compared with Standard Products of Refinery

The density of noncatalytic product by 0.863 g/cm$^3$ and density of product with lowest catalyst ratio (0.5 % wt) by 0.852 g/cm$^3$ was closed to standard properties of gas oil (0.870 g/cm$^3$). Then, the density of product with catalyst ratio (1 % wt) by 0.845 g/cm$^3$ closed to aviation turbine density (0.840 g/cm$^3$), and product density with catalyst ratio (1.5 %wt) by 0.834 g/cm$^3$ almost similar with kerosene density (0.835 g/cm$^3$). While the product density with highest catalyst ratio (2.5 % wt) by 0.797 g/cm$^3$ has closed to gasoline properties. As can be seen from the figure above, the density has been decreasing as a catalyst to feed ratio increased.

So, it can be explained that in the presence of alumina as a catalyst has a function to reduce the density of the liquid product. Product with lower density means the lighter oils properties [2] and it is an important quality indicator for automotive, aviation and marine fuels, where it affects storage, handling and combustion [9].

## CONCLUSION

This research studies the thermal and catalytic cracking of vacuum residue in pyrolysis process and investigated the effects of alumina catalyst ratio and reaction times to quality and quantity of the products. The experimental results concluded the following:

- Liquid product can be produced in shorter reaction times by using double heating elements in the reactor.
- Presence alumina catalyst in this experiment has a great effect on increases the liquid yields and minimized the coke residue, but decrease the gas yields.
- In a thermal process, produce the liquid product with highest saturates content. But in the catalytic

process produce liquid products with highest aromatics and olefins contents.

- More ratio of alumina catalyst to feed has decreased the density of liquid product and increased the API gravity.

## ACKNOWLEDGEMENTS

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