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Upgrading Vacuum Residue By Swelling Of Co_2 Gas And Catalytic Cracking Process By Using Al_2o_3 Catalyst

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Abstract:

Vacuum residue is a waste of the production process in the petroleum refining industry. It still contains hydrocarbon compounds that can be reused as a petroleum derivatives product that have commercial value. Improving the quality of vacuum residue is carried out in several stage of the process. In this study, the swelling process as an initial step to weaken and break the long chain carbon of vacuum residue in order to reduce energy consumption was applied. Furthermore, the swelling products are reprocessed to the catalytic cracking processes to improve the quality and quantity of the product yield. The application of the swelling process can reduce operating conditions temperatures up to 350ºC, and the use of Al_2O_3 catalyst in the cracking process can produces the product yield that have a good quality after performing the GC-MS analysis test. The content of hydrocarbons in the vacuum residue of our research product shows the dominance of aromatic compounds with high octane numbers. Octane number is one of the main indicators in a fuel, regardless of the quality of the fuel. In this research, vacuum residue that obtained from the cracking process contain compounds that have a high octanes number that is equivalent to commercial fuels. The optimum composition of 5%-wt catalyst showed chromatogram composition of 166 compounds with the highest peak at 3.26 retention time owned by toluene with an octane number of 91.

Keywords: Vacuum Residue, Swelling, Catalytic Cracking, GC-MS

Abstrak (Indonesia):

Residu vakum merupakan limbah dari proses produksi di industri penyulingan minyak bumi. Masih mengandung senyawa hidrokarbon yang dapat digunakan kembali sebagai produk turunan minyak bumi yang memiliki nilai komersial. Peningkatan kualitas residu vakum dilakukan dalam beberapa tahapan proses. Pada penelitian ini dilakukan proses swelling sebagai langkah awal untuk melemahkan dan memutus rantai panjang karbon residu vakum guna mengurangi konsumsi energi. Selanjutnya produk swelling diolah kembali ke proses catalytic cracking untuk meningkatkan kualitas dan kuantitas rendemen produk. Penerapan proses swelling dapat menurunkan temperatur kondisi operasi hingga 350ºC, dan penggunaan katalis Al2O3 dalam proses cracking dapat menghasilkan rendemen produk yang memiliki kualitas yang baik setelah dilakukan uji analisis GC-MS. Kandungan hidrokarbon dalam residu vakum produk penelitian kami menunjukkan dominasi senyawa aromatik dengan angka oktan tinggi. Angka oktan merupakan salah satu indikator utama dalam suatu bahan bakar, terlepas dari kualitas bahan bakarnya. Dalam penelitian ini residu vakum yang diperoleh dari proses perengkahan mengandung senyawa yang memiliki angka oktan tinggi yang setara dengan bahan bakar

komersial. Komposisi optimum katalis 5% -wt menunjukkan komposisi kromatogram 166 senyawa dengan puncak tertinggi pada waktu retensi 3,26 dimiliki oleh toluena dengan bilangan oktan 91.
Kata kunci: Residu Vacum, Pembengkakan, Katalitik, GC-MS

1. Introduction

Upstream oil and gas industry have an impact on the environment with emergence of waste, both exploration and production stages. The main waste in the form of sludge oil is classified into toxic and hazardous waste (B3). In government regulation (PP) No. 104 of 2014 concerning of Management of Hazardous and Toxic Waste [1], it is mentioned that *B3 is a substance, energy, and/or other components in which due to their nature concentration and/or amount, both directly and indirectly, are able to pollute and/or damage the environment, and/or endanger the environment, health, and the survival of humans and other living things.*

From this context, it can be interpreted that B3 waste generated from oil and gas exploration and production activities must be handle specifically, B3 waste cannot be disposed of directly into the environment without processing. The management of B3 waste must be carried out with due regard to the longterm impact and having a permit from both SKK MIGAS and the Ministry of Environment and Forestry (KLHK).

Waste can occur during exploration and production, where the production stage starts from the production well that has been drilled to the completion of the extraction process of oil and gas from the reservoir. Generally, the waste generated from this stage is production water, chemical residues to sludge/bottom. Waste production stage is oil sludge/bottom waste, which contains ammount of hydrocarbons, heavy metals and chemicals. Until 2014, petroleum production has reached 860 thousand barrels per day, and there was a waste of sludge oil of around 51 thousand m^3 per year [2].

Vacuum residue is a waste of petroleum production. Separation or extraction process and cracking process from vacuum residue produce derivative products such as gasoline and diesel. In Indonesia, the derivative product market is very good, but the service providers that can process waste into usable product and constraints in the licensing process at KLKH [3].

Vacuum residue contains undesirable materials such as organic and inorganic compounds, as well as toxic substance that are harmful to the environment caused by pathogenic diseases of microorganisms [4]. Disposal of oil sludge which contains toxic substances such as aromatic hydrocarbons (benzene, toluene, ethyl benzene, and xylene), poly-aromatic hydrocarbons and high total hydrocarbon content,without further processing can cause pollution to environment, especially soil contamination [5] Initially, vacuum residue waste made into asphalt or heavy oil or bunker fuel oil. However, the use of vacuum residue as a fuel has stalled due to stringent environment regulation about air emission thresholds [6].

Quality improvement effort of vacuum residue is a reflection Minister of Environment Regulation No. 13 of 2007 concerning Requirements and Procedures for Waste Management for Oil, Gas and Geothermal Businesses [7]. Work procedures on the management of oil and gas production operations are regulated later by PT. PERTAMINA and SKK MIGAS [8].

Generally, to improve the quality of vacuum residue is done by the process of pyrolysis and cracking. Cracking process is the best process in an effort to improve the quality of vacuum residue, but the operating conditions are quite high.

In the last few decades, most researchers have emphasized the development of refining techniques to produce high-value fuels, especially in the cracking process. Hosseinpour et al, conducted a study on increasing residual vacuum with the catalytic cracking method that use of the $SiO_2/\alpha\text{-}Fe_2O_3$ catalyst. The result obtained are an increase conversion in coke yield, but the operating conditions are very high (T = 550ºC and P = 610 atm) [9].

Eshragian et al, continued their research on catalytic cracking and vacuum residue. The research process was carried out in a batch reactor with the use of Al_2O_3 nanoparticles catalyst (NPs) and drill cuttings (DC). Operating condition still high at 420ºC or 450ºC, with a mixing speed of 500 ppm of DC and NPs without mixing. From this research, an increase in liquid yield conversion is obtained [10].

Previous research shows that the catalytic cracking process is still carried out at high operating conditions, especially temperatures. For this reason, researchers are looking for effort to reduce energy consumption by doing a weakening process, namely the swelling process.

2. Material and Methods

This research defined the composition of vacuum residue obtained by refinery unit III PT. PERTAMINA (Persero), Sungai Gerong – Palembang. The characteristic of vacuum residue shown in Table 1.

Table 1. Characteristics of Vacuum Residue Refinery Unit III PERTAMINA - Plaju

Properties	Test Methods	Typical Specification
SG at 60/60º	ASTM D-1298	Max 0.9800
Conradson Carbon Residue	ASTM D-189	Max 12.5
Metal Content		
- Vanadium	AAS	Max 2.0
- Sodium	AAS	Max 90.0
Pour Point	ASTM D-97	Max 120
Sulphur Content	ASTM D-4294	Max 0.35
Water Content	ASTM D-95	Max 0.5
FlashPoint PMCC	ASTM D-93	Max 190
Kinematic Viscosity (170ºF)	ASTM D-445	Max 360.0

Al_2O_3 was used as a catalyst. It was produced by W.R Grace & Co. as a global aluminium oxide manufacturing and distribution company, and has been licensed by the United State Environmental Protection Agency (USEPA) has shown in Table 2.

Table 2. Characteristic of Alumina Catalyst

Description	Specification
Molecular Weight	101,96 g/mol
Appearance/Physical State/Colour	White odorless powder
Melting Point /Freezing Point	2000ºC
Boiling Point	2980ºC
Density	3.2 – 4 g/cm^3
Vapor Pressure	1 hPa at 2158ºC
Surface Area	100 m^2/g
Particle Size	70% between 0.063 – 0.200 mm
Water Solubility	Very low (0.00002 g/L at 20ºC)
PH value (10% suspension)	9.0 – 10.0
Purity/Impurities/Additives	95%+ with trace amounts of other metal oxides, sulfates and/or chlorides

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The steps of this research consist of swelling process with supercritical gas of CO_2 and catalytic cracking process as shown in Fig. 1

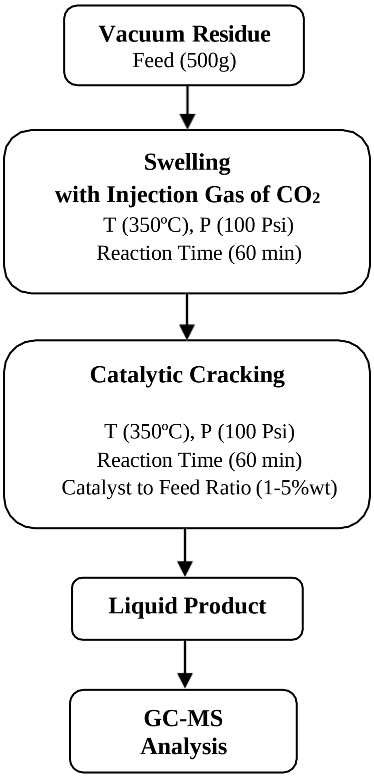

Fig. 1 Steps of The Swelling – Cracking Process and GC-MS Analysis

The process was carried out in a fixed bed reactor with operating conditions of 350ºC, pressure of 100 Psi, and reaction time up to 60 minutes.

Vacuum residue as a feed is put into the reactor, then after reaching the desired temperature do the CO_2 gas injection. The stage is called swelling process the purpose is to observe the liquid product, whether it can cracking at temperatures lower than the literature.

Swelling is a process of increasing the volume of the initial state and the final state, and is influenced by temperatures or thermal conditions. The aromatic structure in the dual bond like a benzene molecule in asphaltene vacuum residue induce the bond to be rich in electrons and alkaline, which is difficult to break and weaken, so that the swelling process by CO_2 gas injection with its acidic (H^+) and supercritical properties can attack dual covalent bonds [11].

The product of the swelling was processed by the catalytic cracking process. Catalytic cracking is a process of breaking with the assist of catalyst to speed up the reaction and control it without being consumed by the reaction [12]. This research utilizing the Al_2O_3 catalyst which was varied to the feed (1, 2, 3, 4, and 5%-wt) to obtain the liquid product yield.

The product will be analyzed using the GC-MS (Gas Chromatography – Mass Spectroscopy). GC-MS analysis was carried out to see the content in the sample of product obtain from catalytic cracking process. The goal of this research is to obtain the octane number from the final product. The compounds contained in the sample will be grouped based on their chain structure [13].

3. Result and Discussion

Waste treatment of petroleum production (vacuum residue) was carried out by swelling method and catalytics cracking.

The liquid product from the catalytic cracking process were analyzed using the GC-MS analysis method. The product test shown in Fig.2. The purpose of its analysis is to determine the quantity and quality of hydrocarbon content in the vacuum residue, which are saturated, olefin, and aromatic compounds.

The GC-MS analysis is done by injecting a small number of samples into the instrument. When the analysis time is over, the peak produced on the chromatogram will be matched with the compounds in the library, so it can be known the content of the compound in the sample.

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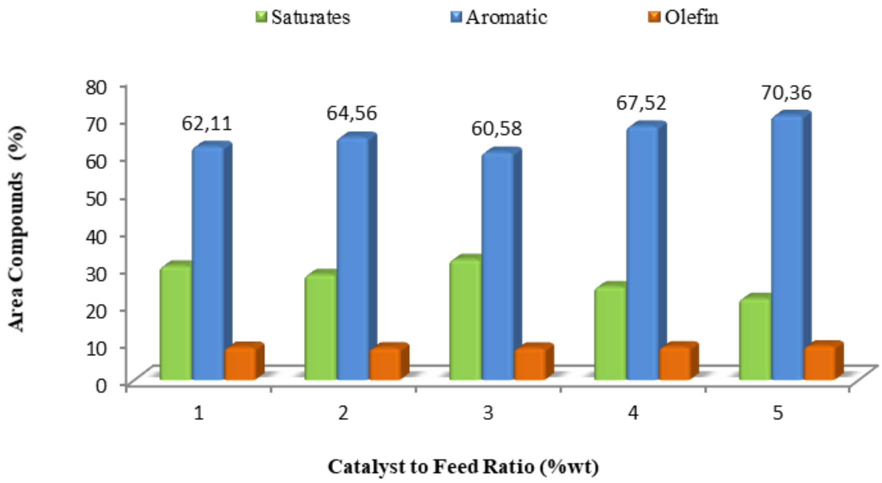


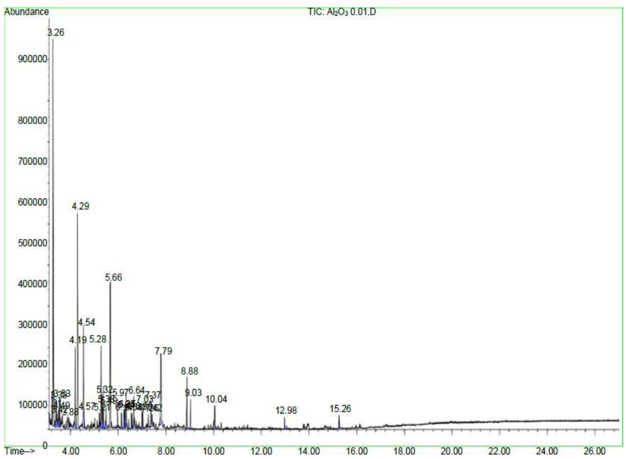
Fig. 2 Results of Liquid Product Analysis of Catalytic Cracking Process with GC-MS

The figure above shows the fluctuation between the content of saturates, olefins, and aromatics based on the ratio of alumina catalyst to vacuum residue feed. However, it can be seen from the figure that the aromatic content still has the highest percentage of compound area than saturates and olefins even in the presence of fluctuation.

The lowest percentage of aromatic compounds has in the ratio of 3%-wt catalyst is 60.58%, saturates compounds is 32.04% and olefin compounds is 8.47%. Whereas the catalyst ratio of 5%-wt has the highest percentage of aromatic compounds, which is 70.36%, with a lower percentage of saturates compounds of 21.68% and higher olefin compounds of 9.05%.

By references, the components of saturated (paraffin and naphtanes) are lighter fraction than aromatic and olefins. However, in liquid products such as gasoline, aromatic and olefins components are the most important, because liquid product that have high component of aromatic and olefins also have high octane numbers. It means that the products have better product quality [14].

The types of gasoline produced and marketed by PT. PERTAMINA (Persero) that we called premium currently has an octane number 88 with a maximum lead content of 3 g/l and a maximum sulfur content of 2%-wt [15].



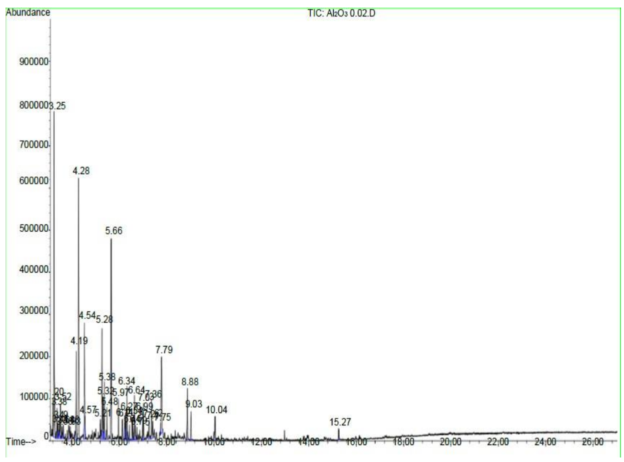


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Fig. 3 GC-MS Chromatogram Ratio Al_2O_3/VR (1%-wt)

Fig. 4 GC_MS Chromatogram Ratio Al_2O_3/VR(2%-wt)

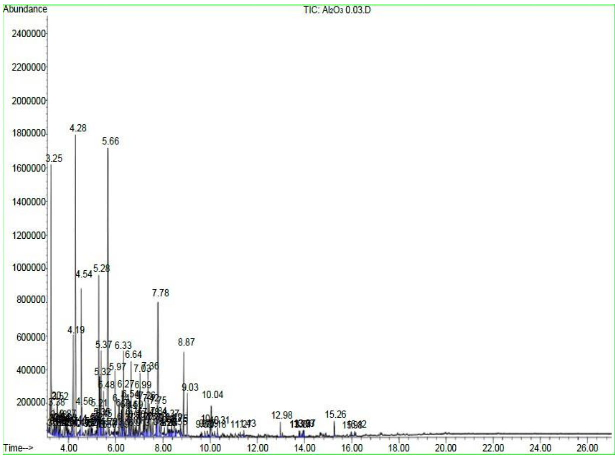

Fig. 5 GC-MS Chromatogram Ratio Al_2O_3/VR (3%-wt)

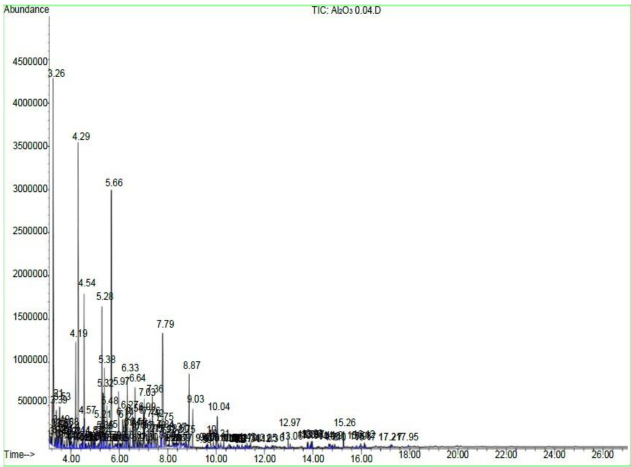

Fig. 6 GC-MS Chromatogram Ratio Al_2O_3/VR (4%-wt)

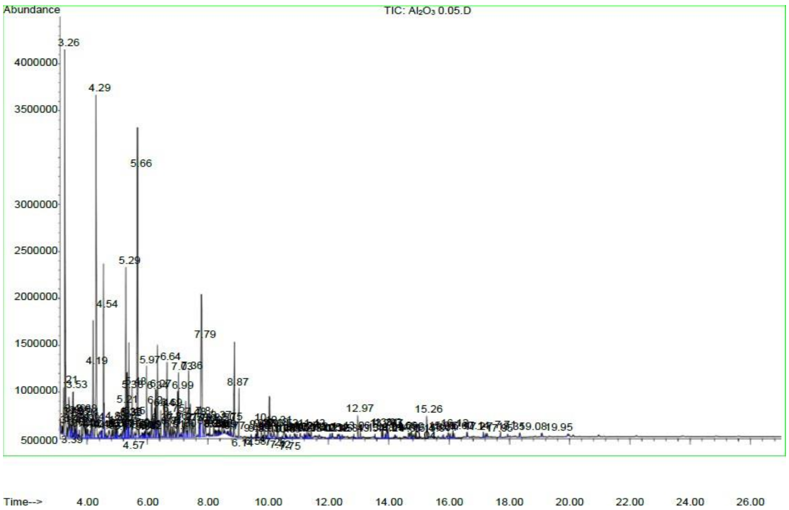

Fig. 7 GC-MS Chromatogram Ratio Al_2O_3/VR (5%-wt)

Fig.3 shows the GC-MS chromatogram reading 36 compositions of compounds in a liquid product of catalytic cracking process with variation of Al_2O_3/VR is 1%-wt.

Fig.4 shows the GC-MS chromatogram reading 42 compositions of compounds in a liquid product of catalytic cracking process with variation of Al_2O_3/VR is 2%-wt.

Fig.5 shows the GC-MS chromatogram reading 106 compositions of compounds in a liquid product of catalytic cracking process with variation of Al_2O_3/VR is 3%-wt.

Fig.6 shows the GC-MS chromatogram reading 144 compositions of compounds in a liquid product of catalytic cracking process with variation of Al_2O_3/VR is 4%-wt.

Fig.7 shows the GC-MS chromatogram reading 166 compositions of compounds in a liquid product of catalytic cracking process with variation of Al_2O_3/VR is 5%-wt.

The chart of GC-MS analysis above shows the same result, is the composition of aromatic compounds dominating the product, followed by olefins and saturated compounds (paraffin

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and naphtene). The charts above that the higher the variation of the ratio of catalyst to feed, the more composition of hydrocarbon contained.

The composition of aromatic compounds at a catalyst ratio of 1%-wt was 62.11%; catalyst ratio of 2%-wt is 64.56%; catalyst ratio of 3%-wt is 60.58%; catalyst ratio of 4%-wt is 67.52%; and catalyst ratio of 5%-wt is 70.36%.

The most composition is shown in fig.7. From this figure, it can be seen that the peak is quite high at the retention time of 3.26, 4.29, 4.54, 5.29 and 5.66. GC-MS data shows that the retention time of 3.26 belongs to the toluene with an octane number of 91, at a retention time of 4.29 owned by a benzene (p-xylene) with an octane number 97, a retention time of 4.54 owned by a benzene (o-xylene) with an octane number 97, a retention time of 5.29 owned by benzene (1-ethyl-2-methyl) with an octane number 94, and retention time of 5.66 owned by propanoic acid with octane number 94. All of these compounds are high-octane aromatic compounds.

4. Conclusion

Swelling process is able to weaken and break the hydrocarbon chain of vacuum residue. This is evidenced by the low temperature cracking process of vacuum residue has occurred at 350ºC.

Thermal cracking has produced a liquid product which has a high aromatic content at the optimum catalyst composition of 5%-wt.

Aromatic compounds have high octane numbers. The GC-MS results for the retention time of 3.26 belonging the toluene compound have an octane number of 91, and a retention time of 4.29 owned by benzene (p-xylene) having an octane number of 97.

Waste treatment of oil production into derivative products that can be reused has been able to reduce the composition of B3 waste in the environment.

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