**UPGRADING VACUUM RESIDUE BY SWELLING OF CO2 GAS AND CATALYTIC CRACKING PROCESS BY USING AL2O3 CATALYST.**

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**ABSTRACT**

Vacuum residue is a waste of the production process in the petroleum refining industry. Even though vacuum residue is waste, it still contains hydrocarbon compounds that can be reused as a petroleum derivatives products that have commercial value. Improving the quality of vacuum residue from waste to commercial products is carried out in several stage of the process. In this research, we applied the swelling process as an initial step to weaken and break the long chain carbon of vacuum residue in order to reduce energy consumption. Furthermore, the swelling products will be reprocessed in 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 Al2O3 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 this vacuum residue shows the dominance of aromatic compounds with high octane numbers. 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

1. **Introduction**

Upstream oil and gas industry has 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 0f 2014 concerning of Management of Hazardous and Toxic Waste, it is mentioned that *B3 is a substance, energy, and/or other components which, due to their nature, concentration and/or amount, both directly and indirectly, can polluting and/or damaging the environment, and/or endangering the environment, health, and the survival of humans and other living things.*

From this context we can interpret 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 long term 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 amount of hydrocarbons, heavy metals and chemicals. 2014, oil production amounting to 860 thousand barrels per day, there is sludge oil waste of around 51 thousand m3 per year (Helmy and Kardena, 2015)

This sewage sludge is like a deep black paste, sometimes mixed with soil, gravel, water, and other ingredients. This mud is caused by the deposition of fine oil particles. These sediment accumulate more and more at the bottom of the storage tank or in the pipeline of petroleum distribution. This silt is called vacuum residue.

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 (Adhitya et al., 2017).

Vacuum residue contains undesirable materials such as organic and inorganic compounds, as well as toxic substance that are harmfull to the environment caused by pathogenic diseases of microorganisms (Ayotamuno et al., 2007). 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 sil contamination (Vilia et al., 2012).

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 (BOPK, 1999).

Quality improvement effort of vacuum residue is a reflection of Minister of Environment Regulation No. 13 of 2007 concerning Requirements and Procedures for Waste Management for Oil, Gas and Geothermal Businesses. Work procedures on the management of oil and gas production operations regulated later by PT. PERTAMINA and SKK MIGAS (Implementing Working Unit, 2018).

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. For this reason, researchers are looking for effort to reduce energy consumption by doing a weakening process, namely the swelling process.

1. **Experimental Pprocedures**

**2.1 Feed Material and Catalyst**

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

Table 1. Characteristics of Vacuum Residue

Refinery Unit III PERTAMINA - Plaju

|  |  |  |
| --- | --- | --- |
| **Properties** | **Test Methods** | **Typical Specification** |
| SG at 60/60ºConradson Carbon ResidueMetal Content* Vanadium
* Sodium

Pour PointSulphur ContentWater ContentFlashPoint PMCCKinematic Viscosity (170ºF) | ASTM D-1298ASTM D-189AASAASASTM D-97ASTM D-4294ASTM D-95ASTM D-93ASTM D-445 | Max 0.9800Max 12.5Max 2.0Max 90.0Max 120Max 0.35Max 0.5Max 190Max 360.0 |

Al2O3 is used in this research as a catalyst, and 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), shown in Table 2.

Table 2. Characteristic of Alumina Catalyst

|  |  |
| --- | --- |
| Description  | Spesification |
| Molecular WeightAppearance/Physical State/ColourMelting Point /Freezing PointBoiling PointDensityVapor PressureSurface AreaParticle SizeWater SolubilityPH value (10% suspension)Purity/Impurities/Additives | 101,96 g/molWhite odorless powder2000ºC2980ºC3.2 – 4 g/cm31 hPa at 2158ºC100 m2/g70% between 0.063 – 0.200 mmVery low (0.00002 g/L at 20ºC)9.0 – 10.0 95%+ with trace amounts of other metal oxides, sulfates and/or chlorides |

* 1. **Research Methods**

The steps of this research consist of swelling process with supercritical gas of CO2 and catalytic cracking process, where the product obtained from swelling process will be continued to catalytic cracking process as shown in Fig. 1

**Vacuum Residue**

Feed (500g)

**Swelling**

**with Injection Gas of CO2**

T (350ºC), P (100 Psi)

Reaction Time (60 min)

**Catalytic Cracking**

T (350ºC), P (100 Psi)

Reaction Time (60 min)

Catalyst to Feed Ratio (1-5%wt)

**Liquid Product**

**GC-MS**

**Analysis**

Fig. 1 Steps of The Research Process

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 CO2 gas injection. The stage is called swelling process whose 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 asphalthene 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 CO2 gas injection with its acidic (H+) and supercritical properties can attack dual covalent bonds (Abedini et al., 2014).

The product of the swelling are then 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. This research utilizing the Al2O3 catalyst which was varied to the feed (1, 2, 3, 4, and 5%-wt) to obtain the liquid product yield.

Al2O3 catalyst is a type of catalyst that is absorbent, it’s a catalyst that is able to absorb free electron pairs from vacuum residue, so its can to increase the quality and quantity of vacuum residue.

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 groped based on their chain structure (Rhezia, 2012).

1. **Result and Discussion**

Waste treatment of petroleum production (vacuum residue) is carried out by swelling method followed by catalytic cracking.

The liquid product from the catalytic cracking process were analyzed using the GC-MS analysis method. The product test are 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.

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 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 is 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 reference, the components of saturated (paraffin and naphtenes) are lighter fraction than aromatic and olefins. However, in liquid products such as gasoline, aromatic components and olefins are the most important because liquid product with high aromatic and olefin contents have higher octane numbers, its means that have better product quality.

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 (Kurniawan, 2014)



Fig. 3 GC-MS Chromatogram Fig. 4 GC\_MS Chromatogram

 Ratio Al2O3/VR (1%-wt) Ratio Al2O3/VR(2%-wt)



 Fig. 5 GC-MS Chromatogram Fig. 6 GC-MS Chromatogram

 Ratio Al2O3/VR (3%-wt) Ratio Al2O3/VR (4%-wt)



Fig. 7 GC-MS Chromatogram Ratio Al2O3/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 Al2O3/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 Al2O3/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 Al2O3/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 Al2O3/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 Al2O3/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 (parrafin 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 ois 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 show 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.

1. **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.

Basically, in principle from chemical compounds, octane number is highly correlated with the type of hydrocarbon compounds. Aromatic, naphtane (cyclic carbon chains), or branched carbon chains compounds is a hydrocarbon compounds that is good for increasing octane numbers.

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.

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 octane number that is equivalent to commercial fuels. Its means that the process of improving the quality of vacuum residue as petroleum waste with the application of swelling with supercritical gas of CO2 and cracking has obtained the desired results.

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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