

Electromagnetic Catalytic Cracking Process of Vacuum Residue Using Fe₂O₃/Al₂O₃Metta Wijayanti^{1*}, Sri Haryati¹, Muhammad Djoni Bustan¹¹Chemical Engineering Department, Postgraduated Program, Faculty of Engineering, Sriwijaya University
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Abstract: Vacuum residue is well known as waste product from crude oil refinery. Need a further process to improve its quality. In this study, a catalytic cracking process of vacuum residue in electromagnetic field was investigated using Fe₂O₃/Al₂O₃ as catalyst. The optimization process is conducted by combination vacuum residue and catalyst in the ratios of 1:5, 1:6, 1:7, 1:8, and 1:9 in 75 min of reaction time, 400°C and 10A applied current. Liquid product is analyzed using gas chromatography mass spectrometry (GCMS). The result showed the formation of p-xylene, paraffin, and naphthalene were detected 11.38% in the retention time of 4.3 min, 1.04% in the retention time of 7.76 min, and 3.28% in the retention time of 7.80 min, respectively.

Key words: vacuum residue, electromagnetic catalytic cracking (ECC), gas chromatography mass spectrometry (GCMS)

1. Introduction

Crude oil is a mixture of organic compounds that consist of hydrocarbon and nonhydrocarbon compounds. It is generated by the fossil material of microorganisms, plants, and animals, which are covered by the past million years. The content of hydrocarbon compounds are more than 90% and the rest are nonhydrocarbon compounds such as sulphur, nitrogen, oxygen in the different content of volatility, specific gravity, and viscosity [1].

There are large amounts of oil residues in the oil refineries, including atmospheric and vacuum residues, which can be upgraded into valuable light fuels [2]. A vacuum distillation column typically produces 45% vacuum residue and 54.2% vacuum gas oil. The atmospheric residue is typically 53%, and vacuum residue is 25% of crude oil as refinery feed [3]. The vacuum residue resulting from heavy crude oil is 2 to 3 times more than that from medium and light crude oil [4].

The residue of crude oil is generated from a waste product from refinery, which is inexpensive and not maximally used by the industry. In the refinery unit, crude oil is used as feed in the atmospheric distillation column, it produces some oil fractions with the different distance temperature. Light fractions are used as fuel and residue as the heavy fractions have a low selling price [5].

Hydrocarbons are organic compound consist of hydrogen and oxygen. It was one of a contaminant, which can give a bad impact on human and

environment. Hydrocarbons were found in crude oil that is used by human in life and potentially stain the environment [6].

The environment can be stained by industrial activity in the refinery, start from downstream until upstream. The exploration includes the geology investigation, seismic, and the drilling to find crude oil sources and in the phase of production, distribution, storage, and trade potentially caused the environmental stain [7].

Industrial pollutants, which came from crude oil potentially endanger organism. This pollutant consist of hydrocarbon aliphatic and aromatic compound, which has light until heavy molecule weight [7].

With increasing consumption of fossil fuels, much effort has been focused on upgrading heavy oils in the recent years. There are large amounts of atmospheric residue (AR) and vacuum-distilled residual (VR) oil in the petroleum refineries that could be transformed into valuable light fuels [8].

There are some technologies, which can be used to upgrading the vacuum residue to produce fuel in the good quality. Moreover, to improve the quality, it can minimize the waste of refinery, which can stain the environment. The negative impact can be decreased. Vacuum residue is a heavy fraction product on the bottom distillation unit in refinery crude oil. Vacuum residue contains Ni, V, N, S, and asphalt. This fraction contains of undesirable compound (some heteroatomic component) such as metal V and Ni [9].

As heavy fraction product, vacuum residue contains complex compound, such as hydrogen which has high boiling point (above 813K) and heteroatom, 3–5% sulphur, 0.2–1.0% nitrogen, and 0.1% metal. Moreover, vacuum residue which contains undesirable compound such as 5-30% of asphaltene, rich of polyaromatic and heteroatom, affects the precipitation and coke formation that depend on the reaction condition [10]. Saturates are heavy fraction oil consisting of non-polar hydrocarbon with linear structure, branches, and cyclic which saturate with hydrogen. The higher saturates in the crude oil means the increasing of production heavy fraction oil with higher boiling point [12].

Based on distribution of compound in the refinery unit, vacuum residue has a high boiling point (538°C) and carbon bond more than 25. High boiling point is caused by big molecules compound in the vacuum residue. Vacuum residue consists of complex compounds and form big molecules. Bigger molecules makes it hard to be cracked into smaller molecules. Some basic technology, which can be used to upgrade the quality of vacuum residue are thermal cracking, catalytic cracking and hydro cracking [11].

Asphaltene is the most compound, which can be found in vacuum residue. The result from Pertamina RU III Plaju-Sungai Gerong reported that the value/concentration of asphaltene is around 57.5%. Therefore, asphaltene becomes the focus of vacuum residue cracking. Asphaltene contains polyaromatic and heteroatomic compounds with the number of carbon is above 35. The complex molecules containing in vacuum residue generates a high difficulties in cracking and converting the vacuum residue to a product. Thermal cracking and catalytic cracking are reported to provide the effective processes to crack vacuum residue and catalytic cracking that is consumed a high energy, which is not socio-economically suitable for a large-scale process. Ngunyen et al in 2016 is one of formerly researchers who use the temperature condition above 450°C. It uses high-energy consumption. High temperature indicates the high-energy consumption to process of cracking.

Aromatics are hydrocarbon, which has one or more unsaturated benzene rings, which can be conducted with paraffin or naphtha. Saturates and aromatics are lighter component than asphaltene and naphtha, it can be influence the percentage of light component in crude oil. Resins are polar polyaromatic, which contain heteroatom such as nitrogen, oxygen and sulphur compound. They can be soluble in light alkane

such as n-pentane and n-heptane with molecule weight under 1000 g.mol⁻¹. Residue which contain high asphaltene and resins are aim to produce cokes [12]. It has been reported that the formation of coke could be less severe in gas phase than that in the liquid phase, because much lower agglomeration reactions occurred in the former status [13,14].

The distillation range of VR is mainly above 500 °C, hydrocarbons mainly undergo liquid phase reaction in the existing process. The free radicals which split from hydrocarbon can disperse quickly in the gas phase whereas they are surrounded by surrounding molecules like a “cage” in the liquid phase. Thus, to disperse the formed free radicals, it is necessary to overcome the extra energy barriers spread out from the “cage” in the liquid phase. This is the so-called “radical cage effect” [15,16]. Therefore, how to improve the gas-phase reaction ratio and suppress the liquid-phase reaction will become the key problem for the next generation of heavy oil processing technology [17].

Electromagnetics is necessary for achieving electromagnetic compatibility of products, for understanding high-speed digital electronics and wireless, and for optical computer networking. Electrical word describes a broad range of phenomena in addition to electronics, ranging from X-rays to optics to thermal radiation. In physics courses, we are taught that all these phenomena concern electromagnetic waves.

An important concept to aid understanding of electromagnetics is electrical length. Electrical length is a unit less measure that refers to the length of a wire or device at a certain frequency. When the wavelength is much longer than the wire lengths, the basic rules of electronic circuits apply and electromagnetic [18].

To break down the long chain of vacuum residue, we need media or substance, which can weaken the hydrocarbon bond. Every substance has their own magnetic field, and vacuum residue. So, it can be used to weaken the carbon bond in vacuum residue. Thermal vibration cause ion lattice trembles and electron conduction moves. Higher temperature cause the higher metal vibration.

2. Materials and Method

Based on Nguyen-Huy (2015), the temperature operation of cracking was 500°C and Nguyen-Huy (2016) used 2-4 hours as their reaction time. It gives reference to cracking the vacuum residue with lower temperature and short reaction time than before.

There are some stages to crack by using electromagnetic, catalyst manufacturing, equipment's

preparation, research, and analyzed. This chart represent the stages of research:

The catalyst is combination from two kind of catalyst to improve catalyst performance in cracking vacuum residue.

Equipment and material preparation

1. Equipment

This cracking process uses equipment series consisting of fixed-bed reactor, thermocouple, band heater, and metal winding as electromagnetic source.

2. Material

Vacuum residue came from Pertamina RU III Plaju-Sungai Gerong.

Table 2. Characterization of Vacuum Residue(MSDS Pertamina RU III Plaju-Sungai Gerong)

Uji	Unit	Metode Uji	Typical Specification
Spesific Gravity 60/60°F		ASTM D-1298	Max 0.98
Conradson Carbon Residue	%wt	ASTM D-189	Max 12.5
Vanadium (V)	PPm	AAS	Max 2.0
Sodium (Na)	PPm	AAS	Max 90.0
Pour Point	°F	ASTM D-97	Max 120
Sulphur Content	%wt	ASTM D-4294	Max 0.35
Water Content	%Vol	ASTM D-95	Max 0.5
Flash Point PMCC	°F	ASTM D-93	Min 190
Kinematic Viscosity at 170°F	cSt	ASTM D-445	Max 360.0
Paraffin	%wt		12.00
Naphtene	%wt		4.50
Aromatic	%wt		26.00
Asphaltene	%wt		57.50

Description of research process

Vacuum residue process uses fixed-bed reactor and the operational condition of electromagnetic catalytic cracking (ECC) on 400°C during 75 min, 10 A, and Fe₂O₃/Al₂O₃ as catalyst. Catalyst Fe₂O₃/Al₂O₃ ratio are 1:5, 1:6, 1:7, 1:8, and 1:9. Ratio catalyst to feed is 3:100.

Vacuum residue is introduced into the reactor as much as 1000g, with the condition 400°C during 75 min, and 10 A. Liquid product collected and analyzed the contents by using gas chromatography mass spectrometry (GC-MS).

2.1. Data Analysis

Liquid product ECC process were analyzed using GC-MS to detect the compounds contain which have retention time and peak area to explain their compound. In GC-MS, it used scan method. Identified compound of the liquid sample were appropriated with mass spectrometer in GC-MS.

3. Result and Discussion

ECC product by using catalyst (Al₂O₃/Fe₂O₃) ratio 1:5, 1:6, 1:7, 1:8, and 1:9 produce much liquid product conversion. The highest is 63.5% by using catalyst ratio 1:9. This results show how much liquid

product and the compound contain in it to be used furthermore.

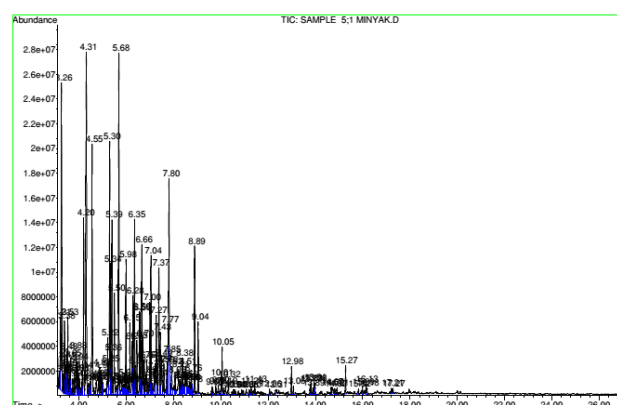


Fig. 5. Chromatogram GC ECC using catalyst (Al₂O₃/Fe₂O₃) ratio 1:5

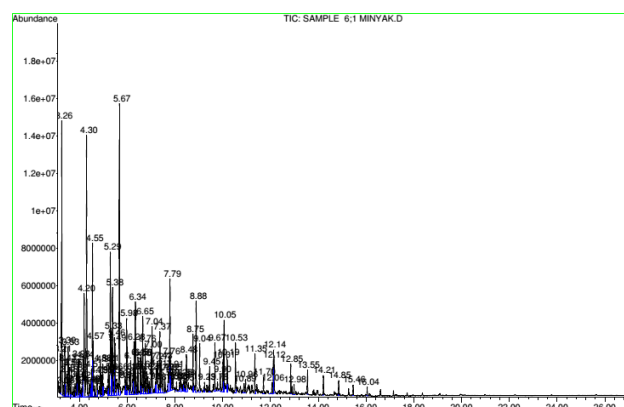


Fig. 6. Chromatogram GC ECC using catalyst (Al₂O₃/Fe₂O₃) ratio 1:6

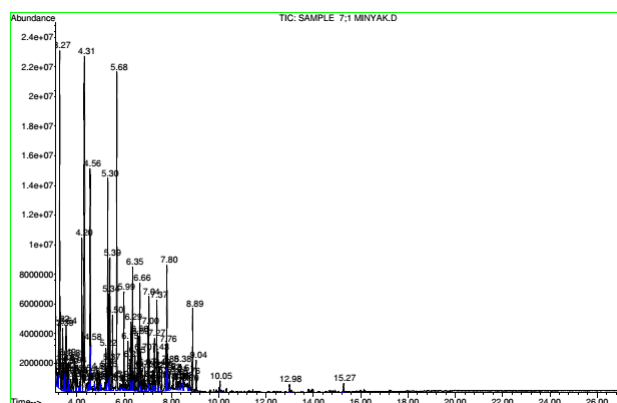


Fig. 7. Chromatogram GC ECC using catalyst (Al₂O₃/Fe₂O₃) ratio 1:7

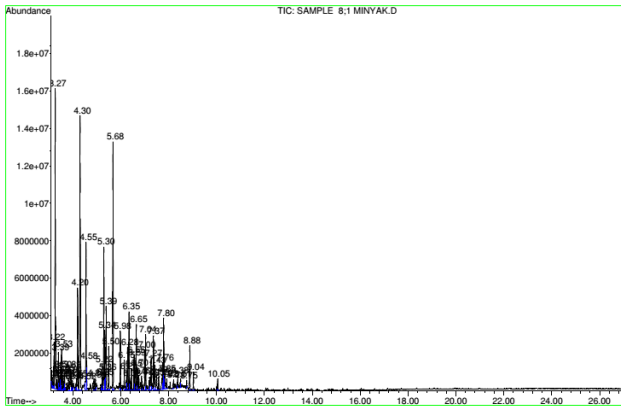


Fig. 8. Chromatogram GC ECC using catalyst ($\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$) ratio 1:8

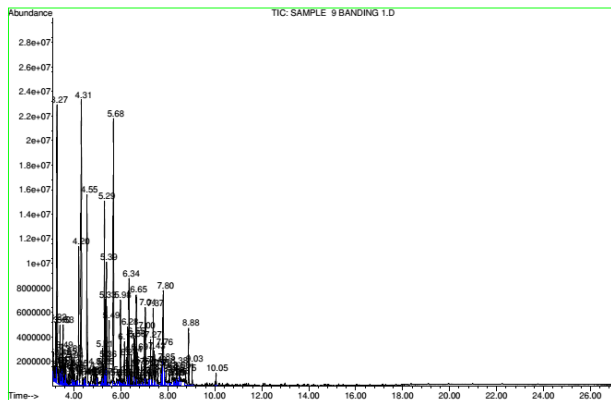


Fig. 9. Chromatogram GC ECC using catalyst ($\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$) ratio 1:9

Table 3. Interpretation of chromatogram GC ECC using catalyst ($\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$) ratio 1:9

Retention time (min)	content (%)	Library
3.22	1.57	Heptane,2-methyl-
3.27	8.6	Toluene
3.4	1.17	Cyclohexane,1,3-dimethyl-,cis-
3.54	1.32	Heptane, 2,4-dimethyl-
4.30	11.38	p-Xylene
4.55	5.44	p-Xylene
5.29	4.21	Benzene,1-ethyl-2-methyl-
5.33	1.74	Benzene,1-ethyl-2-methyl-
5.39	2.51	Benzene,1,3,5-trimethyl-
5.49	2.51	Benzene,1,3,5-trimethyl-
5.68	6.73	Benzene,1,3,5-trimethyl-
5.98	1.91	Benzene,1,2,4-trimethyl-
6.28	1.30	Benzene,1-methyl-3-propyl-
6.34	2.45	Benzene,2-ethyl-1,4-dimethyl-
6.65	2.03	Benzene,1-methyl-3-(1-methylethyl)-
7.00	1.26	Benzene,1,2,3,4-tetramethyl-
7.04	1.7	Benzene,1,2,3,4-tetramethyl-
7.27	1.44	Benzene,2-butenyl-
7.37	2.30	Benzene,2-ethenyl-1,4-dimethyl-
7.76	1.04	1H-Indene,2,3-dihydro-1,6-dimethyl-
7.80	3.28	Naphthalene
8.88	1.36	tridecane

Based on Table 2, paraffin, olefin, naphthenic and aromatics (PONA) were found in the liquid product

ECC using catalyst ($\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$) ratio 1:9. PONA compound indicates that asphaltene was successfully cracked resulted in the simple compounds. To be more specific, the retention time indicated that 11.38% of p-xylene, 1.04% paraffin, 3.28% naphthenic were found in retention time of 4.3, 7.3, and 7.80 min, respectively.

The result confirmed that the electromagnetic Catalytic Cracking (ECC) using catalyst $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ can break complex bound in vacuum residue. In previous research, Khalil (2015), vacuum residue can be cracked in 2-4 hours at 743 K and 1-2 atm in fixed bed reactor [19].

The formation of 1-alkenes was attributed to the rupture of alkyl free radicals. The formation of iso-alkenes was mainly due to the cracking of isomeric alkyl substituents attaching to aromatic rings and naphthenic rings [20]. Meanwhile, the aliphatic free radicals and naphthenic free radicals produced by the cracking reaction could capture H radicals and then produce alkanes, which is the cause of formation of nalkanes and iso-alkanes and cycloalkanes [21].

The result also proved that the electromagnetic field can break the hydrocarbon bond of vacuum residue, initiated by $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$. Fe_2O_3 has bigger pore than Al_2O_3 , it makes the compounds with big molecule size can absorb to the pore. Group OH in Fe_2O_3 is a receiver or pulls electron from double bond in saturates bond of vacuum residue. It caused the bond more weak and easy to be cracked.

The electrical conduction mechanism produces heat via electrical resistance. The electrical field of ECC oscillates the electrons or ions in a conductor and leads to an electric current. This current encountered internal resistance, heating the conductor.

Hydrocarbons cracking reactions is well known in an electric arc or electric discharge. In the presence of a Journal Pre-proof 11 catalyst, more valuable products can be formed from free radicals produced in an electric discharge. When the thickness of metal is small compared to the penetration depth, the surface is hot. Under these conditions, electrons are released from the material and are accelerated in the electric field [22]. This electron energy is sufficient to crack the chemical bonds in the molecules constituting free radicals.

Fe_2O_3 has big surface area. It can minimize the sintering effect and increase catalytic activity. The combination of Fe_2O_3 and Al_2O_3 can be more increase catalytic activity and active sites [24].

Nasri [23] told the effect of increased Fe catalyst on asphaltene reduction is significant at higher amounts of activated carbon (15 and 20 %). With an increase in activated carbon content, the effect of Fe catalyst on asphaltene reduction has significantly increased. It also can be observed that the reduction of asphaltene is sharp at initial addition of activated carbon and thereafter decreases slowly with increasing activated carbon.

Hydrocarbon spill on the soil and water would envenom the animals and plants whose life in that environment, not only them but also can envenom the human. Therefore, it has to tackling step on field contamination oil in order to minimize the contamination area. The usage of the waste product of crude oil (VR) by upgrading the quality is the one of the way to minimize the quantity of waste oil.

Result analysis of GC-MS showed that product ECC contain of PONA compound. It can be used as fuel. ECC can upgrade the quality of vacuum residue which known as waste product in refinery. The usage of this product will decrease oil waste, which is harmful for the environment and the life creature in it.

4. Conclusion

Process of Electromagnetic Catalytic Cracking (ECC) and catalyst $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ can crack the complex hydrocarbon bond in vacuum residue faster and being the simple compound. It is PONA compound, which is fuel contents. Catalyst ($\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$) ratio 1:9 give the best result in vacuum residue cracking. It is shown on GC-MS result. In retention time 4.3 min was found 11.38% p-xylene which count as aromatic compound. 1.04% paraffin was found in retention time 7.76 min. Then, 3.28% naphthenic was found in retention time 7.80 min. The usage of vacuum residue product which is waste refinery product can be reduced the waste and bad effect to environment.

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