

# The Effect of Swelling Factor Vacuum Residue on Fuel Product Using Supercritical Gas CO<sub>2</sub>

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**Abstract**—Vacuum residue is a by-product of the petroleum refining industry process that has low quality and low selling price under crude oil with hydrocarbon compound content consisting of carbon and hydrogen atoms. It can be utilized by improving the quality of vacuum residue from waste into commercial products is carried out through several stages of the process that become a new interest to convert this raw material into valuable fuel oil by using swelling process. The effect of the swelling process with supercritical gas CO<sub>2</sub> is to weaken and break the long carbon chain vacuum residue to lower the process's energy consumption. It is swelling with supercritical CO<sub>2</sub> gas results in the mixing of CO<sub>2</sub> into the oil phase, increasing vacuum residue volume. This process takes place on a fixed bed reactor with temperature operating conditions (200°C, 250°C, 300°C, and 350°C), CO<sub>2</sub> pressure (100Psi, 120Psi, 140Psi, 160Psi, and 180Psi) and reaction time (60 minutes and 90 minutes). The result of liquid product from swelling process with supercritical of CO<sub>2</sub> gas is done by analysis method of Gas Chromatography-Mass Spectrophotometer (GCMS) instrument using optimal time in pressure operating conditions 160Psi, the temperature of 350°C and reaction time of 90 minutes resulted in a percent swelling factor of an excellent vacuum residue of 7.14%. Hydrocarbon compound content in the research products showed the dominance of aromatic compounds by 71.53%, saturates compound 35.79%, and olefin compound by 10.05%.

**Keywords**— Vacuum residue; swelling factor; GC-MS.

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## I. INTRODUCTION

The world demand for fuel oil and petrochemical products has increased rapidly, while the supply of petroleum fuels from oil reservoirs in Indonesia has continued to decline, resulting in the fuel oil crisis in Indonesia. The increasing demand for light fuels, especially gasoline, is important for extracting many useful ingredients from crude oil. Heavy oil and vacuum residue as a by-product of refineries have low quality and low prices [1].

Vacuum residue as a cheaply available raw material has shown alternative sources of useful oil production ranging from 30-60% by weight of crude oil [2]. The loss of vacuum residue quality is due to asphaltene, heavy metals, and heteroatoms. Therefore, increasing vacuum residue is interested in turning this raw material into valuable fuel oil using the swelling process. Increasing vacuum residue aims to reduce the viscosity, density, and boiling point, becoming a lighter fuel with a high ratio of Hydrogen and Carbon content [2].

In research on residual vacuum [3] manage research in converting residual vacuum within under boiling liquid products through environmentally friendly channels into high value under boiling liquid products. Bimetal Ni-Mo is used as a supporter of goethite minerals and is well characterized using a variety of analytic techniques. The catalytic activity of VR hydrocracking was examined in a batch reactor, catalyst Ni (1%) - Mo / Goethite (4.5%) gave a yield of liquid products with a low boiling point, 69.8%, with vacuum residue conversion of 80% at 420°C, and a first hydrogen load of 70 bar in 3 hours. The resulting liquid product contains 8.6% naphtha, 51.4% middle distillate, 9.8% of vacuum gas oil (VGO) with saturated point 28.1%, 8.4% resin, 62.5% aromatic, and more than 1% asphalt content.

Research on residual vacuum requires an effective process method to get the best results [4]. One of the processing methods that can give the best results without a catalyst is swelling [5]. Another research [6] determines the effect of swelling gas (CO<sub>2</sub>) and interfacial methods (IFT) on crude oil. The results obtained, namely, the swelling process, has a dominant effect on the results obtained at different

temperatures (300°C = 0.9847), (500°C = 0.9889), (800°C = 0.9918). The balance of the IFT increases with the increasing temperature. Among all types of gas injection processes, CO<sub>2</sub> injection has been widely employed because of its high potential for enhanced oil recovery. CO<sub>2</sub> reacts with the reservoir rock and fluids and modifies their properties, providing more favorable conditions for oil production. Oil viscosity and interfacial tension reduction, oil swelling, and extraction of lighter oil components by CO<sub>2</sub> are the principal mechanisms that contribute to CO<sub>2</sub> enhanced oil recovery processes [7]. The improvement in volume was due to the solubility of gas (CO<sub>2</sub>) into the raw oil state. In other own [4] CO<sub>2</sub> is one of the media to enhance oil recovery (EOR) that has been used successfully in the oil processing industry with a relatively low-temperature reservoir [8]. The safe absorption of CO<sub>2</sub> in geological formations and aquifers is also very interesting. In this study [7], the chemical properties and physical properties of CO<sub>2</sub> consist of crude oil and brine, as well as the interaction between these compounds are very important, i.e., a binary system in each EOR process.

CO<sub>2</sub> injection has become one technique that produces the most common improvements in EOR. CO<sub>2</sub> can be injected in mixed conditions during oil manufacturing or not combined into a completed oil reservoir to increase EOR. The ability of CO<sub>2</sub>-based EOR systems depends largely on the solubility of CO<sub>2</sub> in the oil phase as it results in increased viscosity volume [9]. CO<sub>2</sub> injection with oil can be achieved at low temperatures that contain the API relatively higher than 36°API and use a high pressure [10]. When injected under insoluble conditions, CO<sub>2</sub> increases oil through viscosity, increases the volume of vacuum residue, and replaces the gas solution. A laboratory experiment [11] of CO<sub>2</sub> injection of stock tank oil (STO), as referred to at the beginning of CO<sub>2</sub> injection, a process of mixing CO<sub>2</sub> into the oil phase occurs to increase the volume of vacuum residue (swelling). Higher than the amount of CO<sub>2</sub> injected can occur in transferring a portion of the light hydrocarbon component into CO<sub>2</sub> gas.

The swelling factor of vacuum residue by dissolved CO<sub>2</sub> and the reduction in viscosity of vacuum residue are the two main physical mechanisms of the CO<sub>2</sub> EOR method [12]. If CO<sub>2</sub> is injected into this reservoir, including contact by vacuum residue, CO<sub>2</sub> dissolution occurs, causing an increase in the volume of vacuum residue (swelling) [11]. The system expansion process can reduce the viscosity of the vacuum residue significantly and therefore increase the mobility of the vacuum residue when the pressure increases and the amount of CO<sub>2</sub> injected can occur, moving some light hydrocarbon components into CO<sub>2</sub> (extraction). With the extraction of light hydrocarbons and some heavy hydrocarbons, a condition in which CO<sub>2</sub> dissolves with the oil phase is obtained. Likewise, the injection of CO<sub>2</sub> EOR at a specific pressure and temperature reservoir can extract lighter hydrocarbon compounds into the CO<sub>2</sub> phase and will condense again into the oil phase [11]. This event will encourage the process of dissolved displacement, swelling of vacuum residue due to saturation of CO<sub>2</sub>, decreased viscosity of vacuum residue that expands due to mixing CO<sub>2</sub>, which has a viscosity far below the vacuum residue, extraction of light hydrocarbons into the CO<sub>2</sub> phase, and fluid movement.

This research discusses to study the effect of the swelling process of CO<sub>2</sub> gas injection on the distribution of residual

vacuum hydrocarbon bond energy generated. This research aims to produce residues that have low bond energy and low viscosity and are more valuable under operating conditions of optimal temperature, pressure, and reaction time.

## II. MATERIAL AND METHOD

### A. Vacuum Residue

Vacuum Residue is the main ingredient in this study using the swelling process with CO<sub>2</sub> gas injection. The initial stage of residual vacuum as a feed is carried out the CO<sub>2</sub> gas injection process to determine the reduction of the molecular energy bonds from the residual vacuum by observing liquid products (liquid) based on variations in temperature, pressure, and reaction time. The raw material used in this study is Vacuum Residue (VR) from the PT. Pertamina RU (III), Sungai Gerong, shows the main characteristics in Table I.

TABLE I  
CHARACTERISTICS OF VACUUM RESIDUE

Properties	Unit	Test Methods	Specification
Specific Gravity 60/60°F		ASTM D-1298	Max 0.98
Conradson Carbon Residue	%wt	ASTM D-189	Max 12.50
Vanadium (V)	PPm	AAS	Max 2.00
Sodium (Na)	PPm	AAS	Max 90.00
Pour Point	°F	ASTM D-97	Max 120
Sulphur Content	%wt	ASTM D-4294	Max 0.35
Water Content	%Vol	ASTM D-95	Max 0.50
Flash Point PMCC	°F	ASTM D-93	Min 190
Kinematic Viscosity 170°F	cSt	ASTM D-445	Max 360.00
Paraffin	%wt		2.00
Olefins	%wt		16.88
Naphthalene	%wt		4.24
Aromatic	%wt		26.43

### B. Experimental Method

This research uses site process swelling with a supercritical gas CO<sub>2</sub>, swelling factor measurement, and analysis product output with GC-MS. The experimental process operates on a fixed bed reactor (Fig. 1). The sample was included in 1000 grams of residual vacuum (Table 1) in the reactor. Before starting the healing process, the system will be cleaned by turning on the vacuum pump to remove the O<sub>2</sub> inert gas in a vacuum for 2-3 minutes (vacuum condition). Residual vacuum feed is fed inside this reactor, next to giving that required temperature a CO<sub>2</sub> gas injection means carried out.

This stage is a swelling process that replaces the resulting liquid product, swelling temperatures lower than the research. Swelling is a method to enhance the specific quantity from some original conditions to the last conditions, including changes in temperature about thermal requirements [13]. Some aromatic composition in the double bond consists of benzene in the asphaltene compound. This vacuum residue binds this bond deep in particles and polymers, which means hard to develop, including a reverse in the swelling method with CO<sub>2</sub> gas with acidic properties (H<sup>+</sup>) including supercritical properties associated with changes in bonding bonds, double covalent [7].

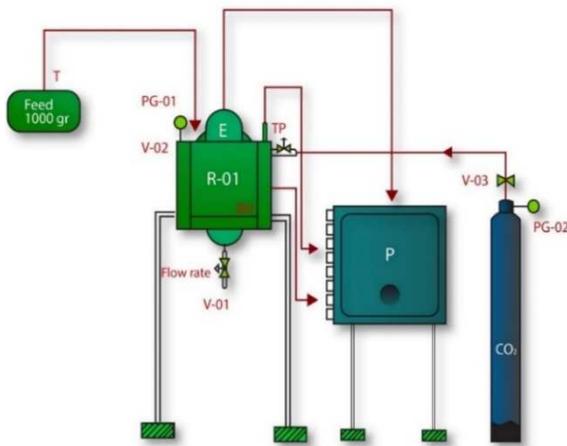
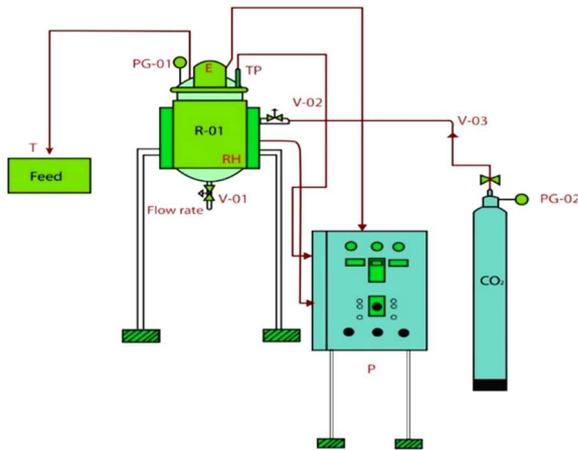


Fig. 1 Schematic Process of Swelling with Supercritical CO<sub>2</sub>

CO<sub>2</sub> gas is injected into the reactor for the swelling process, breaking the aromatic bond and having a strong covalent bond on the vacuum residue molecule [14]. To get accurate data results, the process of injection with CO<sub>2</sub> gas in reactors with varying pressures (100Psi, 120Psi, 140Psi, and 180Psi). Temperature conditions also affect the swelling process [10] with different temperatures (200°C, 250°C, 300°C, and 350°C). The supercritical CO<sub>2</sub> process occurs at temperatures above 300°C and involves temperature conditions below 300°C as a comparison of data on the analysis results. The swelling process is carried out at a reaction time of 60 and 90 minutes. The vacuum residue will change to a low viscosity phase during the swelling and healing process and weakened covalent bonds.

The reaction time will determine the results of the swelling factor measurement for each product produced. The product output results are liquid and gas. The gas produced is exhaust emissions from the reactor. The liquid is the product output in the reactor. Swelling measurement factors pay attention to reaction time by considering the variables of pressure and temperature during the swelling period. This study uses the time variable to compare the best swelling process experiment. Product output is categorized based on the reaction time of 60 and 90 minutes to produce the best swelling factor. After collecting swelling product yields, Gas Chromatography-Mass Spectroscopy (GC-MS) will analyze it to observe the components.

GC-MS analysis is performed to see what compounds are contained in the product output. This GC-MS analysis method is used to analyze samples containing complex organic compounds such as hydrocarbons. GC-MS analysis can produce more accurate data in identifying compounds that are completed with their molecular structure [15]. The purpose does get the significant octane number value of the liquid product by calculating an existing formula based on quantitative data on GC-MS results. The composites received in the specimen command last are grouped individually based on their series composition.

### C. Swelling Factor Measurement

The swelling experiment is an eligible connection state performance analysis that defines the number of hydrocarbons that are secured by CO<sub>2</sub> and evaporated within the CO<sub>2</sub> form with explaining the quantity of any stage.

$$SF = \frac{V_{o,f}(P_s, T_{Exp})}{V_{o,i}(P_{atm}, T_{Exp})} \quad (1)$$

So experiments last frequently handled with containing the swelling factor from some oil under connection by some CO<sub>2</sub> state. During the research, the swelling fuel factor during the crude oil CO<sub>2</sub> method was determined by several running pressures (P=100, 120, 140, 160, and 180 Psi) and consistent temperatures (T=200, 250, 300, and 350°C). Wherever the investigation was conducted, the swelling factor from the oil due to the release of CO<sub>2</sub> in the producing state was defined at some rate from the last volume of the oil to its original condition. The beginning of the experiments [5] was essentially provided [1].

## III. RESULT AND DISCUSSION

### A. Vacuum Residue Swelling Process

Vacuum Residue is the main sample in this research by using a swelling process with CO<sub>2</sub> gas injection. The initial stage of residual vacuum as a feed is carried out the CO<sub>2</sub> gas injection process to determine the reduction of molecular energy bonds from the residual vacuum by observing liquid products based on variations in temperature (200, 250, 300, and 350°C), pressure (100, 120, 140, 160, and 180 Psi), and reaction time (60 and 90 minutes). CO<sub>2</sub> gas has the privilege of acting as a solvent under supercritical conditions and also being miscible in hydrocarbons. The residual vacuum used is short residue, which has lower saturation than CO<sub>2</sub> saturation pressure. This phenomenon (solvent and miscible) will result in changes in PVT Correlation.

Figure 2 shows vacuum residue swelling results at various temperature treatments (200, 250, 300, and 350°C), pressure (100, 120, 140, 160, and 180 Psi), and the reaction time is 60 minutes. The swelling factor of the optimal residual vacuum in this study was 6.25% using a reaction time of 60 minutes, the pressure of 180Psi, and temperature of 350°C. Vacuum residue is a complex compound that is ensured to have internal energy in the form of a large enthalpy (H), so it is very difficult to know the value (H) and (S) [16]. Injection of CO<sub>2</sub> gas into a residual vacuum is very influential on changes in total volume. The greater the CO<sub>2</sub> gas injection, the greater the swelling or total volume change. This can be seen more clearly on the pressure drop until part of the liquid turns into

gas below the saturation pressure. With increasing temperature and pressure, the density of vacuum residue decreases. Supercritical fluid properties in CO<sub>2</sub> solvents cause the decrease in density in vacuum residue, thus affecting the weakening and disconnection of complex compound structures in alkaline vacuum residue molecules [16]. While the results of the supercritical CO<sub>2</sub> swelling process at the reaction time of 90 minutes in Figure 3.

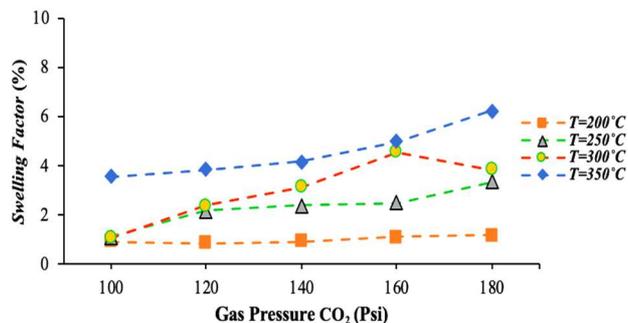


Fig. 2 Swelling Process for 60 Minutes

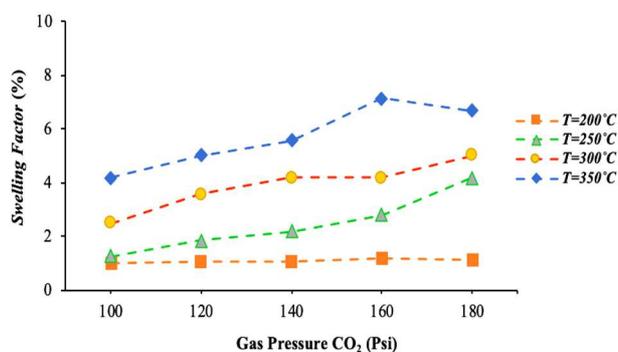


Fig. 3 Swelling Process for 90 Minutes

The diagram above explains the effect of pressure and temperature on changes in the volume of liquid products (liquid) from the swelling process. However, the swelling process shows a large effect on energy reduction in operating conditions where the operating conditions are literature at a temperature of 450-500°C, while in research with the swelling method as bond attenuation produces volume changes at 350°C. Injection of CO<sub>2</sub> gas into a residual vacuum is very influential on changes in total volume. Table 3 and Figure 3 show that at temperature (200, 250, 300, and 350°C), pressure (100, 120, 140, 160, and 180 Psi), and the reaction time is 90 minutes. The overall swelling factor of the optimal residual vacuum in this study was 7.14% using a reaction time of 90 minutes, the pressure of 160Psi, and temperature of 350°C.

### B. Effect of Swelling Process on Total Product and Conversion of Vacuum Residue Feeds

This swelling process is carried out by comparing the percent (%) of total product yield [17] (liquid, gas, and coke residues) and temperature (200, 250, 300, and 350°C). The effect of the swelling process given by the properties of CO<sub>2</sub> gas is supercritical properties that have and also free variables that contribute to the weakening of density, viscosity, and bond energy [16].

The results of this study are presented in Table 2 and Table 3, which are then poured in the form of graphs in Figures 4 and 5, where the results of this study describe the results of the residual vacuum product from the swelling process using reaction time for 60 minutes and 90 minutes.

TABLE II  
LIQUID PRODUCTS IN SUPERCRITICAL CO<sub>2</sub> SWELLING PROCESS IN 60 MINUTES

Product	% Total Product			
	Temperature (°C)			
	200	250	300	350
Liquid	4.98	11.49	14.94	22.82
Gas	25.02	38.51	25.06	27.18
Coke Residu	70.00	50.00	60.00	50.00
<b>Conversion (%)</b>	<b>30.00</b>	<b>50.00</b>	<b>40.00</b>	<b>50.00</b>

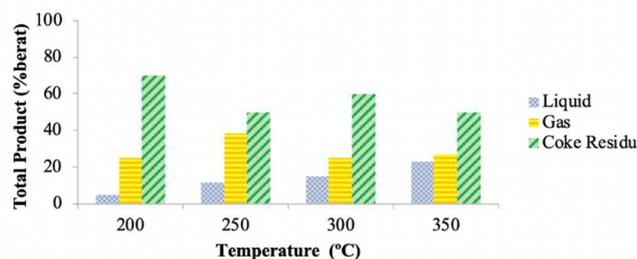


Fig. 4 Product Total from the Supercritical CO<sub>2</sub> Swelling Process 60 Minutes

Figure 4 explains the effect of temperature on the percent (%) of the total production from the swelling process shows that the percentage of residual coke products is very high, especially at 200°C at 70.00%, liquid products at 350°C at 22.82%, and gas products at 250°C at 38.51%. However, as the temperature increases, a percentage change occurs between liquid products, gas, and residual coke. In comparison, the total percent (%) of the product from the supercritical CO<sub>2</sub> swelling process at the 90-minute reaction time is presented in Table 3 and Figure 5.

TABLE III  
LIQUID PRODUCTS IN SUPERCRITICAL CO<sub>2</sub> SWELLING PROCESS IN 90 MINUTES

Product	% Total Product			
	Temperature (°C)			
	200	250	300	350
Liquid	5.38	12.20	19.39	28.51
Gas	14.68	12.80	25.61	26.49
Coke Residu	80.00	75.00	55.00	45.00
<b>Conversion (%)</b>	<b>20.06</b>	<b>25.00</b>	<b>45.00</b>	<b>55.00</b>

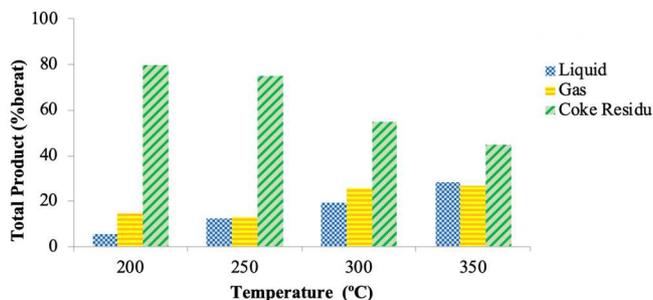


Fig. 5 Product Total from the Supercritical CO<sub>2</sub> Swelling Process 90 Minutes

Figure 5 shows the effect of temperature (200, 250, 300, and 350°C) on the percent (%) of total supercritical CO<sub>2</sub> swelling products. As the temperature rises, the liquid yield also increases, and the gas yield increases at a maximum temperature of 350°C. Vacuum residue (VR), which is fed, is defined as the yield of coke residues that decreases with increasing temperature. Vacuum residues are complex hydrocarbon compounds, azeotropes, and in transition. Vacuum residue is alkaline, with a carbon number reaching more than 40. In addition to being acidic and having high carbon number values, vacuum residue has components that are difficult to separate, so in the process, usually used other compounds in the form of CO<sub>2</sub> gas solvents or by using pressure (MPa). CO<sub>2</sub> gas serves to break the azeotrope bond in the vacuum residue.

The highest temperature used is at a temperature of 350°C and a reaction time of 90 minutes showed a maximum yield of liquid products (liquid) of 28.51%, 26.49% of gas products, and coke residue of 45.00%. The increase in the liquid product is directly proportional to the increase in the temperature of the feed. Using the temperature of the mass of the residual vacuum feed, it can be assumed that a significant increase in the amount of liquid product occurs. In the swelling process, the largest percentage of coke residue is 80%, at a temperature of 200°C. Decreased coke residue [18] is significant enough to prove the effect of temperature on the yield of cracking product liquid.

Feed conversion is defined as the amount of raw material formed into liquid and gas products. Conversion is calculated by dividing the total mass of liquid and gas products by the mass of the feed. A higher percentage of product conversion is achieved with a temperature of 350°C and a reaction time of 90 minutes. Figure 6 illustrates the effect of temperature on feed conversion in the supercritical CO<sub>2</sub> swelling process.

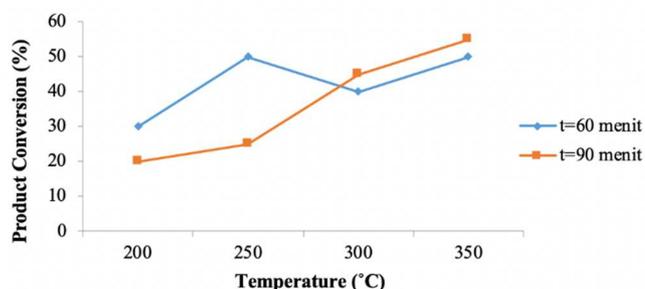


Fig. 6 Effect of Temperature on Swelling Process Conversion Supercritical CO<sub>2</sub>

Product conversion (Figure 6) increases because of the temperature and pressure on the feed increase. In the swelling process, there is a significant increase in conversion from temperatures of 200°C to 350°C. This is due to very low temperatures. Theoretically, the cracking process will occur at the lowest temperature of 350°C, but due to the swelling process in the initial stages of research that causes turbulence between CO<sub>2</sub> gas and residual vacuum so that the residual vacuum molecule chain is weakened and does not require too high a temperature to break the bonds of these molecules. At the reaction time of 60 minutes, the cracking process did not show a significant increase in conversion at each temperature increase (200, 250, 300, and 350 °C). The conversion

percentage was much higher than swelling supercritical CO<sub>2</sub> for the reaction time of 90 minutes at temperature 350°C.

This result shows that by using the temperature of 350°C and 90 minutes reaction time, the weight fraction in residual vacuum molecules can be converted into lighter fractions by breaking down long-chain hydrocarbon molecules into shorter molecules. Residual vacuum molecules that have previously been attenuated by swelling at low temperatures.

### C. Analysis of liquid products by the gas chromatography-mass spectrophotometer (GC-MS) method

The results of liquid products (liquid) from the swelling process with supercritical from CO<sub>2</sub> gas are carried out by the analysis method of the Gas Chromatography-Mass Spectrophotometer instrument. The GCMS instrument analysis method is performed by injecting a small number of specimens to be examined inside the instrument. When the inquiry season is completed, the top produced on the chromatogram command last adjusted to some composites under these archives to find out the contents from the compound during that unit. The purpose of the analysis using the GCMS method is to define the amount and character of hydrocarbon compounds during Vacuum Residue: aromatic, saturates, and olefins [19]. GCMS carried out product analysis on the product swelling process temperature of 350°C and reaction time of 90 minutes. The results of the analysis can be seen in Figure 7.

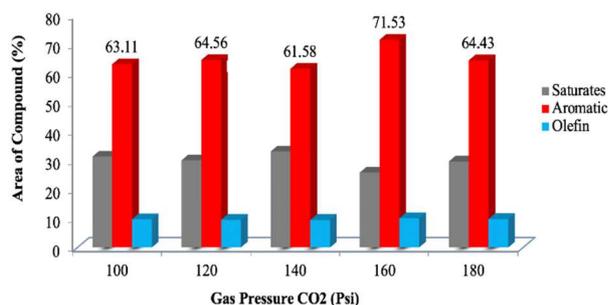


Fig. 7 Liquid Product Analysis with GC-MS

Figure 7 explains the fluctuations among the contents of aromatic compounds, olefins, and saturates (saturated compounds) based on CO<sub>2</sub> gas pressure to residual vacuum feed [20]. However, from Figure 7, we can conclude that the aromatic compounds still possess the leading percentage of olefin compounds and saturates despite fluctuations.

The highest percentage of aromatic compounds at a pressure of 160Psi was 71.53%, with saturates compound at 35.79% and olefin compounds at 10.05%. While the lowest percentage results, namely at a pressure of 140Psi, the temperature of 350°C and reaction time of 90 minutes produced the content of olefin compounds of 9.47%, an aromatic compound of 61.58%, and compounds saturates 33.04%. The elements of saturated compounds (naphthalenes and paraffin) are lighter fractions than olefins and aromatics. Nevertheless, fluid products such as aromatic, gasoline, and olefin elements are the usual heavy because the fluid products with great olefin and aromatic contents have higher octane amounts and thus have better product quality. Looking at the analysis until the product above can be concluded that the results of this experiment have a good liquid product quality.

#### IV. CONCLUSION

Based on the evaluation results and interpretation of experimental data, this study studies the effect of the swelling process with CO<sub>2</sub> gas injection from residual vacuum feeds. The study was conducted to see the effect of swelling, reaction time, temperature, and pressure on product quality and quantity. The experimental results can be concluded that the swelling process occurs under supercritical conditions. This case occurs at a pressure of 160 psi, a temperature of 350°C, and a reaction time of 90 minutes produces an optimal swelling factor of 7.14%. The highest percentage of liquid product analysis using the Gas Chromatography-Mass Spectrophotometer (GC-MS) instrument analysis method is at 160Psi pressure, 350°C temperature, and 90 minutes reaction time, resulting in an aromatic compound content of 71.53%, saturates compound 35.79% and olefin compounds at 10.05%.

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