

CHAPTER V

RESULTS AND DISCUSSIONS

5.1 Experimental Results

The experiment results of cracking of polybutene-1 by Fe/activated carbon catalyst by studying its influences to conversion percentage of the products and yielded oil composition have the following variables; percentage of iron loading on activated carbon, reaction temperature, mass of catalyst, initial pressure of hydrogen gas and reaction time. The results of the experiments from different conditions and those of oil composition analysis are shown in Table A-1 and Table A-2 (Appendix A). The influences of each variable above-mentioned are shown in Figures 5.1, 5.2, 5.3, 5.4, 5.5, 5.6, 5.7 5.8 and 5.9, respectively.

5.1.1 Influences of percentage of iron on activated carbon on composition of oil product

The products yield of variation of percentage loading of Fe 1, 5 and 10% on activated carbon using as catalyst at a fixed condition of 15 g of polybutene-1, with hydrogen pressure of 40 kg/cm², reaction time of 60 min, temperature at 410°C and 0.3 g catalyst were shown in Figure 5.1. The percentage of oil yield was in a range of 81.74 to 91.00%, gases yield of 5.40 to 7.73% and solid yield 3.73 to 5.53%, Table A-2 showed that 1% Fe yielded 50.66% naphtha, 16.94% kerosene, 11.39% light gas oil, 7.5% heavy gas oil while 5% Fe yielded naphtha 51.67%, kerosene 15.55%, light gas oil 10.83%, heavy gas oil 7.78%.

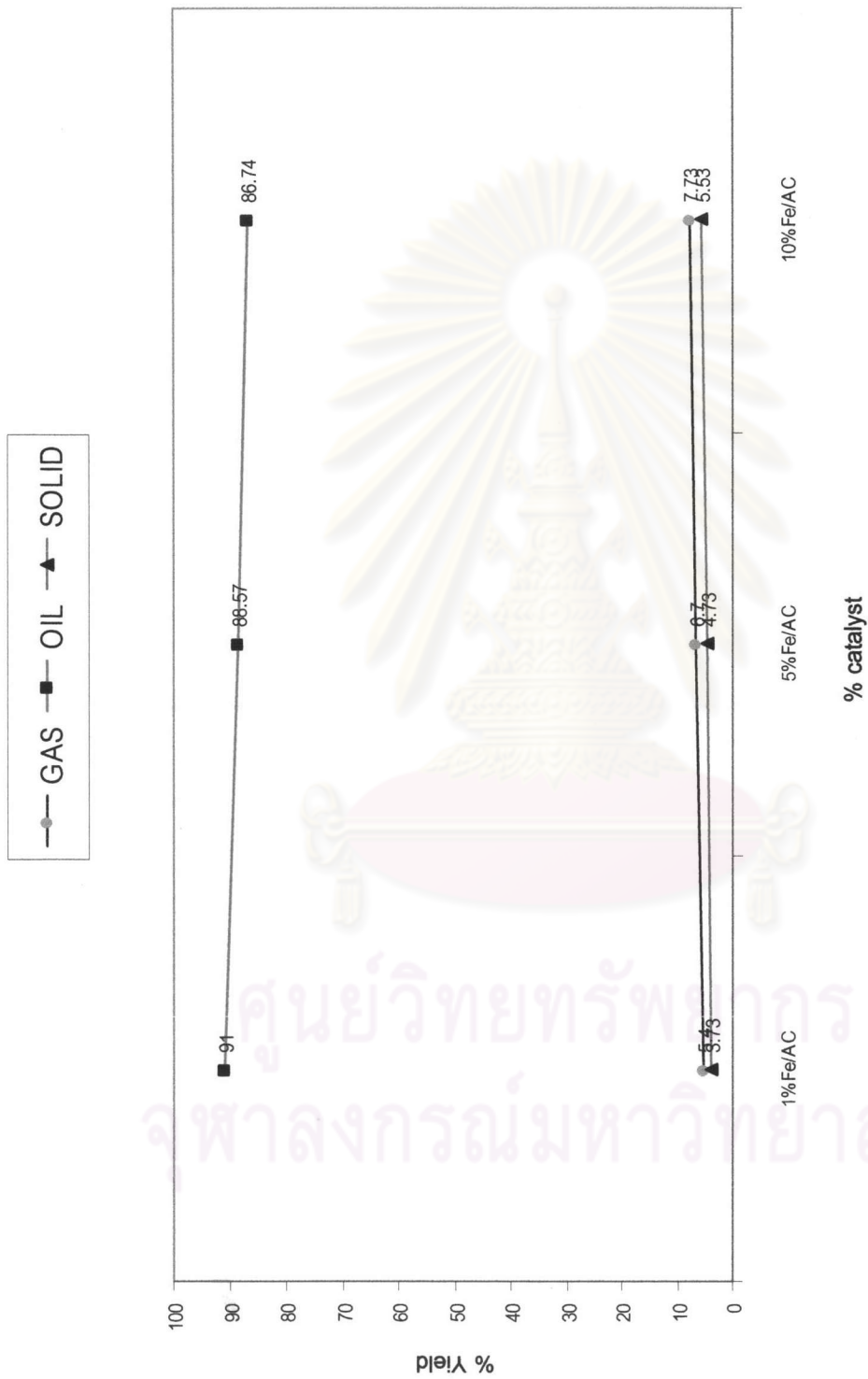


Figure 5.1 Product yield of PB-1 with various %Fe/AC (0.3 mm) catalyst. Reaction conditions : 15 g of PB-1, initial H₂ pressure 40 kg/cm², 60 min and 410 °C.

From these data if considering together with oil yield, it could be concluded that the different percentage of Fe, was no significant effect to the oil yield and composition.

Figure 5.2 shown the percentage of products form reaction that carried out without using catalyst compared with using 0.3 g Fe/Activated carbon (5% Fe) catalyst. The percentage of oil composition was lower quality when compared to using catalyst. It could be explained that without catalyst, the thermal cracking played only the important role in immediately cracking very long hydrocarbon chains to intermediate molecules. The catalytic reaction was simultaneously proceeded by thermal and catalytic cracking; as a result, the distribution of hydrocarbon molecules would obtain better quality oil and increase of naphtha from 34.66 to 45.06%,

5.1.2 Influences of temperature on composition of oil product

The study of the influence of reaction temperature on the cracking of polybutene-1 was performed by operating at various reaction temperatures; 375, 385, 395, 410 and 425 °C by using 0.3 g of 5% Fe/AC catalyst under initial hydrogen pressure 30 kg/cm² and fixing reaction time at 60 min.

The characteristic of obtained product at low reaction temperature, 375 °C, was the mixture of oil and wax and partial oil product still was solid at room temperature. Therefore, in this case, it could not be determined exactly percent of oil and solid. The percentage of oil fraction from cracking as a function of temperature was showed in Figure 5.3 and 5.4. It was found that the percentage of naphtha largely increases from 35.23% to 44.95% with the increase of the temperature from 385 to 410 °C but other composition except solid yield slightly decrease with the increase of the temperature. However when increase temperature to 425 °C oil yield decreased dramatically from 88.57% to 63.11% while gas and solid yield were largely increased from 6.6% and 7.5%

Gas
 Naptha
 Kerosene
 Light Gas Oil
 Heavy Gas Oil
 Long Residues
 Solid

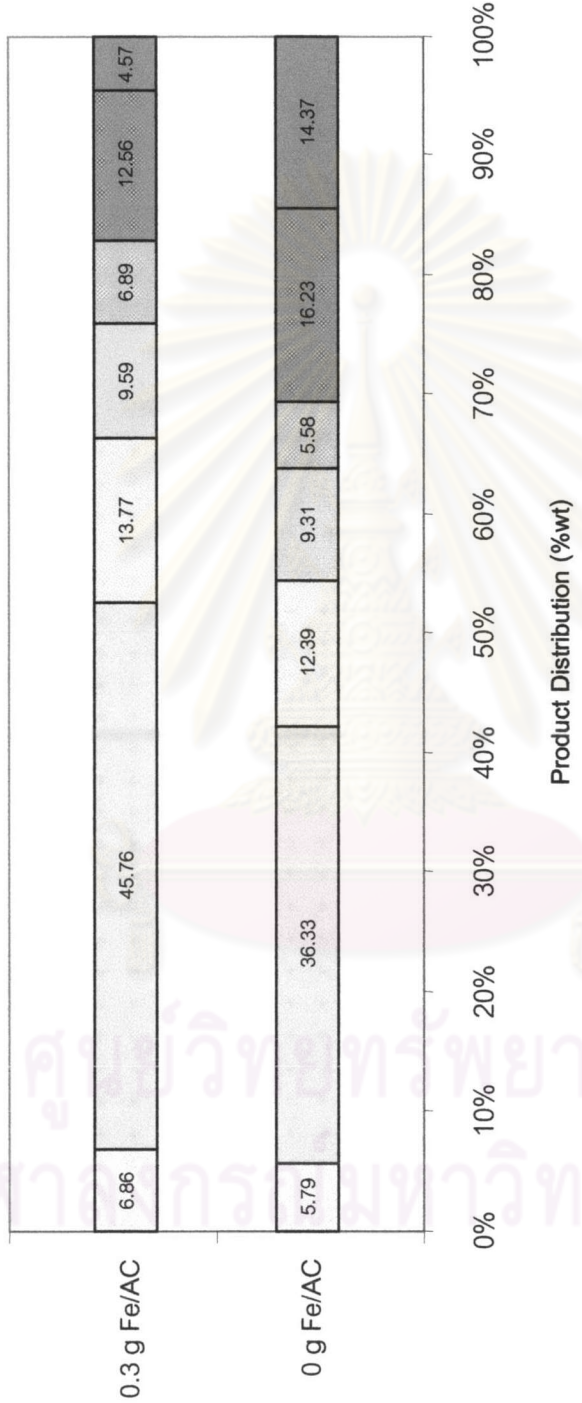


Figure 5.2 PB-1 conversion with and without Fe/AC catalyst. Reaction conditions : 15 g of PB-1, initial H₂ pressure 40 kg/cm², 60 min and 410 °C.

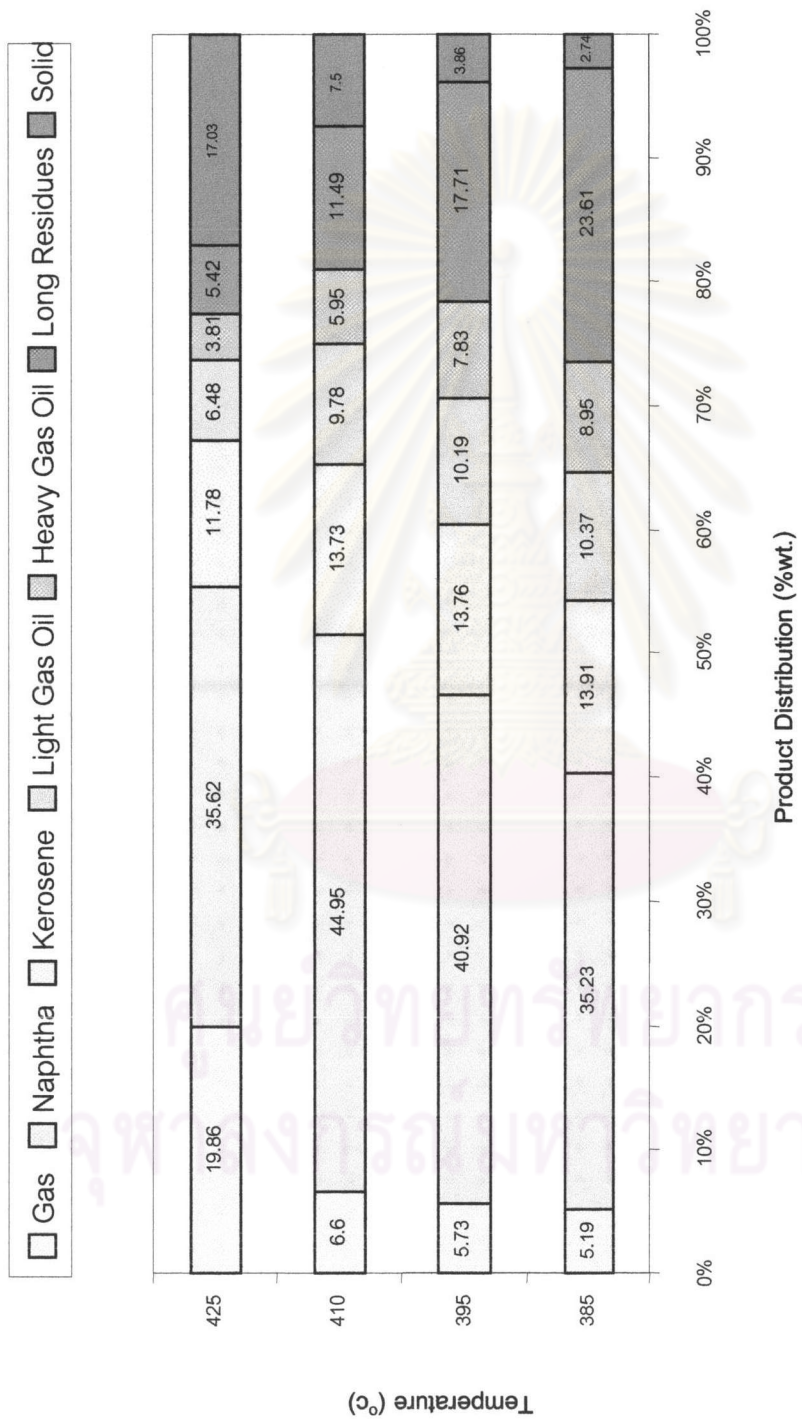


Figure 5.3 PB-1 conversion on 5% Fe/AC (0.3 mm) catalyst with various reaction temperature. Reaction conditions : 15 g of PB-1, initial H₂ pressure 30 kg/cm², 60 min and 0.3 g of catalyst

—●— GAS

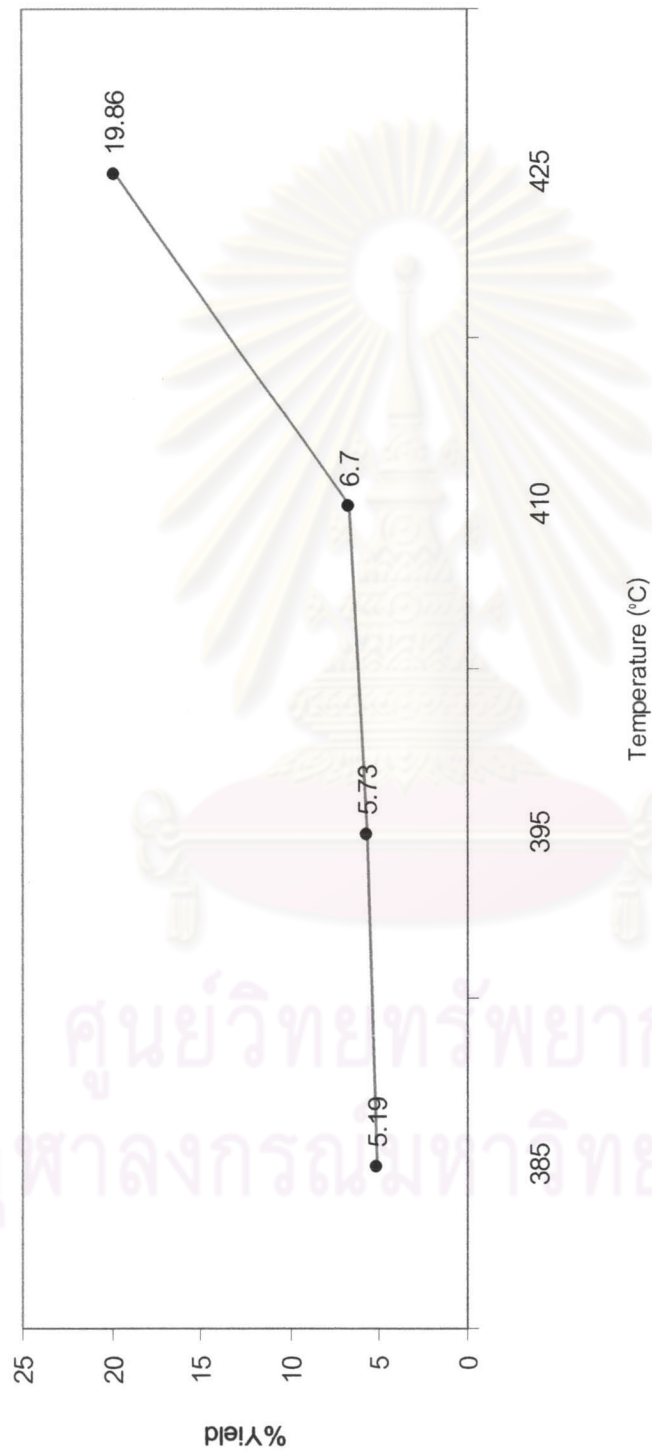


Figure 5.4 Gas yield of PB-1 on 5%Fe/AC (0.3 mm) catalyst with various reaction temperature.

Reaction conditions : 15 g of PB-1, initial H₂ pressure 40 kg/cm², 60 min and 0.3 g of catalyst.

to 19.86% and 17.03%. It can be concluded that low reaction temperature was not suitable condition to crack polybutene-1 because of obtained mixture of oil and wax product. It also shown that thermal cracking of low temperature was not good enough to break down polybutene-1 to be the lower molecular weight hydrocarbon when compared with at high reaction temperature. Moreover, Figure 5.3, showed the comparison of product distribution at various temperature, 385-425°C, gas yield from low reaction temperature was quite low, 5.19%, whereas, increased to 6.7% at 410 °C and largely increased to 19.86% at 425 °C. From this result it was found that too high reaction temperature would create huge amount of gas yield with lower oil yield and higher solid yield. This is because an increase in the temperature inducing a largely amount of thermal cracking of polybutene-1 to be lower hydrocarbon. But too high reaction temperature gave more low molecular weight hydrocarbon, gas and increment of solid yield at high reaction temperature due to coking at catalyst surface. This result was confirmed with the work of Phungtum^[8] who studied the conversion of polypropylene into oil product using iron on activated carbon catalyst in a microreactor by varying operation conditions as pressure of hydrogen gas range of 28 to 50 kg/cm², reaction temperature between 395 and 455 °C and reaction time 30 to 90 min for each catalyst. The analyzed oil product from GC Simulated Distillation was found that iron on activated carbon was suitable and used as catalyst at 435 °C, hydrogen pressure at 30 kg/cm² and reaction time 60 min. The product yield was 2.34% of gas, 96.33% of oil and 1.33 % of solid. Shabtai et al.,^[9] studied the solid superacid-catalyzed depolymerization-liquefaction (DL) reactions of cis-polybutadiene. The samples were systematically investigated as a function of processing conditions, i.e., temperature (350-450°C), time (0.5-3.0 h) H₂ pressure (500-2000 psig), catalyst type and concentration, and the presence of solvents. Catalyst used included SO₄²⁻/Fe₂O₃, SO₄²⁻/ZrO₂, and a Pt-modified SO₄²⁻/ZrO₂. At temperature more than 400 °C, with 1-2 wt% of SO₄²⁻/Fe₂O₃ or SO₄²⁻/ZrO₂ as catalyst. The result obtained 84.00% of oil yield, 5.9%of gas yield and 10.17% of solid yield respectively.

In case of polybutene-1 its structure is quite similar to polypropylene with longer side chain, it means that polybutene-1 easier to crack when compared to polypropylene.

If compared to Shabtai work obtained 84% oil yield at reaction temperature 430 °C. It was confirmed by the result of this work polybutene-1 optimum reaction temperature was 410 °C, and it yielded 45.76% naphtha, 13.77% kerosene, 9.59% light gas oil, 6.89% heavy gas oil and 12.56% long residue respectively.

5.1.3 Influences of initial pressure of hydrogen on composition of oil product

The study of the influence of initial hydrogen pressure was performed by various pressures at 20, 30, 40 and 50 kg/cm². The catalytic cracking of polybutene-1 at the optimum reaction temperature is 410 °C, 60 min of reaction time and 0.3 g of 5%Fe/AC catalyst. The compositions of products and oil yield were shown in Figure 5.5.

Figure 5.5 showed that the product composition changed with changes in initial hydrogen pressure. The increasing of hydrogen pressure from 20-40 kg/cm² increased the % yield of oil product from 78.71 to 88.57%. It can be described that an increase in amount of hydrogen helps to stimulate cracking reaction and causes higher catalytic cracking reaction. This is confirmed in the theory of spill over of hydrogen on catalyst during the reaction, some hydrogen at the surface of catalyst is consumed, so the higher pressure of hydrogen, the more mass transfer from gas phase to solid surface of catalyst. Therefore it causes high conversion and more quantity of recovery product. So it showed a higher result of naphtha from 43.06 to 45.76%. Other composition was stable, gas yield slightly increased while solid reduces from 20.43 to 4.57%. However, at pressure of 50 kg/cm², yield of oil product, naphtha decreased but solid yield increased. This is because there was leakage of H₂ from the safety valve during the reaction because of too high severity in the reaction system so the amount and composition of products were affected.

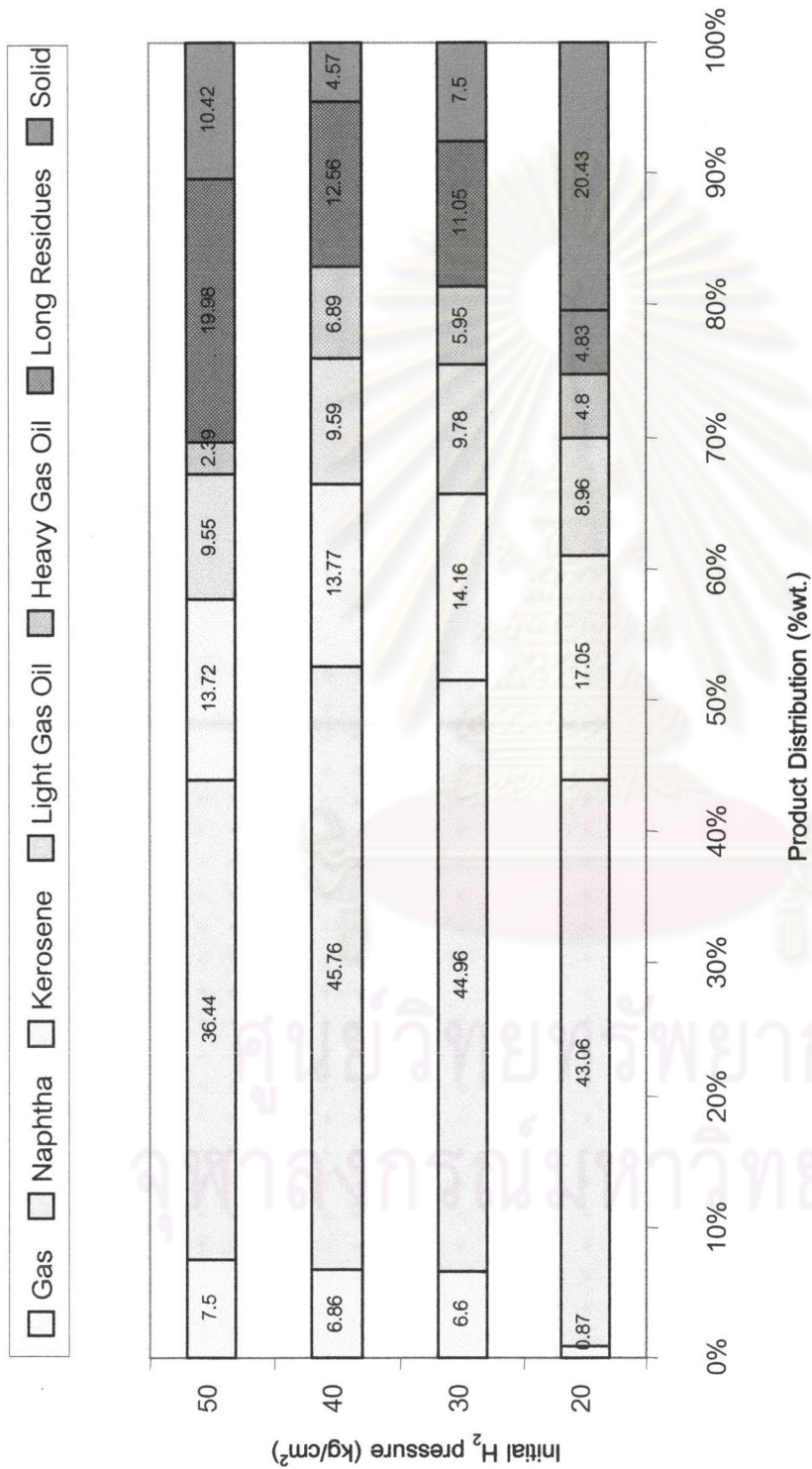


Figure 5.5 PB-1 conversion on % Fe/AC (0.3 mm) catalyst with various initial hydrogen pressure.
 Reaction conditions : 15 g of PB-1, 60 min, 410 °C and 0.3 g of catalyst

The high reactivity of polybutene-1 can be described to the presence of multiple tertiary carbons in the polymeric chains and the consequent stable formation of tertiary carbon radicals in the presence of free radicals initiators. Such carbon radicals undergo the Beta -cleavage reactions to yield lower branched paraffins and olefins by a scheme proposed in Figure 5.6.

From the discussion, It could be said conclusively that the optimum hydrogen pressure was 40 kg/cm^2 . It showed the highest oil product yield (88.57%), the highest naphtha (45.76%) and kerosene (13.77%), while solid was lowest.

5.1.4 Influences of mass of catalyst on composition of oil product

The variation of weight catalyst from 0.15, 0.3, 0.45, and 0.6 g at fixed conditions of 5% Fe/AC, with 15 g of polybutene-1, hydrogen pressure at 40 kg/cm^3 , 60 min reaction time and at $410 \text{ }^\circ\text{C}$ (Figure. 5.7), it was found that a higher mass of catalyst from 0.15 g to 0.3 g induced a slight increase in percentage of oil from 81.10% to 88.57% and slightly decrease from 0.3 g to 0.45 g from 88.57% to 88.25% then dramatically decreased when increase mass of catalyst to 0.6 g from 88.25% to 68.85%, it could be explained that high amount of catalyst increased the cracking reaction it caused the long chain polybutene-1 molecules were cracked to the lower and lower molecular weight hydrocarbon finally it became gas molecules, so gas yield was increased dramatically. This experiment showed that mass of catalyst affected cracking reaction, For 15 g of polybutene-1, hydrogen pressure at 40 kg/cm^3 , 60 min reaction time and at $410 \text{ }^\circ\text{C}$. Catalyst mass at 0.3 g gave the highest oil yield, lowest gas yield and low solid. This can be explained that Fe conducted the catalytic activity, reduce the activation energy of the chemisorption reaction. This mass of catalyst was mixed and contacted well all liquid polybutene-1, therefore, the highest oil yield was obtained.

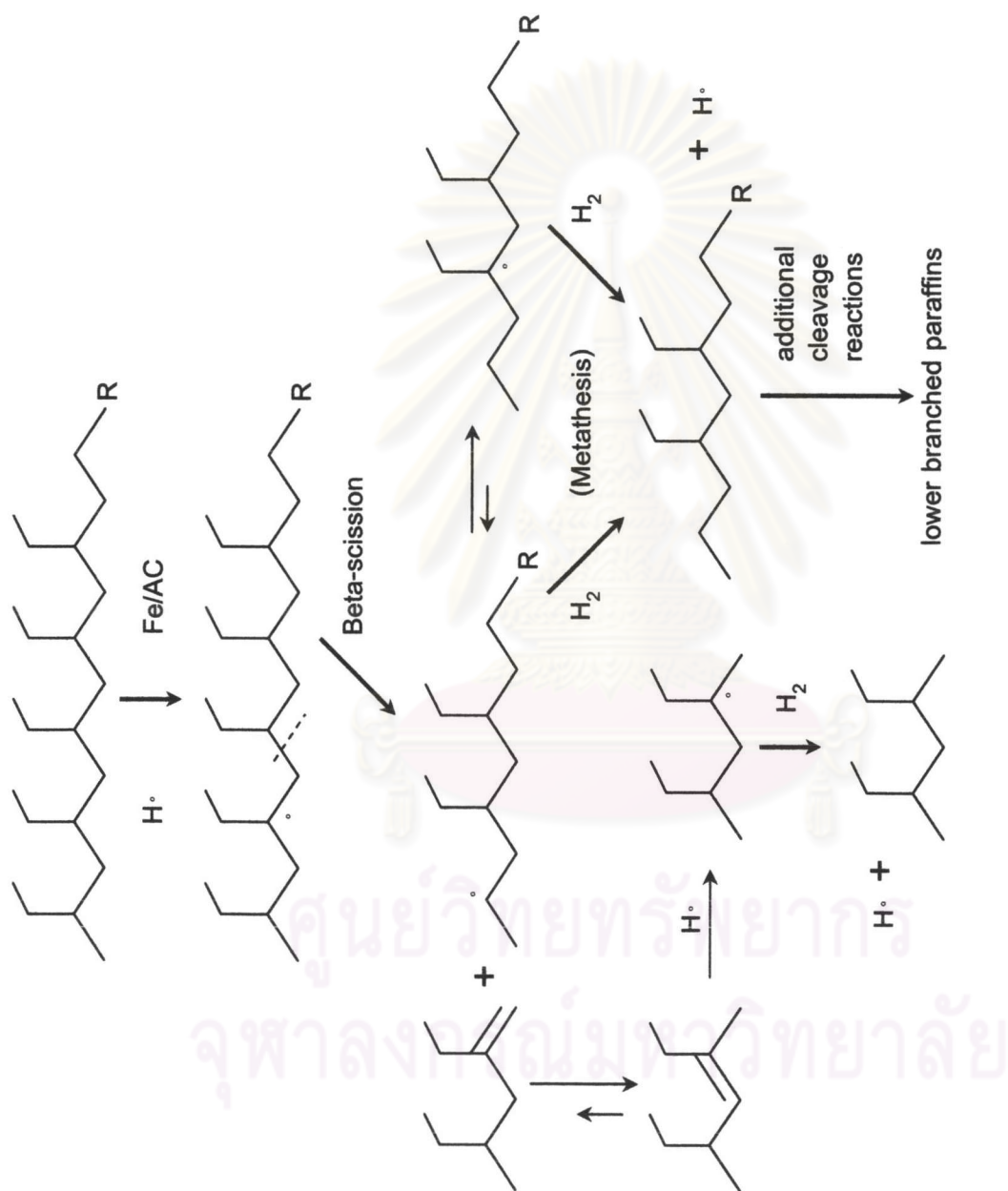


Figure 5.6 Proposed mechanism scheme for hydrocracking polybutene-1.

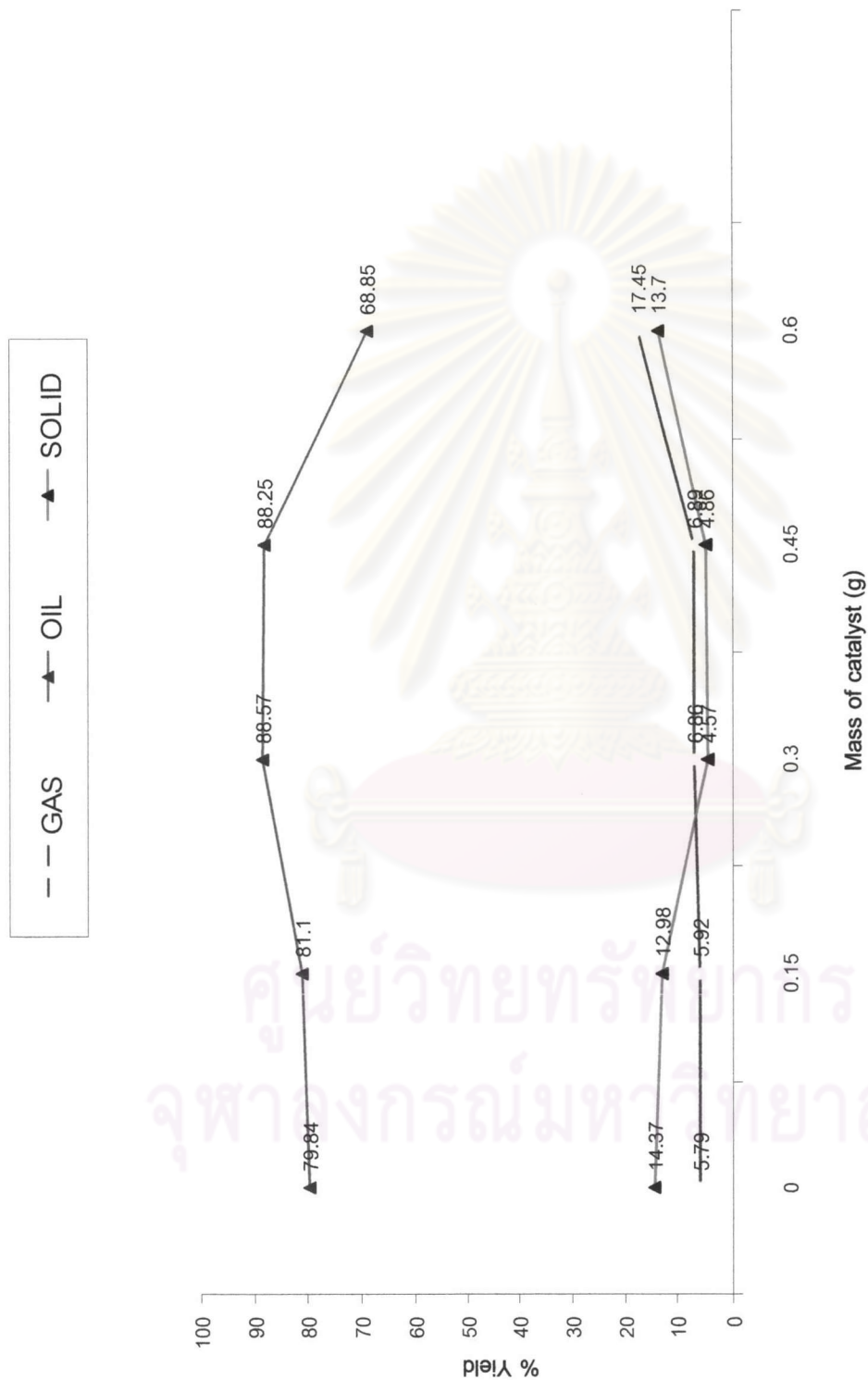


Figure 5.7 Product yield of PB-1 with various mass of catalyst. Reaction conditions : 15 g of PB-1, initial H₂ pressure 40 kg/cm², 60 min and 410 °C.

5.1.5 Influences of reaction time on composition of oil product

The influences of reaction time on the percentage recovered of reaction systems was performed by various time at 30, 60, 75 and 90 min. PB-1 was carried out by fixing the condition at reaction temperature 410 °C, initial hydrogen pressure 40 kg/cm² and 5% Fe/AC catalyst 0.3 g. The compositions of products and oil yield from cracking reaction was shown in Figure 5.8.

Figure. 5.8 showed that when the reaction time increased from 30 to 60 min, the % yields of oil and % naphtha increased whereas kerosene, light gas oil and heavy gas oil being the same quantities. Solid yield decreased from 30 to 60 min, then increased from 60 to 75 min and largely increase with 90 min reaction time. After reaction time more than 60 min, it was observed the decreasing of oil yield and %naphtha, in the contrast it was noticed more increasing of gas. The experiments were fixed the temperature and initial hydrogen pressure, so the thermal and catalytic cracking were occurred the same phenomena when reaction time increased to 60 min. It obtained the maximum oil yield, %naphtha and lowest solid yield, it means that 60 min is the appropriate reaction time. Moreover it could be observed also that when the longer time of reaction, the % of gas largely increased from 7.13 to 24.06%, it means that more reaction time allowed more thermal and catalytic cracking. Longer cracking reaction time was converted hydrocarbon into low molecular weight hydrocarbon; such a result there is a clear increasing in value of gas yield. Longer time also caused coking at the surface of catalyst such a result it was observed the largely increase of %naphtha and %yield. In conclusion, the optimum of reaction time was 60 min, because this reaction time gave the highest oil yield, 88.57% and highest naphtha, 45.06%.

5.1.6 Characterization of Fe/activated carbon before and after using in reaction

Table 5.1 showed the surface specific area before and after using in reaction. It was found that when Fe was impregnated on the surface of pure

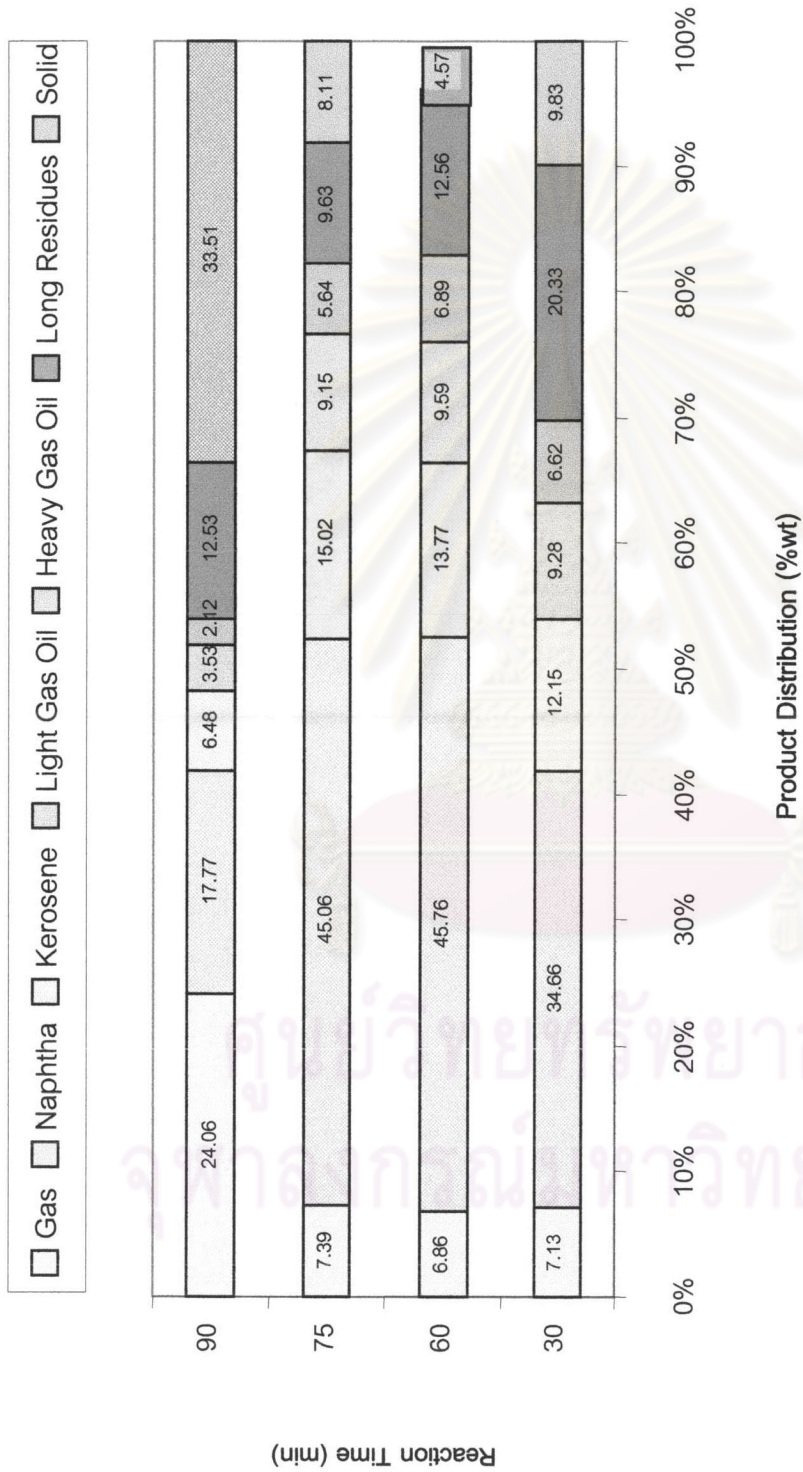


Figure 5.8 PB-1 conversion on 5% Fe/AC (0.3 mm) catalyst with various reaction time. Reaction conditions : 15 g of PB-1, 410 °C, initial H₂ pressure 40 kg/cm² and 0.3 g of catalyst.

activated carbon, the surface decreased slightly about 5.3%, it means that there were attached Fe metal crystals in the pores of activated carbon, and it was not affected to the percentage loading of Fe on surface area. The surface area of each type percentage loading Fe was not significant different. It implied that each percentage loading of iron caused the same covering of plastics on metal crystal situating throughout all the pores of activated carbon, therefore it was observed no effect of surface area on the oil yield and composition of the former experiments.

Table 5.1 showed also the surface specific area of catalyst after using in reaction. It was found that the surface area was decreased largely after being carried out reaction. This was because of some small amount of unconverted polybutene-1 covering the surface of catalyst during cooling to the ambient temperature.

Table 5.1 Surface specific area (BET) of pure activated carbon and any loading of Fe on activated carbon of particle size 0.3 mm, before and after using in reaction at 410 °C, initial H₂ pressure 40 kg/cm².

Fe loading (% by weight)	BET area m ² /g before reaction of polybutene-1 ^[3]	BET area m ² /g after reaction of polybutene-1
Pure activated carbon	746	-
1% Fe/activated carbon	719	58
5% Fe/activated carbon	692	72
10% Fe/activated carbon	706	65

Figure 5.9 showed the surface specific area of catalyst before using in reactor if compare to Figure 5.10. It confirmed that there was coking at the surface of catalyst during the reaction.

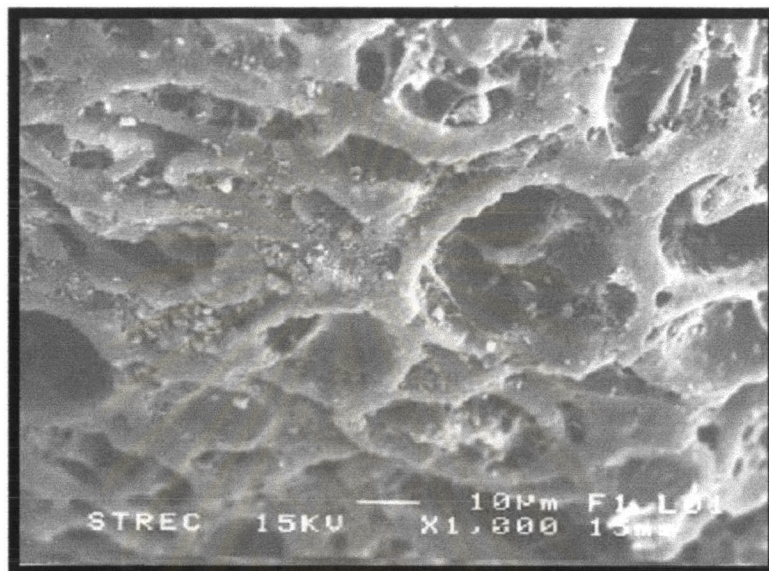


Figure 5.9 The surface specific area of catalyst before using in reactor

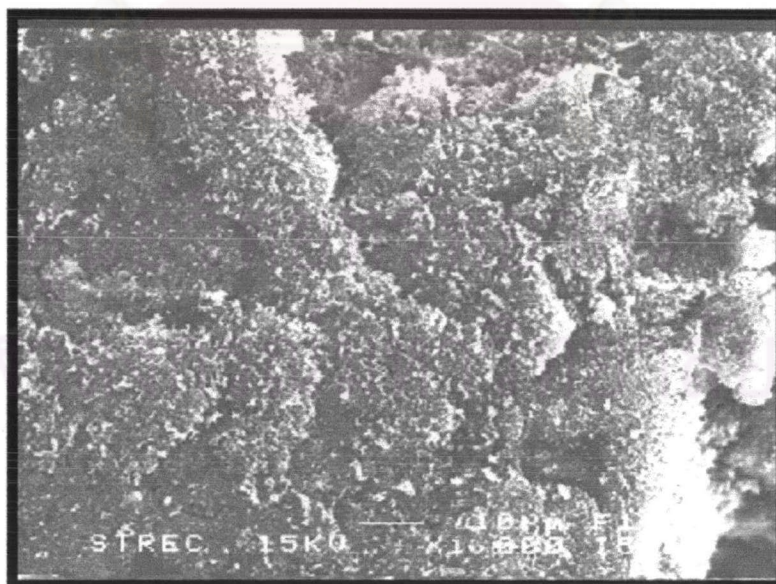


Figure 5.10 The surface specific area of catalyst after using in reactor

5.2 Comparison of this Work with Other Works.

The comparison of this work with Phungtum work and Shabtai et al., work were presented with fractions of gases, oils and solids and expressed in Table 5.2.

Table 5.2 Comparison of this work with Phungtum and Shabtai et al.

Description	This work (2001)	Phungtum ^[8] (2000)	Shabtai et al. ^[6] (1997)
Polymer	polybutene-1	polypropylene	cis-polybutadiene
Reaction scheme	hydrocracking	hydrocracking	superacid-catalyzed depolymerization- liquefaction
Catalyst	Fe/AC	Fe/AC	SO ₄ ²⁻ /ZrO ₂
Reactor	Microreactor (70 ml)	Microreactor (70 ml)	Autoclave (300 ml)
<u>Conditions</u>			
Amount of plastic	15 g	15 g	5 g
Temperature	410 °C	435 °C	430 °C
Reaction time	60 min (total 80 min)	60 min (total 90 min)	60 min (total 60 min)
Atmosphere	H ₂	H ₂	H ₂
Initial Pressure	40 kg/cm ²	30 kg/cm ²	102 kg/cm ²
<u>Results</u>			
Gases (%wt)	6.86	2.34	5.9
Oils (%wt)	88.57	96.33	84.0
Naphtha (%wt)	45.76	62.62	n.a
Kerosene (%wt)	13.77	13.49	n.a
Light gas oil (%wt)	9.59	8.67	n.a
Heavy gas oil (%wt)	6.89	6.74	n.a
Long residues (%wt)	12.66	4.83	n.a
Solids (%wt)	4.57	1.33	10.17

Phungtum^[6] studied hydrocracking of polypropylene into oil product using Fe/activated carbon catalyst in microreactor by varying operation conditions such as pressure of hydrogen as range of 28 to 50 kg/cm², reaction temperature between 395-455 °C and reaction time 30 to 90 min for each catalyst. The results found that reaction temperature of 435 °C hydrogen pressure at 30 kg/cm² and reaction time 60 min was yielded the highest %oil. If compare to this work, the optimum condition (reaction temperature 410 °C initial hydrogen pressure at 40 kg/cm² and reaction time 60 min) was yield 88.57% of oil product which is lower yield, this could be explained that Fe/activated carbon would gave the higher cracking activity when reacting with polypropylene.

Shabtai et al.^[6] studied the solid the solid superacid-catalyzed depolymerization-liquefaction (DL) reactions of *cis*-polybutadiene (PB) samples were systematically investigated as a function of processing condition, temperature (350-450°C), time (0.5-3.0 h) H₂ pressure (500-2000 psig), catalyst type and concentration, and the presence of solvents. Catalyst used included SO₄²⁻/Fe₂O₃, SO₄²⁻/ZrO₂, and a Pt-modified SO₄²⁻/ZrO₂. Experiment was conducted in a batch apparatus using microclave reactor, under atmospheric pressure. The microclave reactor has an internal volume 300 ml. From Table 5.2, result obtained 84.00% of oil yield, 5.9%of gas yield and 10.17% of solid yield respectively, compared to this work obtained 88.57% oil yield, 6.86% of gas yield and 4.57% of solid yield. Although Shabtai used higher activity cracking catalyst but this work showed higher oil yield and lower solid, it is because of the mechanism of cracking polybutene-1. At initiation step, radicals attacked the polybutene-1 molecule at the tertiary carbon which provided more stable hydrocarbon radicals so the catalytic cracking reaction was occurred more effectively.