

CHAPTER V

RESULTS AND DISCUSSION

5.1 The result of research

The experimental results were divided into two parts: hydrocracking of polypropylene with polystyrene and polypropylene with polyethylene.

5.1.1 Polypropylene and polystyrene as raw material

The experimental results of hydrocracking of polypropylene and polystyrene on Iron/activated carbon as catalyst by studying its influences to conversion percentage of the products and yielded oil composition have the following variables: temperature, initial pressure of hydrogen gas, reaction time, mass of catalyst and percent of iron loading on activated carbon as catalyst. The results of the experiments from different conditions and those of oil compositions are summarized in table A-1. The influences of each variable above-mentioned are showed in Figure 5.1, 5.2, 5.3, 5.4 and 5.5 respectively.

5.1.1.1 Influences of reaction temperature on composition of oil product

The reaction temperatures of 405, 415, 425 and 435^oC were carried out and fixed the conditions at 5% Fe/AC, 7.5 g of each polypropylene and polystyrene, hydrogen pressure at 30 kg/cm², 60 min reaction time and 0.45 g of catalyst (shown in Fig 5.1). It is found that when the temperature increased, a percentage of oil was decreased from 56.7 to 52.0%. Normally polystyrene is cracked at a carbon position connecting between benzene rings by thermal or abstracting hydrogen by means of catalytic processes as a result it became majority in the form of cumene, 1,3-diphenylbutane and 1,3,5-triphenylpentane that they were in the range of gas oil long residues. When the temperature was increased from 425 to 435^oC, it caused a larger amount of thermal cracking of polystyrene and polypropylene, as a result, it found obviously the increasing more solid from 5 to 20%(405 to 415^oC). The solid was a large amount increased, because higher temperature induces more cracking process at the surface of catalyst and more possibility to occur coking, owing to high molecular molecule of two polymers. The compositions such as naphtha, kerosene, gas oil and long residues have a trend to be stable while product gases had a trend to be decreased.

In conclusion in case of temperature, the suitable temperature is 415^oC because of high oil yield and low solid. The composition of product was naphtha, kerosene, light gas oil, heavy gas oil, long residues and solid at 15.07, 1.14, 11.37, 4.55, 24.78 and 5.07% respectively with 56.80% of oil yield.

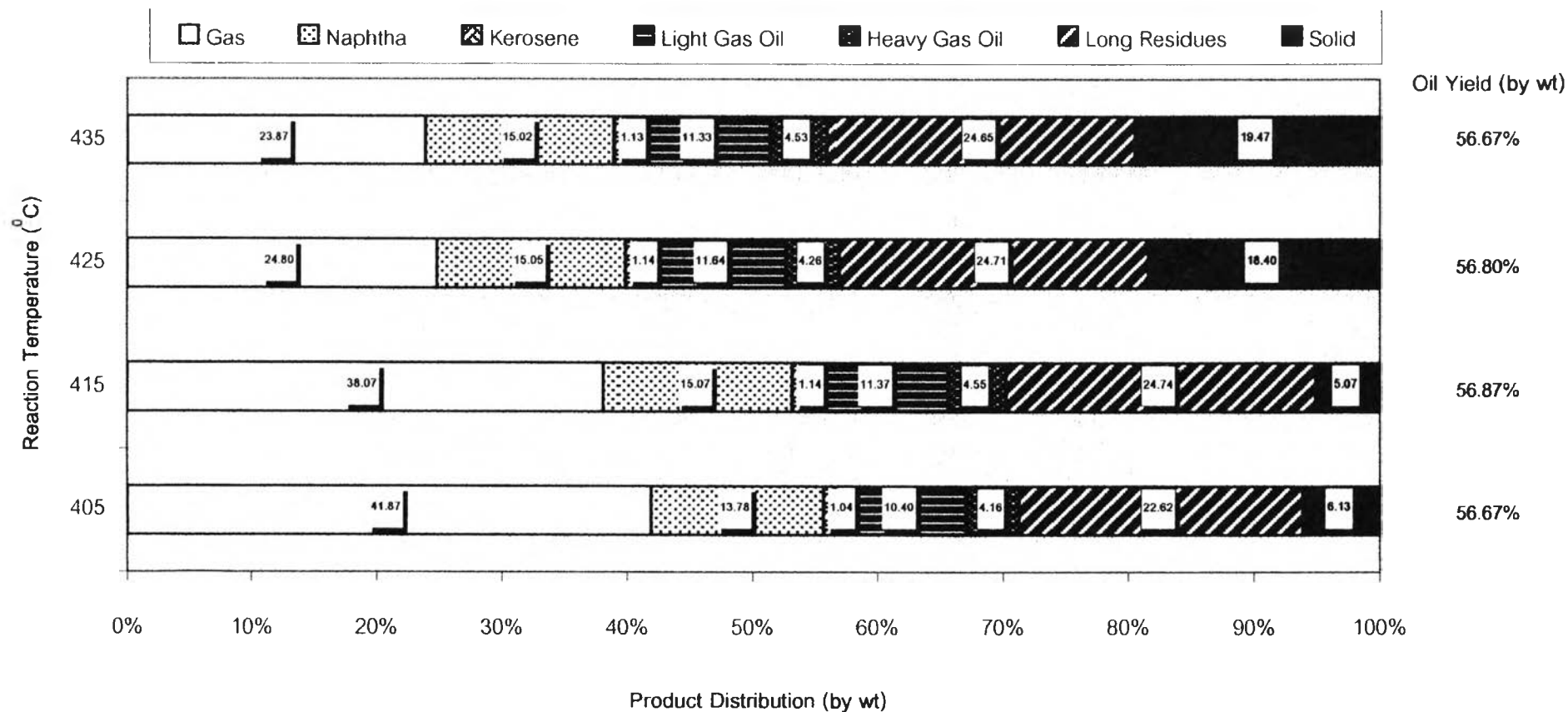


Figure 5.1 Composition distribution from hydrocracking of polypropylene and polystyrene by using various reaction temperature

Reaction condition : 7.5 g of PP + 7.5 g of PS, 30 kg/cm² of H₂, 60 min and 0.45 g of catalyst (5% of Fe/Ac)

5.1.1.2 Influences of initial pressure of hydrogen gas on composition of oil product

The variation of initial pressure of hydrogen gas from 20, 25, 30 and 35 kg/cm² was fixed at the condition at 5% Fe/AC, 7.5 g of each polypropylene and polystyrene, 60 min reaction time, temperature of 415^oC, and 0.45 g catalyst was shown in Fig 5.2. It was found that the pressure of hydrogen at 20 and 25 kg/cm², the oil yield and composition were not different. When the pressure was higher than these, it was observed clearly that the oil yield was considerably decreased about 56% at 30 kg/cm² and 41% at 35 kg/cm², while the long residues was still stable at 5 to 9% of all experiments. Because of more activity at higher pressure of hydrogen. the more cracking to lower molecules and also the more coking as the form of solid and gases.

In conclusion, pressure of hydrogen has an impact on amount of naphtha and solid and gases with its suitable value of pressure between 20 to 25 kg/cm² giving 18% of naphtha, 2% of kerosene, 21% light gas oil, 5% of heavy gas oil, 30% long residue, 6% solid and 74% of oil yield.

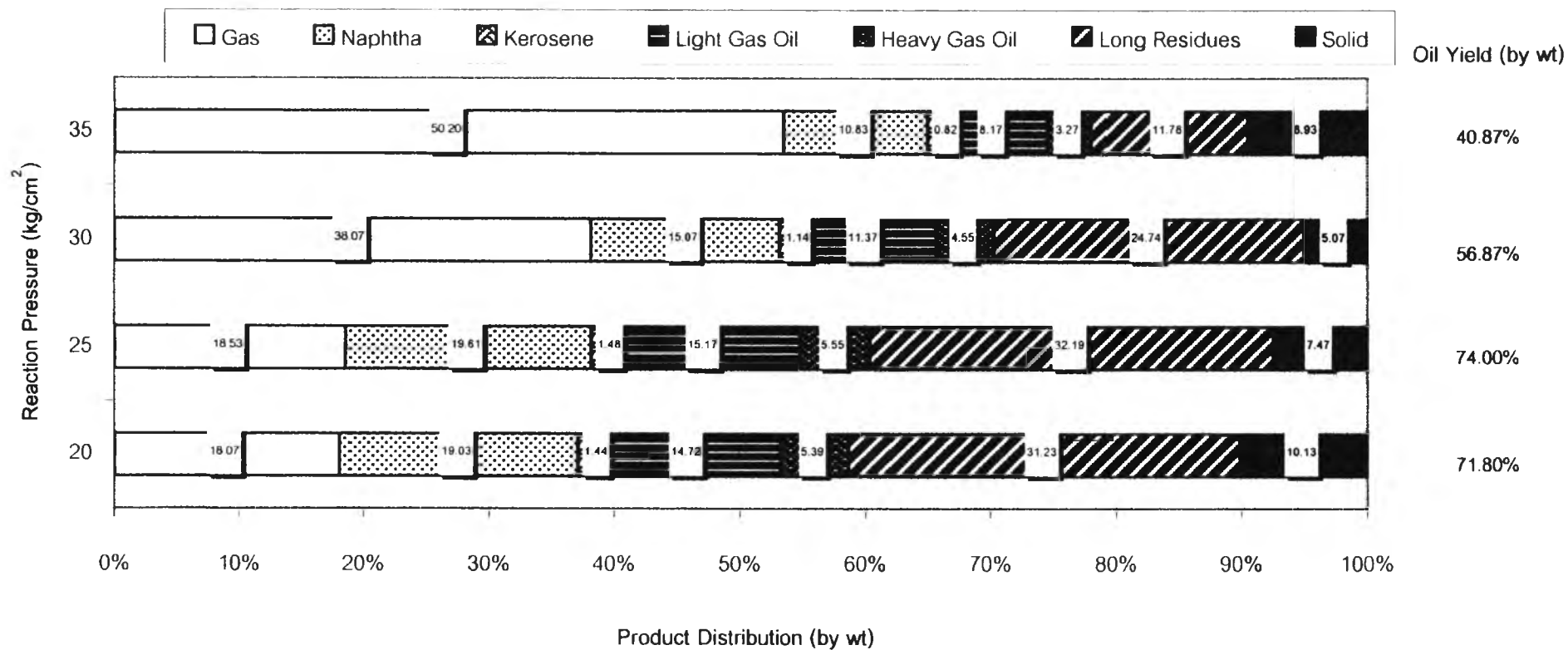


Figure 5.2 Composition distribution from hydrocracking of polypropylene and polystyrene by using various initial hydrogen pressure

Reaction condition : 7.5 g of PP + 7.5 g of PS, 415^o C, 60 min and 0.45 g of catalyst (5% of Fe/Ac)

5.1.1.3 Influences of reaction time on composition of oil product

The variation of reaction time from 30, 45, 60, and 75 min was investigated by fixing the condition at 5% Fe/AC, 7.5 g of each polypropylene and polystyrene, pressure at 25 kg/cm², temperature of 415°C and 0.45 g catalyst (shown in Fig 5.3). It was found that an increase in reaction time induced an increase in percentage of oil yield from 70% to 74% and sharply decreasing to 63% at 75 min. At the reaction time between 30 to 60 min, it seemed to be the same composition of oil, namely observing 18% of naphtha, 2% of kerosene, 15% of light gas oil, 5% of heavy gas oil, 30% of long residue, 6% of solid and about 72% of oil yield. The difference in component of product in each component was gases and solid, namely when it was obtained high composition of gases, the solid would be low. For 75 min. it was found quite different due to longer reaction time and all components of product were shifted to lower molecular weight and finally to gas, it was also observed that the solid was decreased.

In conclusion, a suitable reaction time was 60 min. yielded oil 74%. Percentages of naphtha, kerosene, light gas oil, heavy gas oil, long residues and solid were 19.61, 1.48, 15.17, 5.55, 32.19 and 7.47% respectively.

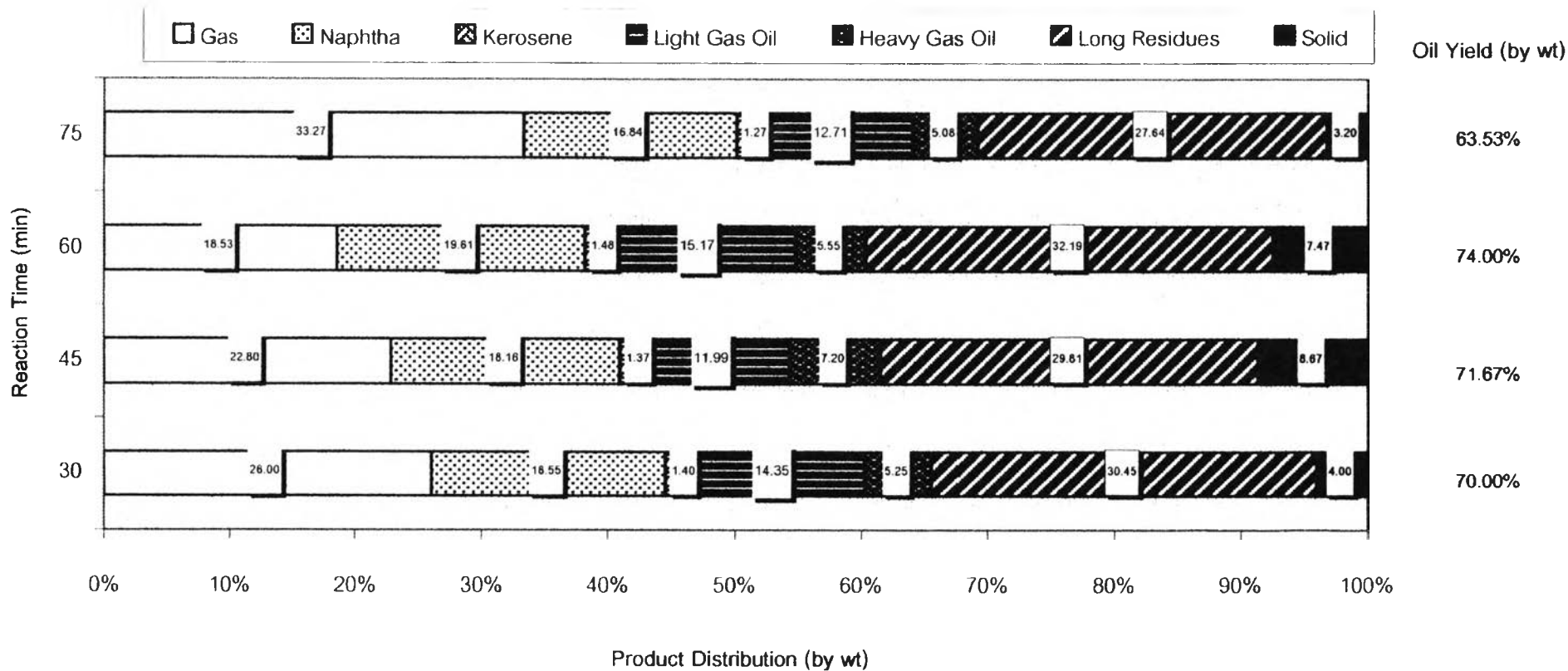


Figure 5.3 Composition distribution from hydrocracking of polypropylene and polystyrene by using various reaction time

Reaction condition : 7.5 g of PP + 7.5 g of PS, 415⁰ C, 25 kg/cm² of H₂ and 0.45 g of catalyst (5% of Fe/Ac)

5.1.1.4 Influences of mass of catalyst on composition of oil product

The variation of weight catalyst from 0.30, 0.45, and 1g was investigated at a fixed condition of 5% Fe/AC, with 7.5 g of each polypropylene and polystyrene, hydrogen pressure at 25 kg/cm², 45 min reaction time and at temperature of 415^oC (shown in Fig 5.4). It was found that a higher mass (lower ratio of mass of polymers to catalyst) of catalyst induced an increase in percentage of oil from 59% to 70% including composition of gas, naphtha, gas oil, long residue and solid being almost stable. Normally the larger quantity of used catalyst, the higher percentage in oil product and composition. This experiment showed that the contacts between reactant and catalyst of different ratio of polypropylene to catalyst might have the same pattern and therefore it has similar oil composition because of very well shaking in reactor to cause entirely catalytic cracking. However it was observed that the higher mass of catalyst, the more solid increased, it implied that the reaction at the surface of catalyst was important to cause more solid and inversely less gases.

In conclusion, a mass catalyst did not affect so much the composition of oil but had influence on solid, gases and oil yield. The suitable mass of catalyst was 0.45 g yielding a percentage of naphtha, kerosene, light gas oil, heavy gas oil, long residues and solid was 18, 1.5, 15, 6, 32 and 6% respectively with 72% of oil yield.

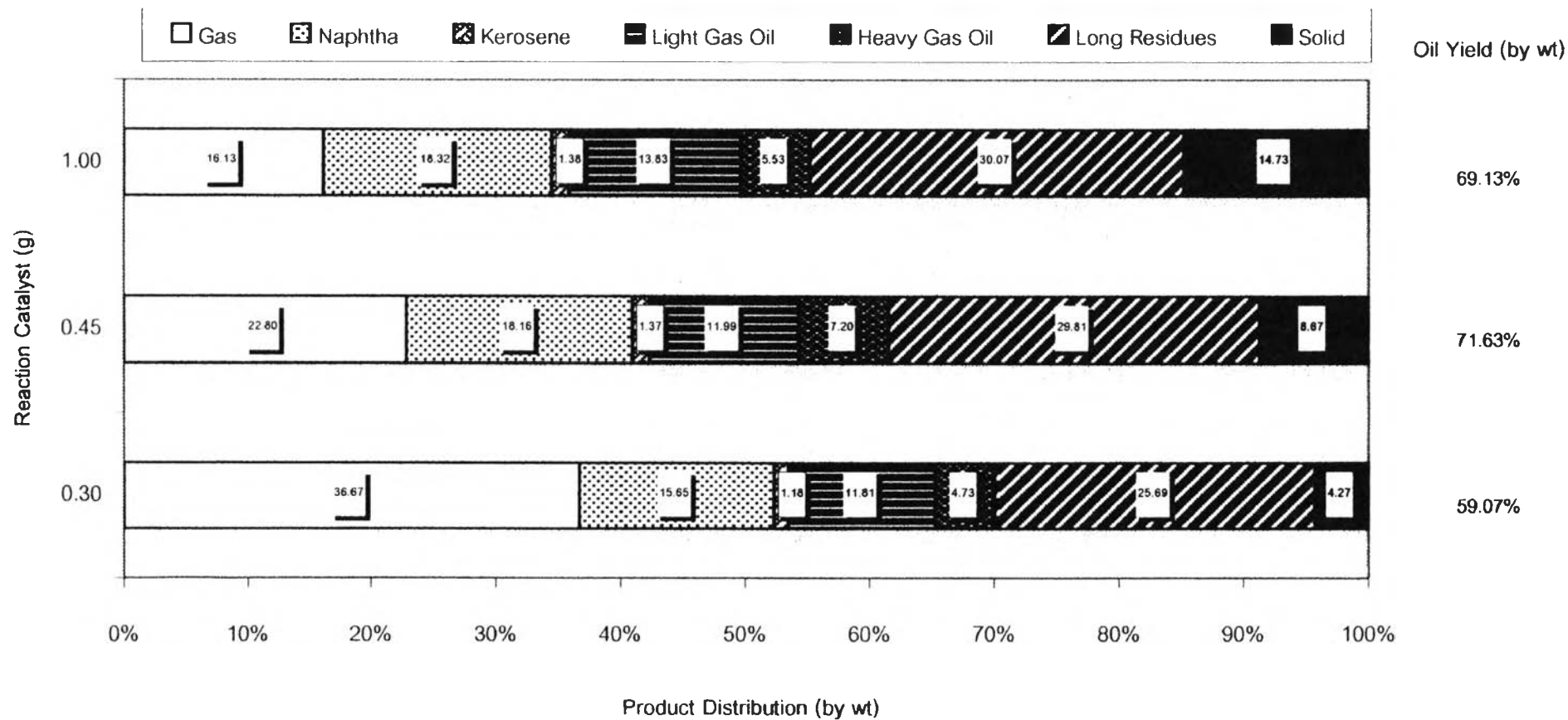


Figure 5.4 Composition distribution from hydrocracking of polypropylene and polystyrene by using various content of catalyst

Reaction condition : 7.5 g of PP + 7.5 g of PS, 415^oC, 25 kg/cm² of H₂, 45 min and catalyst (5% of Fe/Ac)

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

The variation of percentage loading of iron 1, 5 and 10% on activated carbon using as catalyst at a fixed condition of 7.5 g of each polypropylene and polystyrene, with pressure of 25 kg/cm², reaction time of 60 min, temperature at 415°C and 0.45 g catalyst and comparing with non-using catalyst were shown in Fig 5.5. It showed that percents of oil yield and composition were not significant different in percentage loading of iron, the same as in case of using polypropylene as reactant, because the percents of gases in each percentage loading of iron were in the range about of 22.%, naphtha 19%, kerosene 1.5%, light gas oil 14%, heavy gas oil about 5%, long residues 32% solid 6 % and oil yield 72%. While the reaction was carried out without using catalyst, the percents of oil composition were quite less composition of component from that using catalyst. When without catalyst reaction was taken place, the thermal cracking played only the important role in cracking (Fujimoto) immediately very long chains hydrocarbon to intermediate molecules and finally in the form of gases about 36% and oil yield about 56%. The catalytic reaction was simultaneously proceeded by thermal and catalytic cracking, as a result the distribution of hydrocarbon molecules was obtained the higher quality of oil, namely, a increase of naphtha from 17 to 53%, kerosene 7.5 to 13%, light gas oil 8 to 10%.

In conclusion, the catalyst affected directly the oil yield and composition, whereas the percentage of iron on activated carbon was not much influenced on the oil yield and composition. The percentage loading of iron between 1 to 10% did not influenced on composition and oil yield.

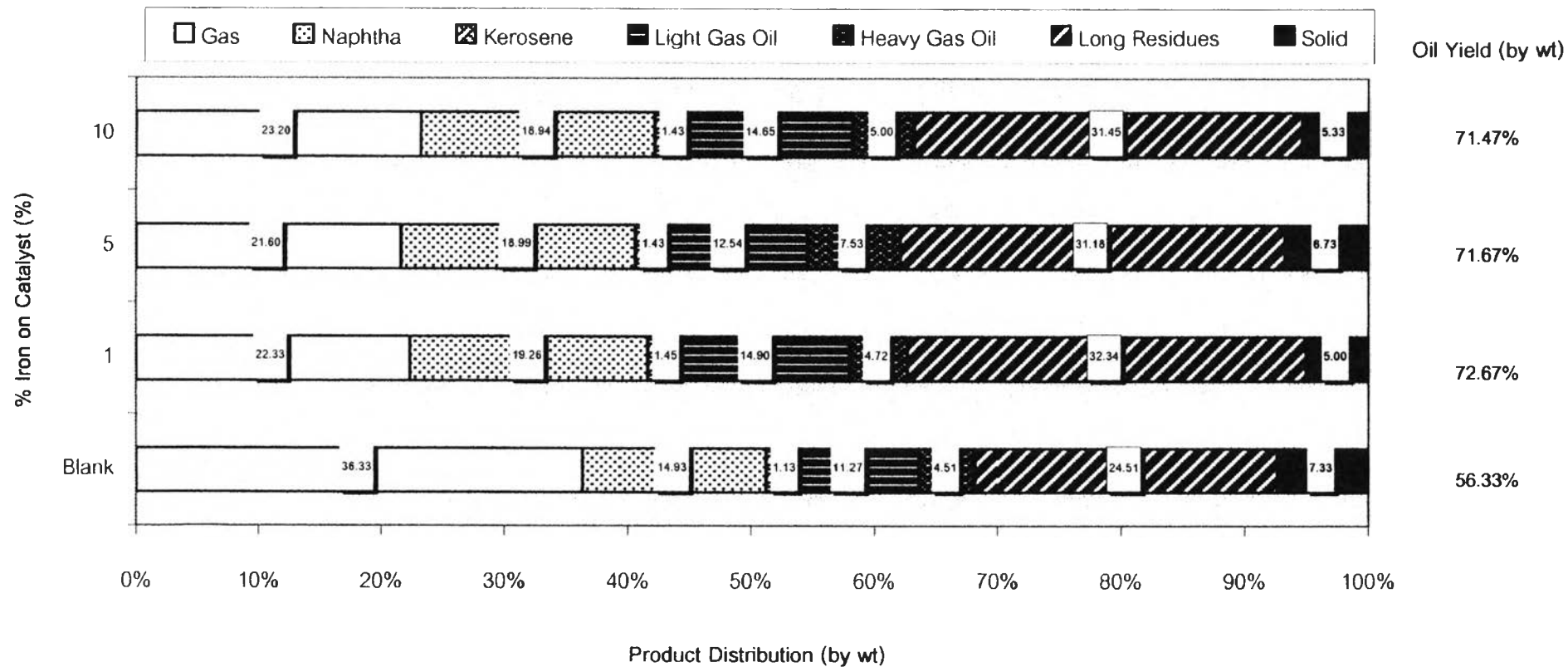


Figure 5.5 Composition distribution from hydrocracking of polypropylene and polystyrene by using various Iron loading on catalyst

Reaction condition : 7.5 g of PP + 7.5 g of PS, 415⁰C, 25 kg/cm² of H₂, 45 min and 0.45 g catalyst (Fe/Ac)

5.1.2 Polypropylene and polyethylene(LDPE) as raw material

The experimental results of hydrocracking of polypropylene and polyethylene on iron/activated carbon as catalyst by studying its influences the conversion percentage of the products and yielded oil composition have the following variables: temperature, initial pressure of hydrogen gas, reaction time by using the mass of catalyst of 0.45g to 15 g of raw material and 5% iron/Activated carbon. This mass of catalyst gave high oil yield and lowest solid. The results of the experiments from different conditions and those of oil composition analysis are summarized in the table A-2. The influences of each variable above-mentioned are showed in the figure 5.7, 5.8 and 5.9 respectively.

Before studying the influences of variables on hydrocracking of polypropylene and polyethylene, the comparison of oil yield and composition of pure polypropylene, pure polyethylene, mixed of polypropylene and polyethylene and without catalyst of mixed of polypropylene and polyethylene(blank) were investigated at the same condition as 30 kg/cm², 50 min. and 445^oC. The result of comparison was shown in Figure 5.6.

5.1.2.1 Comparison of oil yield and composition of pure, mixed (polypropylene and polyethylene) and with and without catalyst of polypropylene and polyethylene

Figure 5.6 showed the comparison of hydrocracking between polypropylene and polyethylene at the same condition. It was found that the oil yield and composition of polypropylene was smaller than polyethylene, whereas the gases were larger. It meant that polypropylene was more easy cracked than polyethylene (Fujimoto). In case of with and without catalyst of polypropylene and polyethylene as the same raw material, the reaction with catalyst gave the higher oil yield and composition, whereas without catalyst being observed more solid meaning that thermal cracking was only taken place.

The composition of oil product of polypropylene and polyethylene as raw material was between that of pure polypropylene and pure polyethylene.

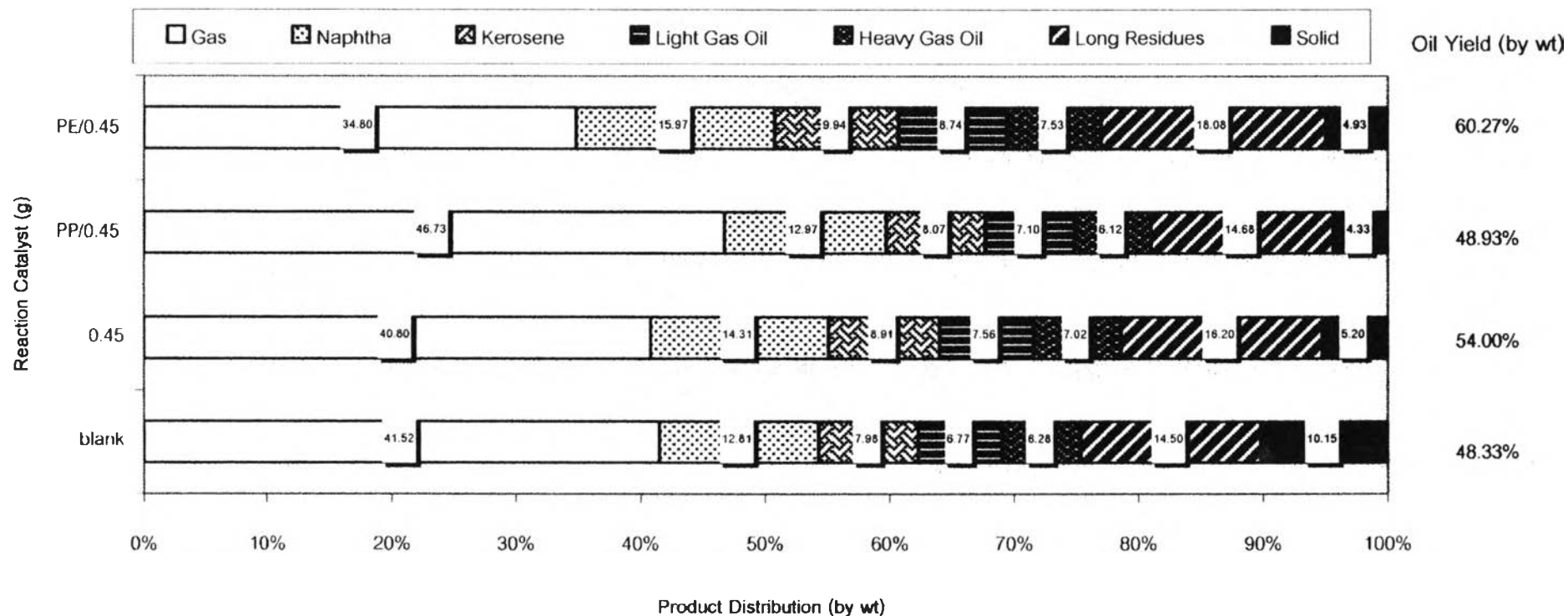


Figure 5.6 Composition distribution from hydrocracking of pure, mixed (polypropylene and polyethylene (LDPE)) and with and without catalyst of polypropylene and polyethylene

Reaction condition : 15 g of PP , 15 g of PE, 445^o C, 30 kg/cm² of H₂, 50 min and 0.45 g of catalyst (5% of Fe/Ac)

7.5 g of PP + 7.5 g of PE ,445^o C, 30 kg/cm² of H₂,50 min and with and without (blank) 0.45 g of catalyse (5% Fe/Ac)

5.1.2.2 Influences of reaction temperature on composition of oil product

The reaction temperature was investigated from 435 - 465⁰C by being fixed the condition at 30 kg/cm², 60 min. and 0.45 g of catalyst. It was observed in Figure 5.7 that when the temperature was increased from 435 to 445⁰C, the oil yield increasing about 6%, whereas the oil composition was kept constant at about 12% of naphtha, 7.5% of kerosene, 12% of gas oil, 13.5 % of residue and 9% solid. The more different was gases about 5%. When the temperature was above 445⁰C, the oil yield decreased with the increase of temperature from 35.73% to 31.47%. It was found a lot of gas about 47-57% because of high activity of thermal cracking being more important than catalytic cracking which could be observed the lower percentage of naphtha and kerosene. The temperature played the role the same as in case of polypropylene and polystyrene.

In conclusion, the optimum temperature was 445⁰C because the product had highest percent oil yield of 51%, naphtha of 13.6%, kerosene of 8.43%, gas oil of 13.78%, residue of 15.32% and lower solid of 8.2 % in product.

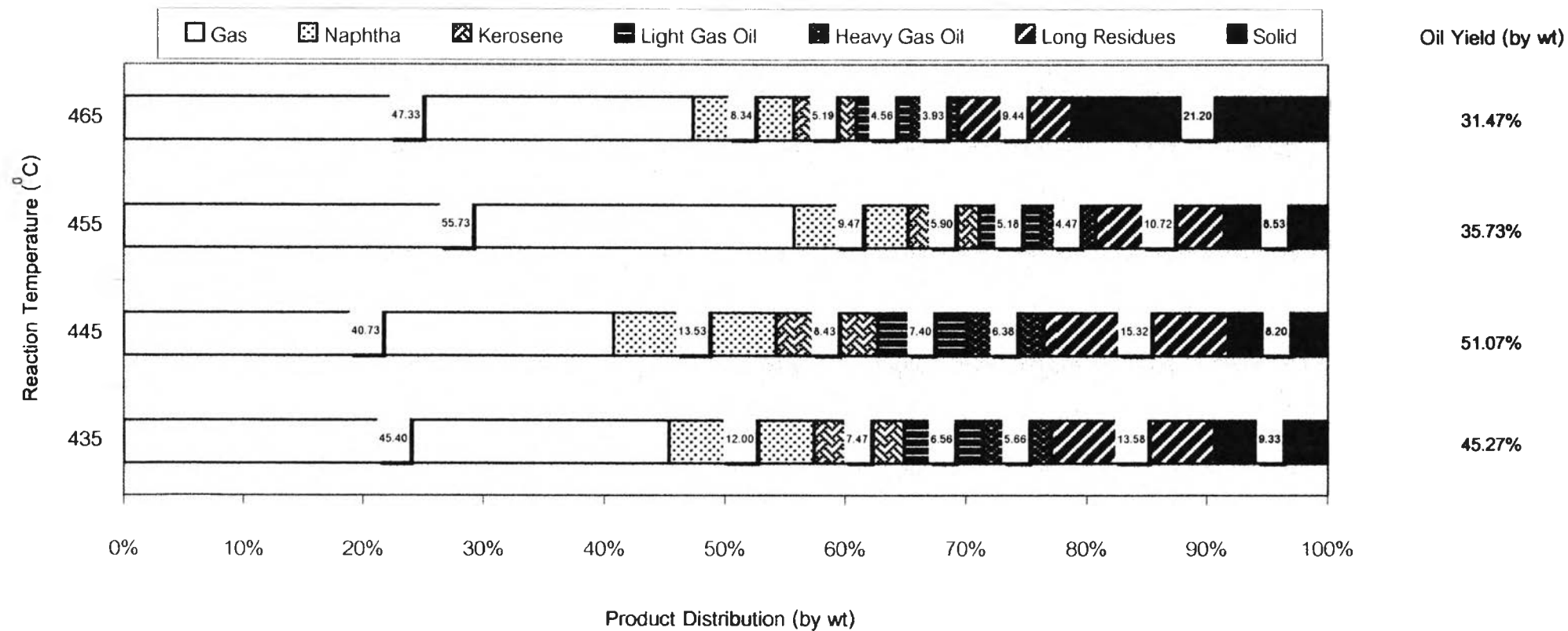


Figure 5.7 Composition distribution from hydrocracking of polypropylene and polyethylene (LDPE) by using various reaction temperature

Reaction condition : 7.5 g of PP + 7.5 g of PE, 30 kg/cm² of H₂, 60 min and 0.45 g of catalyst (5% of Fe/Ac)

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

Figure 5.8 showed the influence of variation of hydrogen pressure range from 25 to 40 kg/cm² on percentage composition and oil yield by being fixed the condition at 445⁰C, 60 min and 0.45g of catalyst. When pressure was raised up from 25 to 30 kg/cm², the result showed that percentage of oil yield increased approximately 8%. After the pressure was raised up more than 30 kg/cm², the result showed that oils yield was reduced and the increase of gas about 20%, whereas all composition in oil was also decreased. It could be explained that the initial hydrogen pressure was responsible to the catalytic cracking step, the higher pressure of hydrogen meant the higher catalytic cracking, as a result the lower oil yield and composition was obtained.

It was noticed that at 30 kg/cm² was the optimum initial pressure with high oil yield of 51%, naphtha of 13.53%, kerosene of 8.43%, gas oil of 13.78%, residue of 15.32% and solid 8.2%.

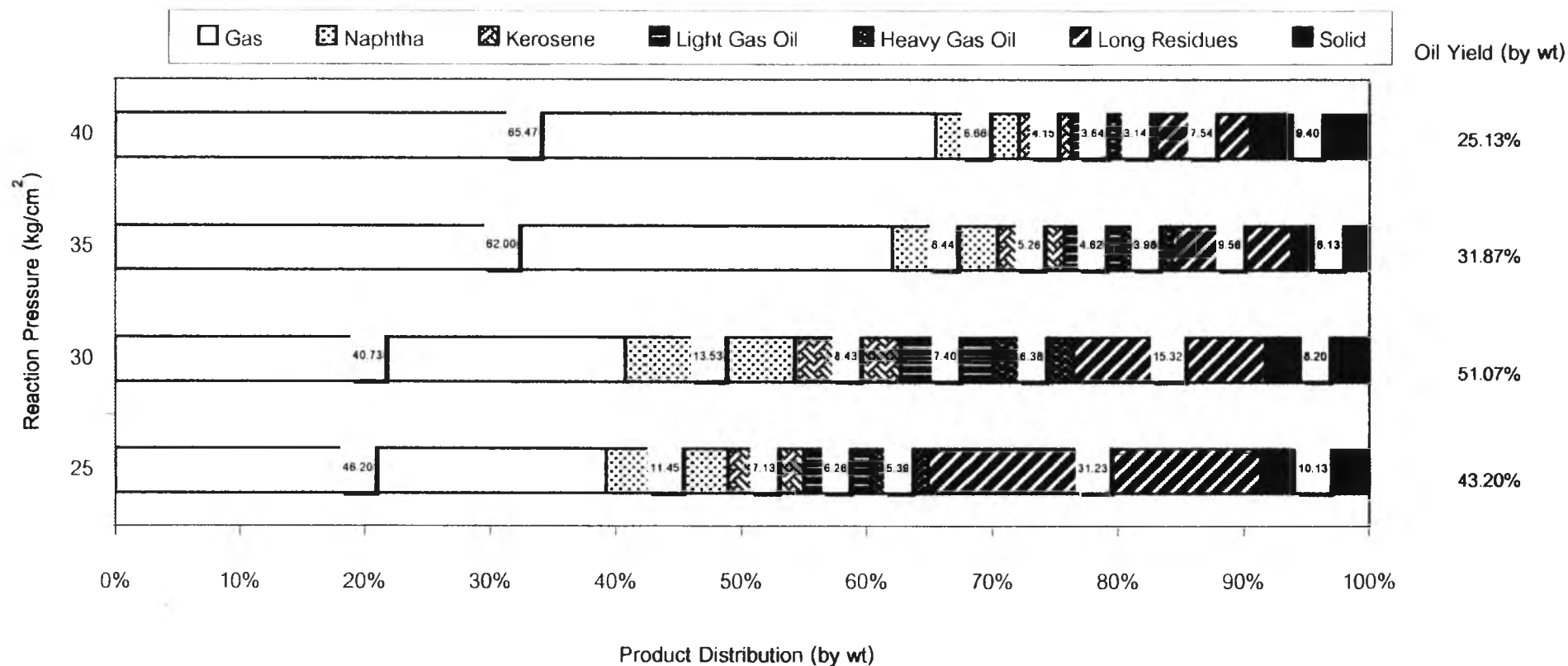


Figure 5.8 Composition distribution from hydrocracking of polypropylene and polyethylene (LDPE) by using various initial hydrogen pressure.

Reaction condition : 7.5 g of PP + 7.5 g of PE, 445⁰ C, 60 min and 0.45 g of catalyst (5% of Fe/Ac)

5.1.2.4 Influences of reaction time on composition of oil product

Figure 5.9 showed the influence of variation of reaction time range from 30 to 60 minutes on percentage of composition and yield of product by being fixed condition at 30 kg/cm^2 , 445°C and 0.45 g of catalyst. The higher reaction time was reasonable to higher thermal cracking than catalytic cracking. When reaction time increased from 30 to 60 minutes, the result showed the small change of percentage of oil yield and composition which was about 50%. The highest value (54%) was at 50 min. It was known that the cracking of polyethylene was more difficult than other polymer ^[7] and this process controls the hydrocracking of the reaction as a result, the small change in oil product.

In conclusion, the reaction time might be 30 to 60 minutes. The maximum yield was carried out at 50 or 60 minutes.

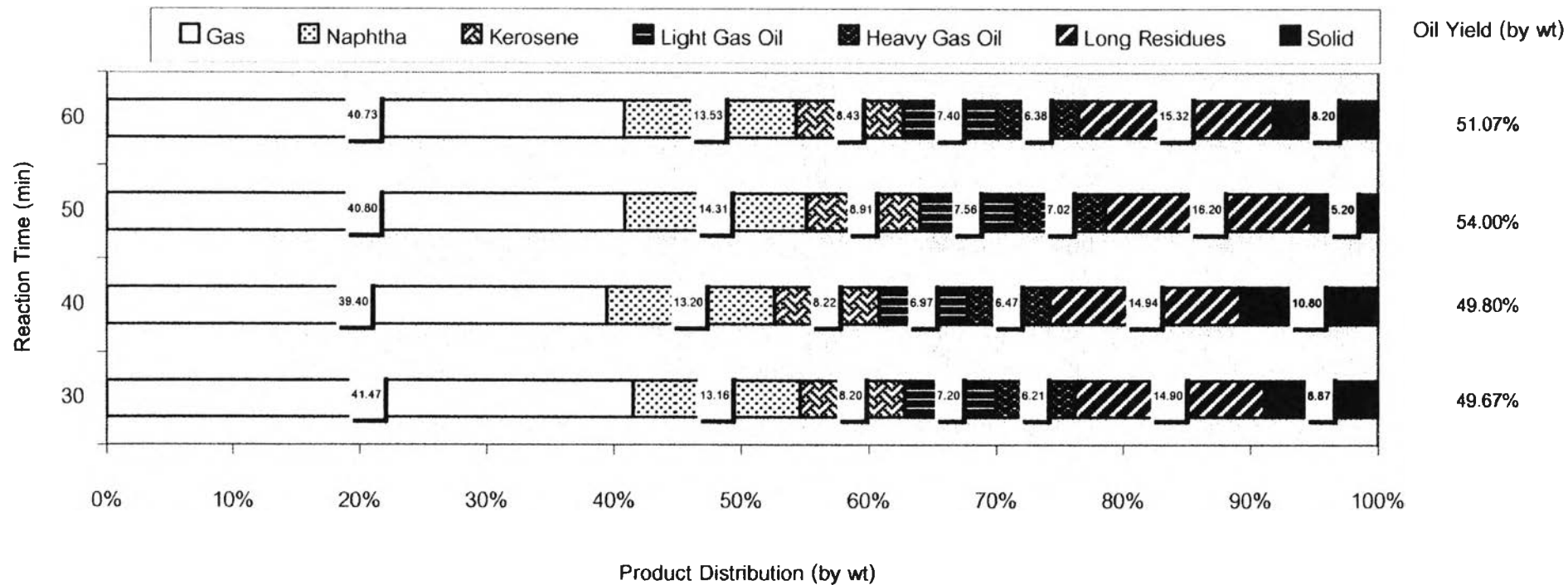


Figure 5.9 Composition distribution from hydrocracking of polypropylene and polyethylene (LDPE) by using various initial hydrogen pressure.

Reaction condition : 7.5 g of PP + 7.5 g of PE, 445⁰ C, 30 kg/cm² of H₂ and 0.45 g of catalyst (5% of Fe/Ac)

5.2 Characterization of iron on activated carbon before and after using in reaction ^[13]

Table 5.1 shows surface specific area (BET) of pure activated carbon and many loads of iron on activated carbon of particle size of 1 mm. before and after using catalyst in reaction at 415°C, 30 atm.

Iron loading % by weight	BET area m ² /g before reaction	BET area m ² /g after reaction of PP	BET area m ² /g after reaction of PP & PS
Pure activated carbon	746	-	-
1% Fe/ activated carbon	719	46	19
5% Fe/ activated carbon	692	37	14
10% Fe/ activated carbon	706	52	13

Table 5.1 shows the surface specific area before and after using in reaction. It was found that when iron was impregnated on the surface of pure activated carbon, the average (1, 5 and 10 % loading) surface decreased slightly about 5.3%, it meant that there were attached iron metal crystals in the pores of activated carbon, and it seemed no influences of percentage loading of iron on surface area. The surface area of each type of percentage loading iron 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 shows 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 by average of 94% for polypropylene and by 98% for polypropylene and polystyrene. This was because of some small amount of unconverted polypropylene or polystyrene covering the surface of catalyst during cooling to the ambient temperature verifying by comparison of pure and used catalyst. It was found more decrease of surface area in polypropylene and polystyrene, because of higher molecular weight of part of polystyrene being used.

5.3 Comparison of product distribution of using three types of raw materials

The oil product distributions of three types of raw materials (polypropylene, polystyrene, mixed polypropylene and polystyrene) were compared in **Table 5.2**

Table 5.2 comparison of oil product distribution of three types of raw materials

Materials	Polypropylene (Puangthum)	Polystyrene (Vitidsant)	Polypropylene and polystyrene	Polypropylene and polyethylene
Temperature	435°C	370°C	415°C	445°C
Reaction time	60 min	60 min	60 min	50 min
Mass catalyst	0.45 g	0.45 g	0.45 g	0.45 g
Composition of oil				
Naphtha	62.62 %	23.83%	19.61%	14.31%
Kerosene	13.48%	1.80%	1.48%	8.91%
Gas oil	15.41%	25.18%	15.17%	14.58%
Long residue	4.83%	39.12%	32.19%	16.20%
Yield	96.33%	89.93%	74.00%	54.00%

Table 5.2 shows the optimum condition of hydrocracking and oil product composition of mixed polypropylene and polystyrene and mixed polypropylene and polyethylene. We observe that mixed polypropylene and polystyrene was easily cracked to oil product, especially polypropylene yielding the components of low molecular weight (higher percentage of naphtha and kerosene). When mixed polypropylene and polystyrene and mixed polypropylene and polyethylene were used, it was difficult to be cracked at low temperature because the polymers became gummy. It could be worked at higher temperature but the oil composition is low which was in the range between oil composition when using polypropylene and polypropylene as reactants.