CHAPTER IV

RESULTS AND DISCUSSION

These experiments involved the search for suitable conditions to convert low-density polyethylene with lignite to oil products in high yield by using Ni-Mo/Alumina as catalyst. The low-density polyethylene was selected for this study, because a large quantity of demand for thermoplastic in the world where some part of this would cause the environment's problem. The catalyst Ni-Mo/Alumina was selected, because Ni and Mo were the active component which give high activity for hydrocracking as well as for hydrogenation reaction. The alumina was chosen as support because it was acidic which was appropriate also for cracking hydrocarbon and was easily impregnated with Ni and Mo by Ni being maintained at high metal dispersion.

4.1 Ultimate and Proximate Analysis of Coal

The ultimate analysis comprised of determinations of percentage of carbon, hydrogen, nitrogen and sulfur. The proximate analysis was the most widely used method for analyzing coal. The proximate analysis expressed percentage of ash, volatile matter and fixed carbon.

The results of ultimate analysis and proximate analysis were shown as Tables 4.1.and 4.2 respectively.

Table 4.1: Ultimate analysis of lignite coal

Time	%C	%H	%N	%S
1	35.204	3.462	1.420	4.040
2	35.308	3.622	1.517	3.893
Average	35.256	3.542	1.468	3.967

Table 4.2: Proximate analysis of lignite coal

Proximate	%
Ash	40.3936
Volatile	37.7096
Fixed Carbon	21.8971

Considering Tables 4.1 and 4.2, it was noticed that lignite was composed of hydrocarbon which could be observed the high %carbon about 35% and hydrogen 3.5% in the ultimate analysis and confirmation also by high volatile matter in proximate analysis. The high content of hydrocarbon in the form volatile matter in lignite had possibility form high oil product.

4.2 Hydrocracking process

The results for all parameter from catalytic coprocessing of low density polyethylene with lignite coal shown in Appendix A (Table A.1), This table indicates the optimum conditions for hydrocracking of used low density polyethylene with lignite. In this research, the hydrocracking reaction was studied as a function of processing variables, i.e. reaction temperature, hydrogen pressure, reaction time and ratio of LDPE/Coal. Products were identified by Simulated Distillation, follow the ASTM D-2887 method. The change in % component of oil product as a function of the above variables allowed for the selection of suitable conditions.

4.2.1 Effect of reaction temperature on oil composition.

The study of the effect of temperature on the catalytic coprocessing of used low density polyethylene with lignite was performed by operating at various reaction temperatures: 400, 420, 435 and 450^{0}C by using 0.45 g of Ni-Mo/ Alumina as catalyst under hydrogen pressure 60 kg/cm^2 and fixing reaction time as 60 min. The composition of oil products from catalytic coprocessing as a function of temperature were shown in Table 4.3 and Figure 4.1 respectively.

Table 4.3: Effect of catalytic coprocessing temperature on product composition at 60 kg/cm^2 of hydrogen, 60 minutes of reaction time and ratio of LDPE/ lignite 15:1

Temperature (°C)	Gas product (% yield)	Oil products (% recovered)					Solid (% yield)	% Yield (Oil product)
		Naphtha	Kerosene	Light Gas Oil	Heavy Gas Oil	Long Residue		
400	13.7	Wax	Wax	Wax	Wax	Wax	-	0
420	13.7	44.3	9.6	6.3	3.2	4.7	18.2	68.1
435	21.4	36.5	8.6	5.5	3.2	3.8	21.1	57.5
450	36.0	24.8	6.9	5.0	3.4	4.9	18.8	45.0

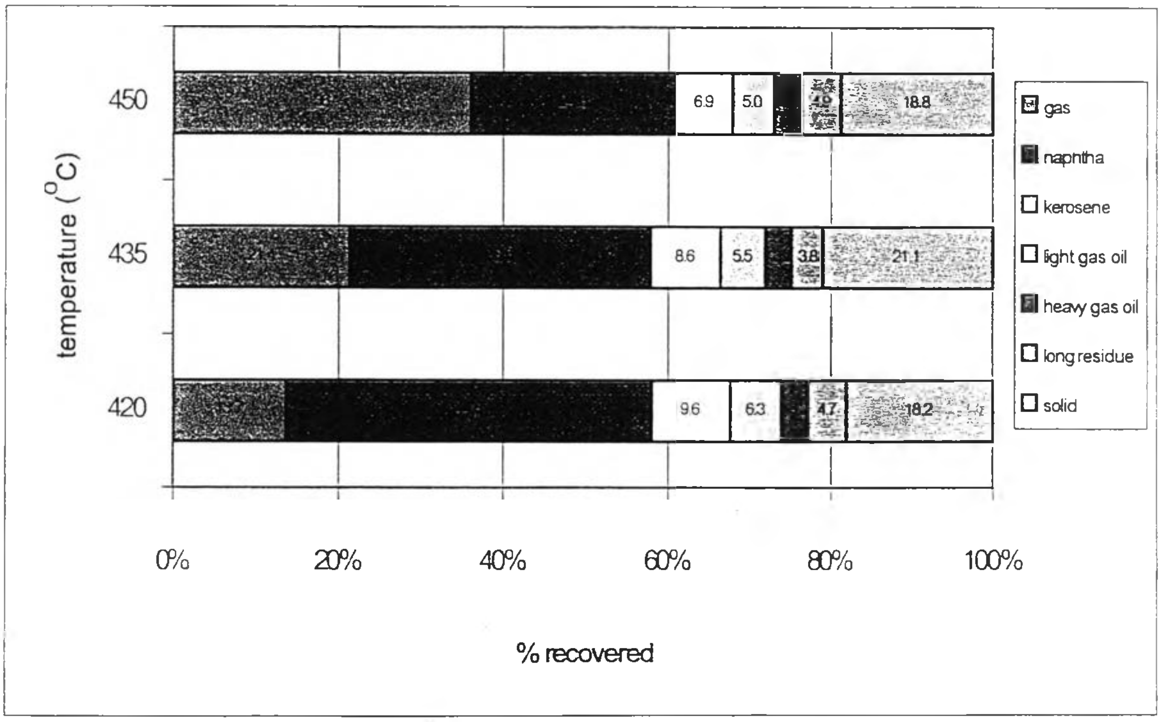

Figure 4.1: Effect of catalytic coprocessing temperature on product composition as a function of reaction temperature at 60 kg/cm^2 of hydrogen, 60 minutes of reaction time and ratio of LDPE/ lignite as 15:1

From the Table 4.3 and Figure 4.1; the effect of reaction temperature on the catalytic coprocessing of used low density polyethylene with lignite coal under 60 kg/cm^2 of hydrogen and 60 min of reaction time. When the reaction temperature increases from 420 to 450^{0}C, the thermal cracking of long chain hydrocarbon from LDPE and lignite firstly broke down with high temperature to form lower hydrocarbon such as gases (C_1-C_5) kerosene and gas oil. Naphtha, kerosene and gas oil were converted also to gases. Nevertheless thermal and catalytic cracks were the competitive reactions, but Ni-Mo/Alumina was not so active as zeolite. For these reasons the percentage of gaseous product increased with an increase reaction temperature. The percentage of recover of naphtha decreases largely with an increase reaction temperature from 44% to 24%, because catalytic was dominated by thermal cracking. In the contrary, the increase of temperature, the gaseous product increased largely from 13% to 36%, this confirmed the idea above.

In conclusion, it was found that, the optimum reaction temperature was 420^{0}C because it gave high naphtha 44%, kerosene 9.6%, gas oil 9.5% and low gaseous product 9.5%. This temperature was used to study for other variables.

4.2.2 Effect of pressure of hydrogen on oil composition

The study of the effect of hydrogen pressure was performed by various pressures at 30, 45, 60 and 75 kg/cm^2. The catalytic coprocessing of low density polyethylene with lignite coal at the optimum reaction temperature is 420^{0}C, 60 min of reaction time and ratio of LDPE/lignite as 15:1. The compositions of products from hydrocracking oil were shown in Table 4.4 and Figure 4.2 respectively.

Table 4.4: The effect of hydrogen pressure on product composition at 420°C of reaction temperature, 60 minutes reaction time and ratio of LDPE/ lignite as 15:1.

Pressure (kg/cm^2)	Gas product (% yield)	Oil products (% recovered)					Solid (% yield)	% Yield (Oil product)
		Naphtha	Kerosene	Light Gas Oil	Heavy Gas Oil	Long Residue		
30	9.3	Wax	Wax	Wax	Wax	Wax	-	0
45	10.9	34.9	7.9	5.1	3.7	5.4	32.1	57.1
60	13.7	44.3	9.6	6.3	3.2	4.7	18.2	68.1
75	20.7	38.3	8.6	5.3	3.6	3.6	19.9	59.4

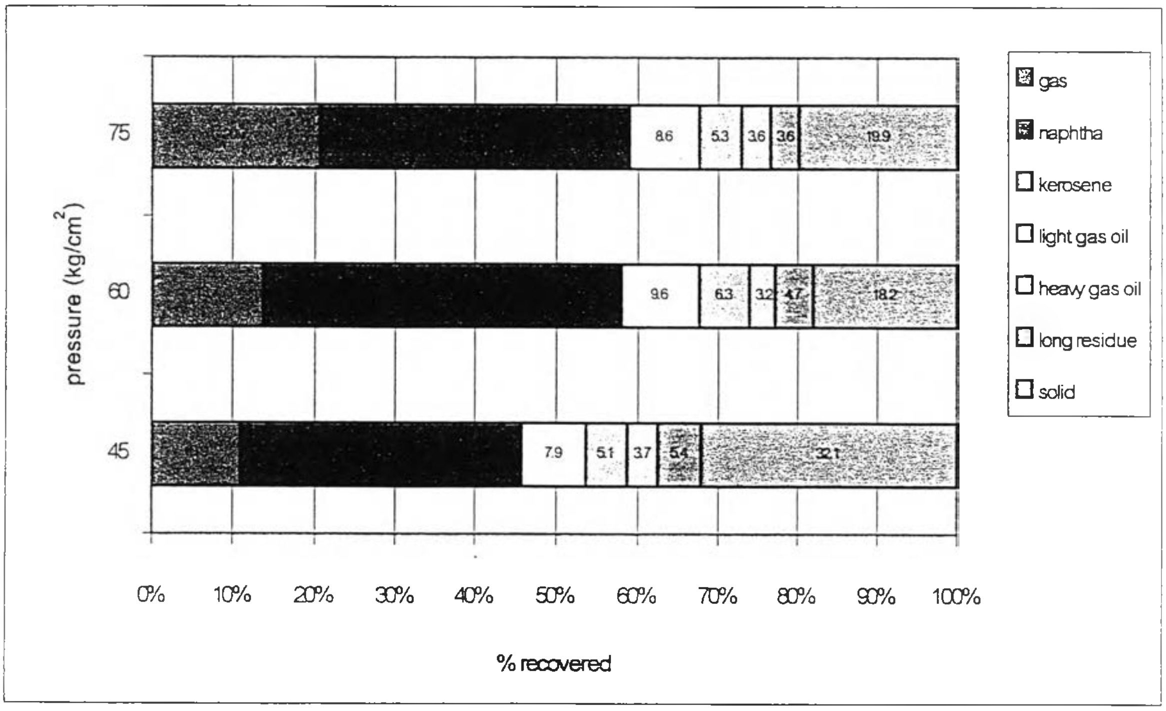

Figure 4.2: The effect of hydrogen pressure on product composition at 420°C of reaction temperature, 60 minutes of reaction time and ratio of LDPE/ lignite coal as 15:1 as a function of hydrogen pressure.

increased the %yield of oil product by 11% while at pressure of 75 kg/cm^2 the %yield of oil product decreased. It was mentioned before that the thermal and catalytic cracking seemed having the same rate of reaction. When hydrogen concentration increased it would promote the catalytic reaction by increasing more hydrogen free radical. Thus catalytic cracking could be occurred than thermal cracking at 75 kg/cm^2 of hydrogen pressure as a result, a decreased the %yield of oil product, naphtha, kerosene, gas oil, but gaseous product increased, whereas solid increased which it confirmed more reaction at the surface of lignite. The hydrocracking reaction could not occur at 30 kg/cm^2. However, as seen in Table 4.4 and Figure 4.2, when the hydrogen pressure was increased from 30 to 75 kg/cm^2, the percentage of recovered of naphtha was increased until hydrogen pressure at 75 kg/cm^2 in which the percentage of recovered was seemed decreased.

The optimum hydrogen pressure condition was 60 kg/cm^2 of hydrogen for high percentage yields of the oil product was 68.1% and the highest product distribution was 44.3 %and 9.6 % recovered of naphtha and kerosene respectively.

4.2.3 Effect of reaction time on oil composition

The effect of reaction time on the percentage recovered of reaction systems, Coal/LDPE was carried out for the reaction time by fixing the condition at 420°C of reaction temperature, 60 kg/cm^2 of hydrogen and ratio of LDPE/Lignite coal as 15:1. The composition of the oil product was analyzed and presented in Table 4.5 and Figure 4.3 respectively.

From Table 4.5 and Figure 4.3 it showed that when the reaction time increased from 30 to 60 min, the % yields of oil and % naphtha increased, whereas other components being the same quantities. After reaction time more than 60 min, we observed the decreasing of % yield of oil and % naphtha, in the contrast we noticed the increasing of long residue and solid. The experiments were fixed the temperature and pressure of hydrogen, so the thermal and catalytic cracking were occurred the same phenomena when the reaction time increased to 60 min. We obtained the maximum % yield, %naphtha and lowest %solid, it means that this appropriate condition cause. Thermal cracking (changing long hydrocarbon to moderate chain) corresponding to catalytic cracking the moderate chain hydrocarbon from thermal cracking in the same time. When the reaction time more than 60 min the catalytic reaction was nearly faster than thermal cracking and long time also caused coking at the surface of catalyst; as a result we observed the %decreasing of %naphtha, kerosene and % yield.

In the same way we observed also that when the longer time of reaction, the overall %of moderate long chain such as kerosene, gas oil and long residue decreased, while %solid increased, it mean that this time caused the decrease the activity of catalytic cracking, but thermal cracking still working.

Table 4.5: The effect of reaction time on product composition at 420^{0}C of reaction temperature, 60 kg/cm^2 of hydrogen and ratio of LDPE/lignite as 15:1

Time (min)	Gas product (% yield)	Oil products (% recovered)					Solid (%yield)	% Yield (Oil product)
		Naphtha	Kerosene	Light Gas Oil	Heavy Gas Oil	Long Residue		
30	13.4	26.1	8.3	7.5	6.3	14.4	24.0	62.6
60	13.7	44.3	9.6	6.3	3.2	4.7	18.2	68.1
90	17.1	18.1	8.2	6.5	5.5	11.7	32.9	49.8
120	18.4	15.2	5.5	6.5	5.5	15.1	33.8	47.8
180	20.9	11.5	4.6	7.2	6.0	15.0	37.8	44.5

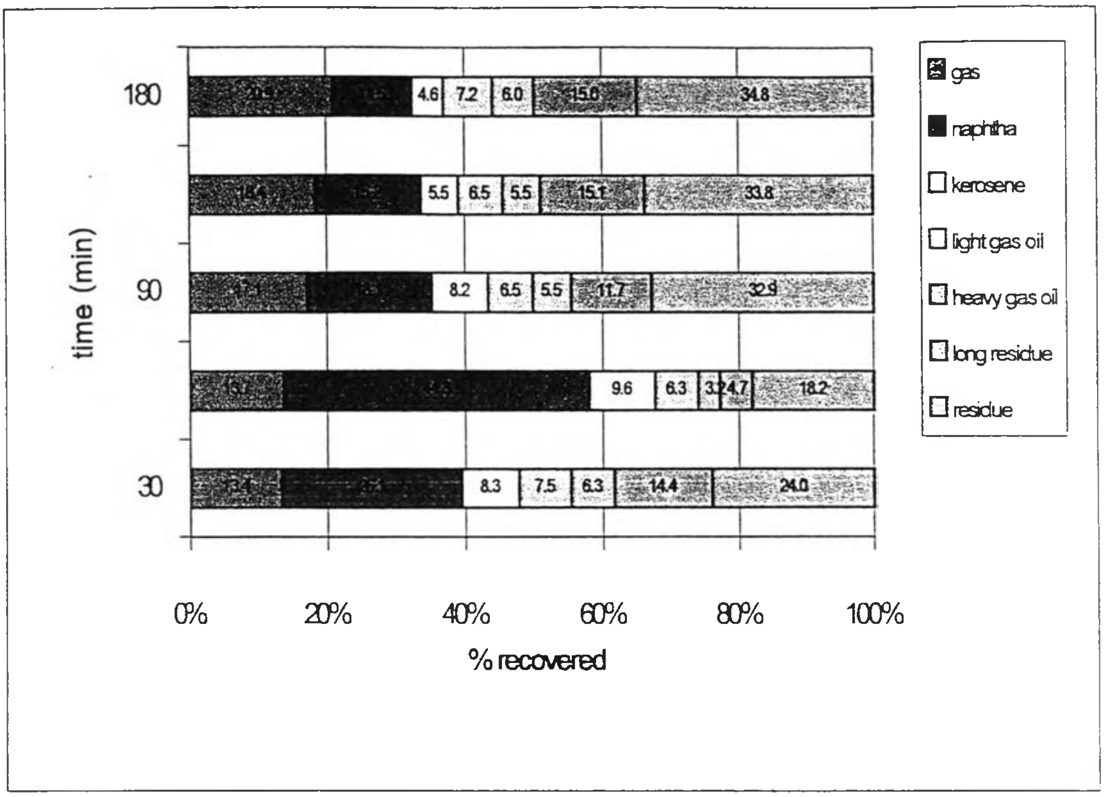

Figure 4.3: Oil product as a function of reaction time, at 420°C of reaction temperature, 60 kg/cm ^{2} of hydrogen and ratio of LDPE: lignite as 15:1.

The optimum of reaction time was 60 min, because this time gave the highest %yield of oil 68.1 and % naphtha 44.3 at condition of 420°C of reaction temperature, 60 kg/cm^2 of hydrogen and ratio of LDPE: lignite as 15:1.

4.2.4 Effect of ratio of LDPE/lignite on oil composition

The study of the effect of ratio of LDPE/Coal on catalytic coprocessing of used low density polyethylene with lignite coal was performed by operating at various ratios of LDPE/lignite: 15:.0.5, 15:1, 15:2.5, 15:3 and 15:5, using 0.45g of Ni-Mo/Alumina as catalyst, at condition of 420°C of reaction temperature, 60 min of reaction time and 60 kg/cm^2 of hydrogen.

The product composition changed with ratio of LDPE/lignite. Shown in Table 4.6, the increasing ratio of LDPE/lignite had not a beneficial effect on % yield of oil product distribution. Therefore, as seen in Table 4.6 the ratio of LDPE/lignite of 15:1 a good condition. The best percentage yield was 68.1 low-density polyethylene with lignite converted to oil product using Ni-Mo/Alumina catalyst as in Figure 4.4.

Table 4.6: The effect of ratio of LDPE/ lignite on product composition at 420^0C of reaction temperature, 60 kg/cm^2 of hydrogen and 60 minutes of reaction time.

Ratio (LDPE/Coal)	Gas product (% yield)	Oil products (% recovered)					Solid (%yield)	% Yield (Oil product)
		Naphtha	Kerosene	Light Gas Oil	Heavy Gas Oil	Long Residue		
15:0.5	21.3	38.3	8.3	6.4	3.8	7.0	14.9	63.9
15:1	13.7	44.3	9.6	6.3	3.2	4.7	18.2	68.1
15:2.5	14.7	37.5	8.0	5.1	2.8	3.4	28.5	56.8
15:3	13.7	24.5	5.6	3.6	2.1	2.7	47.8	38.4
15:5	12.7	18.6	3.9	2.5	1.4	2.6	58.3	27.7

When the ratio of LDPE: lignite was decreased from 15:1 to 15:5, the percentage of recover of naphtha was increased until the ratio of LDPE: Lignite at 15:1 the percentage of naphtha decreases with decreasing ratio of LDPE: lignite, which considering from these results as decreasing ratio of LDPE: lignite from 15:1 to 15:5 so that the cracking reaction could be occurred better than the higher ratio of LDPE: lignite, because long molecular chains from lignite coal could be cracked to short molecular chains. Thus the percentage of recovered of naphtha increases with decreasing ratio of LDPE: lignite.

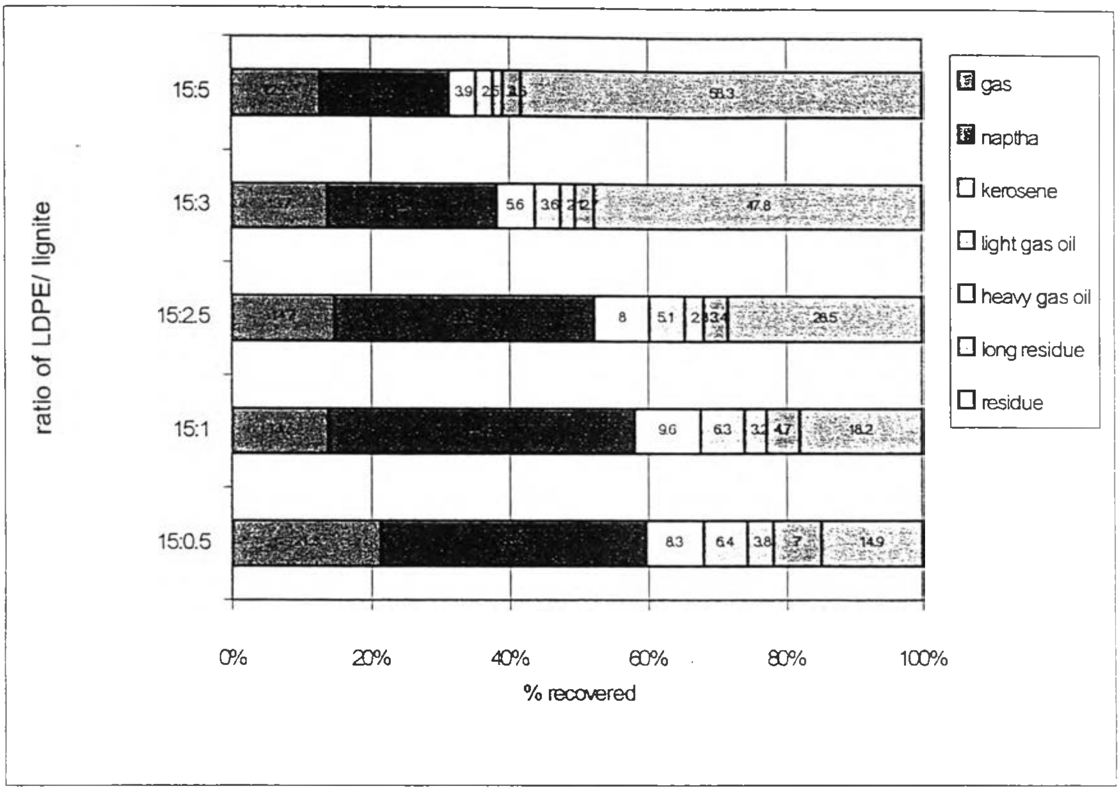

Figure 4.4: The effect of ratio of LDPE: Lignite on product composition at condition of 420°C of reaction temperature, 60 kg/cm^2 of hydrogen and 60 minutes of reaction time.

When the ratio of LDPE/ lignite decreased at the same condition, we observed that the %naphtha, kerosene, gas oil and long residue also decreased whereas %solid increased. It mean that when we used more lignite, it seemed that catalyst might contact directly with lignite and causing coking at the surface of catalyst, as a result we noticed clearly the %decreasing from 63.9 to 27.7 % of %yield of oil and 44.3 (the optimum) to 18.6 % of naphtha.

The optimum ratio of LDPE: lignite was 15:1 at the condition of 420°C of reaction temperature, 60 kg/cm^2 of hydrogen and 60 min of reaction time, It gave the highest 68.1% yield of oil, 44.3% naphtha, 9.6% kerosene, 14% gas oil and 18.2% solid.

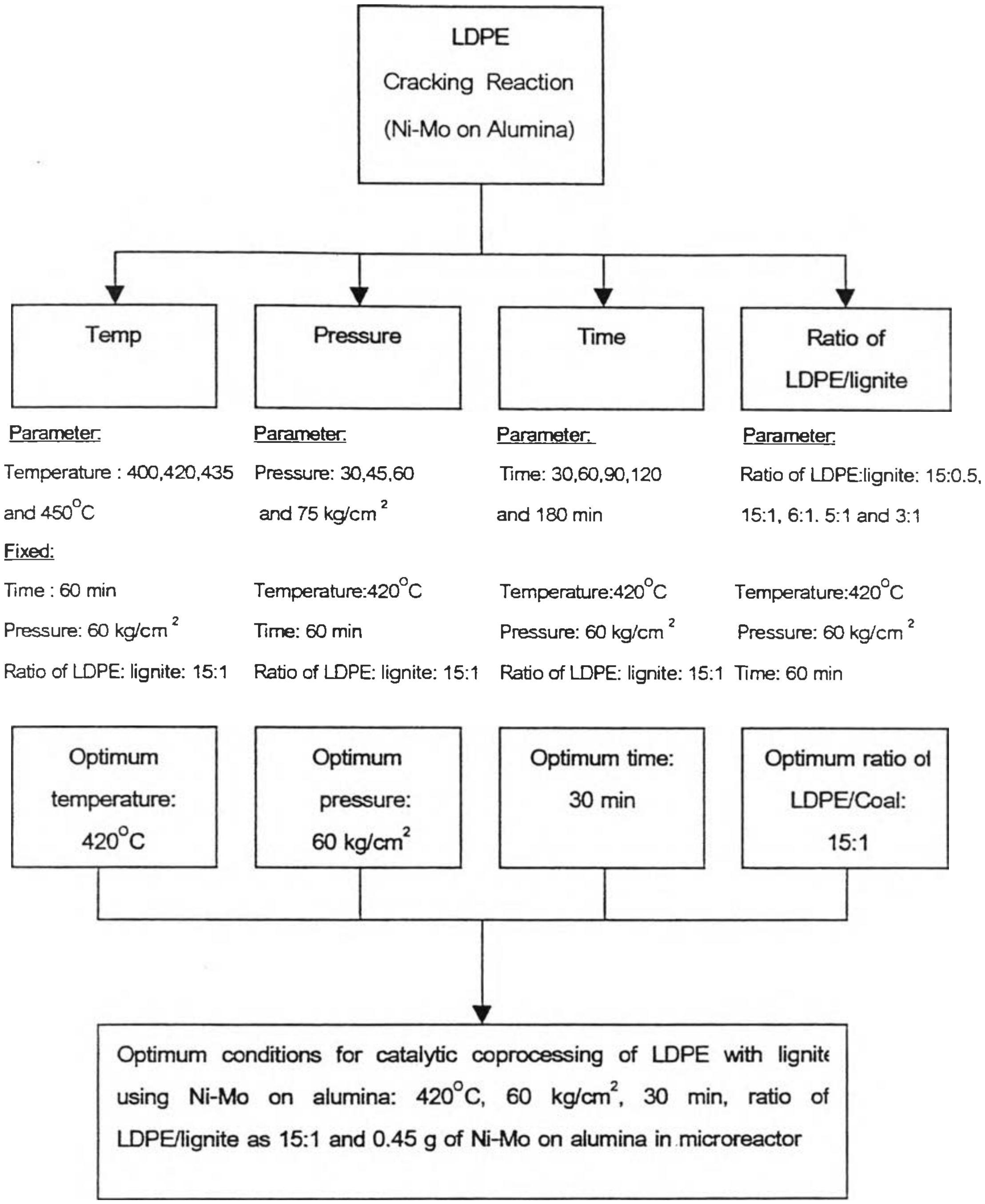

Figure 4.5: The optimum condition of catalytic coprocessing of LDPE with lignite using Ni-Mo on alumina.