

CHAPTER IV

RESULT AND DISCUSSION

This research involved the search for suitable conditions to convert used polyethylene to fuel in high yield by hydrocracking with dual function catalysts. Pt/F on Al₂O₃ catalyst, Pt/Sn/Cl/F on Al₂O₃ catalyst, Ni/Sn/Cl/F on Al₂O₃ catalyst and Co/Sn/Cl/F on Al₂O₃ catalyst were selected because platinum, tin, nickel and cobalt are the components which are active for hydrocracking as well as for hydrogenation reaction. Fluorine and chlorine act as promoters by increasing the activity of the acidic function. Alumina was chosen because it is inexpensive and is easily impregnated with platinum, tin, nickel and cobalt to maintain a high metal dispersion.

4.1 Characterization of Catalysts

Plots of x-ray fluorescence data of alumina and catalysts are shown in Figures A1, A2, A3, A4 and A5. Alumina showed peaks characteristic of aluminium, iron, calcium, titanium, palladium and silver. The Pt/F on alumina showed peaks characteristic of aluminium, platinum, palladium and silver. The Pt/Sn/Cl/F on alumina catalysts showed peaks characteristic of aluminium, platinum, tin, chlorine, titanium, calcium, iron, palladium and silver. The Ni/Sn/Cl/F on alumina catalysts showed peaks characteristic of aluminium, nickel, tin, chlorine, iron, calcium, titanium, palladium and silver. The Co/Sn/Cl/F on alumina showed peaks characteristic of aluminium, cobalt, tin, chlorine, calcium, palladium and silver. The catalysts did not show fluorine peaks because these cannot be detected by x-ray fluorescence.

4.2 Hydrocracking process

The yield of oil products shown in Tables 4.1-4.6, indicate the optimum catalyst type and conditions for hydrocracking of used polyethylene. In this research, the hydrocracking reaction was studied as a function of processing variables, i.e. catalyst type, catalyst concentration, reaction time, temperature and hydrogen pressure. Products were identified by GC/MS. Quantitative analysis was performed by gas chromatography. The change in product as a function of the above variables allowed for the selection of suitable conditions.

4.2.1 Effect of Catalyst Types

The comparison of five catalyst types for hydrocracking of used polyethylene was performed using various catalyst types (commercial catalyst, Pt/F on Al₂O₃ catalyst, Pt/Sn/Cl/F on Al₂O₃ catalyst, Ni/Sn/Cl/F on Al₂O₃ catalyst and Co/Sn/Cl/F on Al₂O₃ catalyst), catalyst concentrations (40%wt) and operating at a temperature 400°C, under 600 psig hydrogen pressure for 12 hours. The result of GC/MS analysis and composition of products from hydrocracking of used polyethylene as a function of catalyst types, keeping other processing conditions constant are shown in Figures B1, B2 and B3 and Tables B1 and B2 respectively. Used polyethylene conversion and the composition trend as a function of above processing variables are shown in Table 4.1 and Figure 4.1 respectively.

It can be seen that products consist of C₁₀-C₂₂ hydrocarbons with C₁₀-C₁₄ found as the main components. The products of the hydrocracking reaction using Pt/Sn/Cl/F on alumina catalyst were the shortest hydrocarbon chains (branch chain and straight chain) compared

with the other catalysts. Because the product consisted of C₁₀-C₂₀ hydrocarbons.

Table 4.1 Oil product yield from hydrocracking as a function of catalyst type

Catalyst type	Oil product (%yield)
<u>Type 1</u> : Commercial catalyst	83.84
<u>Type 2</u> : Pt(0.3%)/F(0.5%)	0.00
<u>Type 3</u> : Pt(0.3%)/Sn(0.15%)/Cl(1.21%)/F(0.5 %)	90.78
<u>Type 4</u> : Ni(5%)/Sn(0.15%)/Cl(1.21%)/F(0.5 %)	21.20
<u>Type 5</u> : Ni(5%)/Sn(5%)/Cl(1.21%)/F(2%)	55.88
<u>Type 6</u> : Ni(10%)/Sn(5%)/Cl(1.21%)/F(2%)	55.15
<u>Type 7</u> : Co(5%)/Sn(5%)/Cl(1.21%)/F(2%)	40.19

As seen in table 4.1, the Pt/F on Al₂O₃ catalyst was not active but the Pt/Sn/Cl/F on Al₂O₃ catalyst was very active. Because tin and chloride increased the activity of the acidic function which were the high cracking activity for hydrocracking reaction. Platinum is more effective for the hydrogenative stabilization of free radical fragments than nickel and cobalt. Therefore, the product of hydrocracking reaction using Ni/Sn/Cl/F on Al₂O₃ and Co/Sn/Cl//F on Al₂O₃ had less percentage yield than the product of hydrocracking reaction using Pt/Sn/Cl/F. From these reasons, the optimum catalyst type was Pt/Sn/Cl/F on Al₂O₃ catalyst. The best percentage yield was 90.78 %.

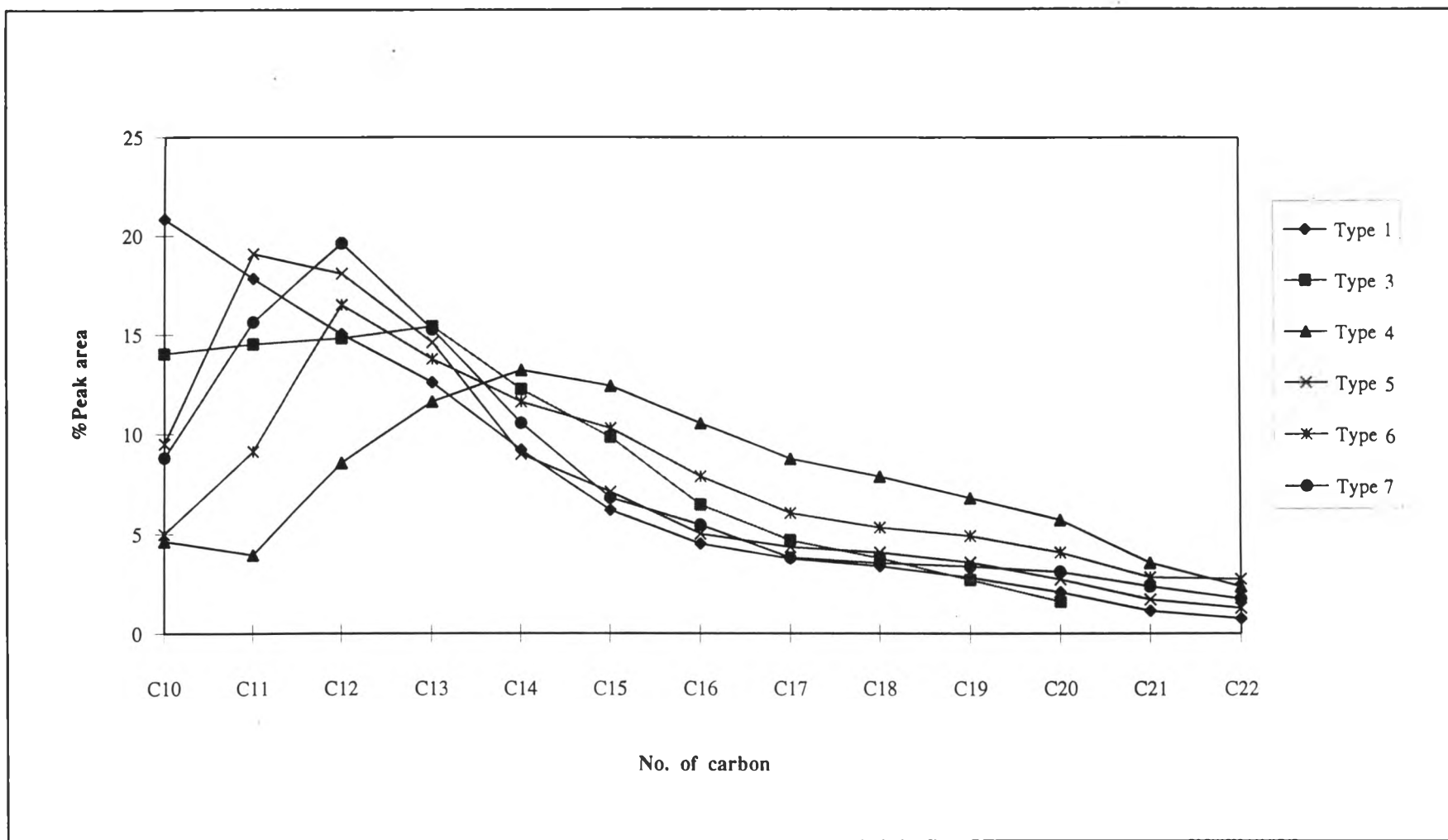


Figure 4.1 Composition trend of product from hydrocracking as a function of catalyst type

4.2.2 Effect of composition of Pt/Sn/Cl/F on alumina catalyst

The effect of composition of the Pt/Sn/Cl/F on Al_2O_3 catalyst was studied by varying %component of this catalyst; Pt(0.3%)/Sn(0.15%)/Cl(1.21%)/F(0.5%) catalyst, Pt(0.3%)/Sn(0.15%)/Cl(1.21%)/F(2%) catalyst, Pt(0.3%)/Sn(0.3%)/Cl(1.21%)/F(0.5%) catalyst, Pt(0.6%)/Sn(0.15%)/Cl(1.21%)/F(0.5%) catalyst. The reaction was operated at 400°C , under 600 psig hydrogen pressure for 12 hours and 35%wt catalyst concentration. The percentage of chlorine was not varied because chlorine acts as a promoter in the same fashion as fluorine but fluorine has stronger acid sites than chlorine. Therefore, this investigation was done on percent of fluorine. The GC/MS chromatogram and composition of products from hydrocracking as a function of the composition of the Pt/Sn/Cl/F catalyst, under the same conditions are shown in Figures B4, B5 and Tables B3, B4 respectively. Used polyethylene conversion and the composition trend as a function of above processing condition are shown in Table 4.2 and Figure 4.2.

The composition of the products was found to be $\text{C}_{10}\text{-C}_{23}$ hydrocarbons with $\text{C}_{10}\text{-C}_{15}$ as the main components. It was observed that hydrocracking using Pt(0.6%)/Sn(0.15%)/Cl(1.21%)/F(0.5%) on alumina catalyst had a beneficial effect on increasing the yield of lower molecular weight components because the product consisted of $\text{C}_{10}\text{-C}_{21}$ hydrocarbons. The results in Table B3 showed that the product from the hydrocracking reaction performed using Pt(0.6%)/Sn(0.15%)/Cl(1.21%)/F(0.5%) catalyst had more branched chain hydrocarbons than those obtained from other catalysts. In Table 4.2, it could be seen that increasing the fluorine and tin content had no effect on the hydrocracking process of used polyethylene. But increasing the platinum content had more effect on the hydrocracking process because platinum catalysts are the most active in hydrogenation-dehydrogenation reaction. So the Pt(0.6%)/Sn(0.15%)/Cl(1.21%)/F(0.5%)

on Al_2O_3 catalyst was considered to be the best. The best percentage yield was 67.22 %wt.

Table 4.2 Oil product yield from hydrocracking of used polyethylene as a function of composition of catalyst

Catalyst	Oil product (%yield)
Component A: Pt(0.3%)/Sn(0.15%)/Cl(1.21%)/F(0.5%)	55.12
Component B: Pt(0.3%)/Sn(0.15%)/Cl(1.21%)/F(2%)	54.09
Component C: Pt(0.3%)/Sn(0.3%)/Cl(1.21%)/F(0.5%)	56.87
Component D: Pt(0.6%)/Sn(0.15%)/Cl(1.21%)/F(0.5%)	67.22

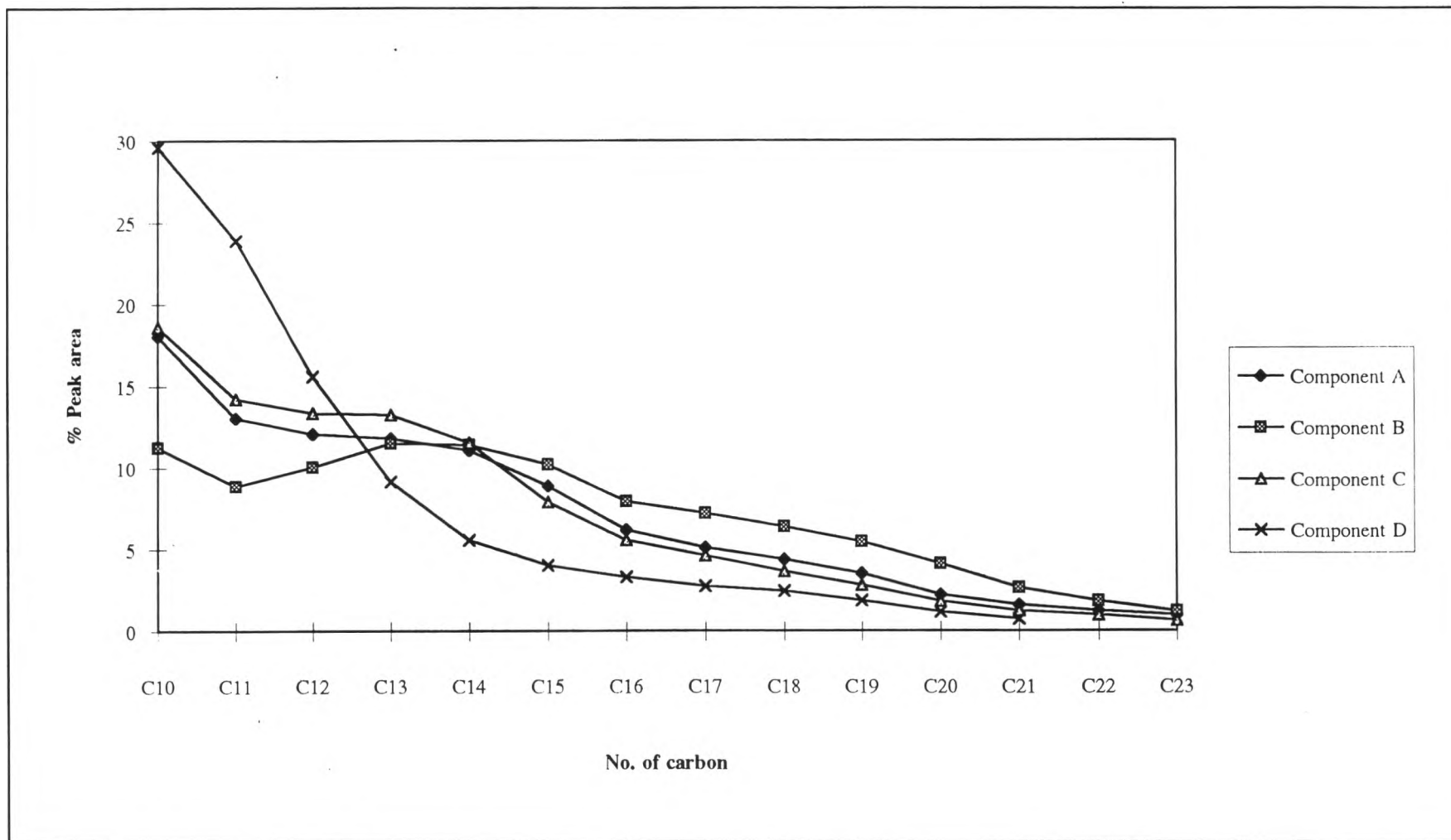


Figure 4.2 Composition trend of product from hydrocracking as a function of %component of Pt/Sn/Cl/F catalyst

4.2.3 Effect of Catalyst Concentration

The study of catalyst concentration was performed by varying catalyst concentration at 30, 35 and 40 %wt. The catalyst used in this study was Pt(0.6%)/Sn(0.15%)/Cl(1.21%)/F(0.5%) on Al₂O₃ with the operating conditions at 400°C, 600 psig hydrogen pressure, 12 hours. The result of GC/MS analysis and composition of the products from the hydrocracking of used polyethylene as a function of catalyst concentration under the same processing conditions are shown in Figures B6, B7 and Tables B5, B6. Used polyethylene conversion and the composition trend as a function of the above processing variables are shown in Table 4.3 and Figure 4.3.

It can be seen that the products from hydrocracking performed with 30 and 35 %wt consisted of C₁₀-C₂₁ hydrocarbons with C₁₀-C₁₂ as the main components. The composition of products from hydrocracking performed with 40 %wt catalyst were C₁₀-C₁₆ hydrocarbons. In Figure 4.3 Increasing catalyst concentration had a beneficial effect on decreasing number of carbon of hydrocracking product. As seen in Table 4.3, the catalyst concentration in the range of 30-40%wt was satisfactory and the catalyst concentration in the vicinity of 40%wt could be considered optimal. Because it was found to give the highest hydrocracking product yield and the shortest hydrocarbon chains. The best percentage yield was 94.8 %wt.

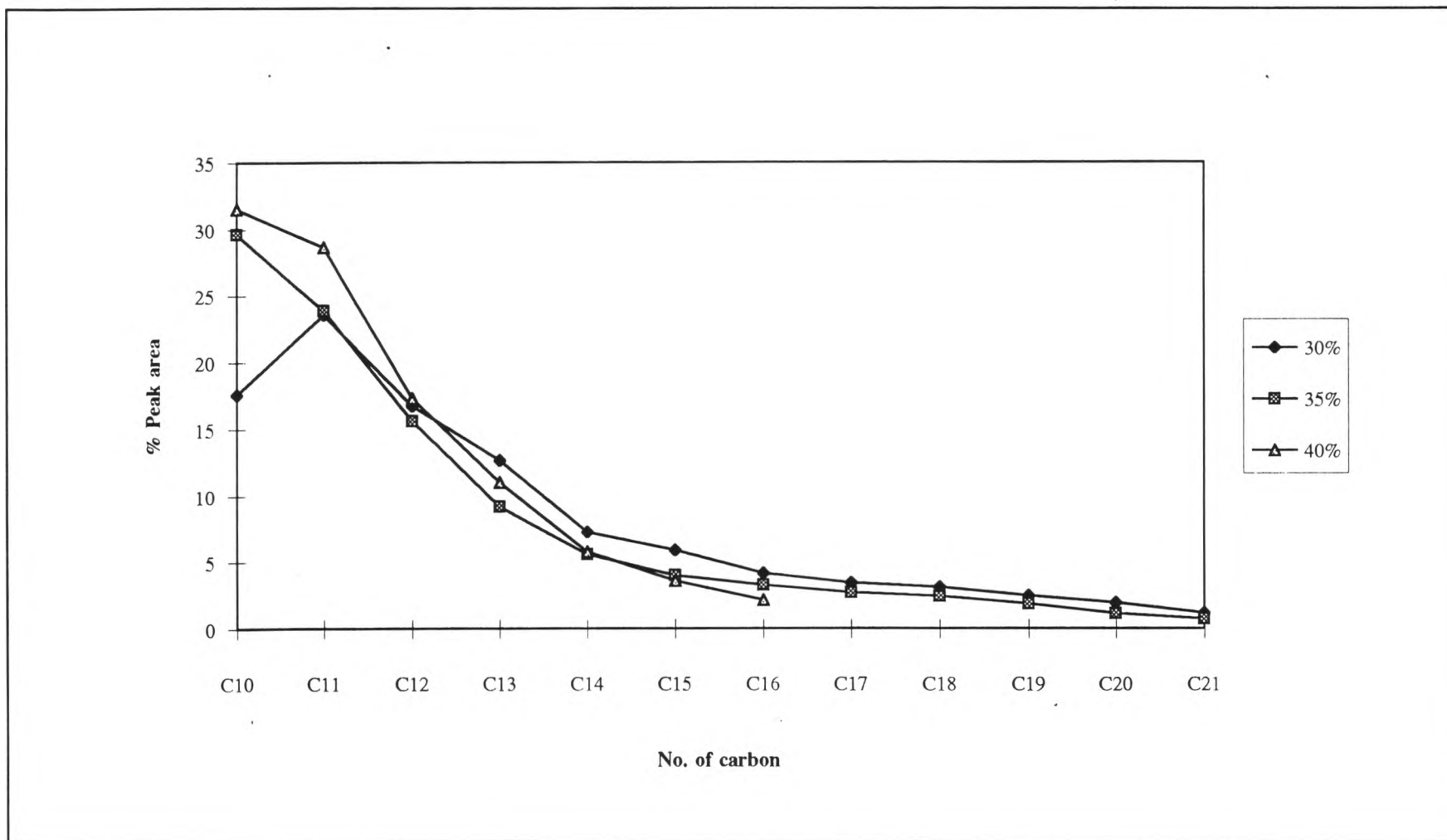


Figure 4.3 Composition trend of product from hydrocracking as a function of catalyst concentration

Table 4.3 Oil product yield from hydrocracking as a function of catalyst concentration

Catalyst concentration (%wt)	Oil product (%yield)
30	33.9
35	67.2
40	94.8

4.2.4 Effect of Reaction Time

The study of the effect of reaction time was performed by varying reaction time at 4, 8, 10 and 12 hours under the operating conditions of 400°C, over 40%wt of the Pt(0.6%)/Sn(0.15%)/Cl(1.21%)/F(0.5%) on Al₂O₃ catalyst (the optimum catalyst concentration and catalyst type) under 600 psig hydrogen pressure. The GC/MS chromatogram and composition of products from hydrocracking as a function of reaction time, using an otherwise identical set of reaction condition are shown in Figures B8, B9 and Tables B7, B8 respectively. Used polyethylene and the composition trend as a function of above processing variables are shown in Table 4.4 and Figure 4.4

The result showed that the composition of products (reaction time 8-10 hours) were C₁₀-C₂₀ hydrocarbons with C₁₀-C₁₄ as the main components. The composition of product from hydrocracking for 4 hours was C₁₀-C₂₄ hydrocarbons with C₁₂-C₁₆ as the main components. The composition of product from hydrocracking for 12 hours were C₁₀-C₁₆

hydrocarbon. Increasing reaction time had a beneficial effect on decreasing number of carbon of hydrocracking product. Therefore, the suitable reaction time at the optimum processing condition was 12 hours. Because it was found to give the highest product yield and the lowest molecular weight of hydrocarbon. The best percentage yield was 94.8 %wt.

Table 4.4 Oil product yield from hydrocracking as a function of reaction time

Reaction time (hours)	Oil product (%yield)
4	50.8
8	66.9
10	81.8
12	94.8

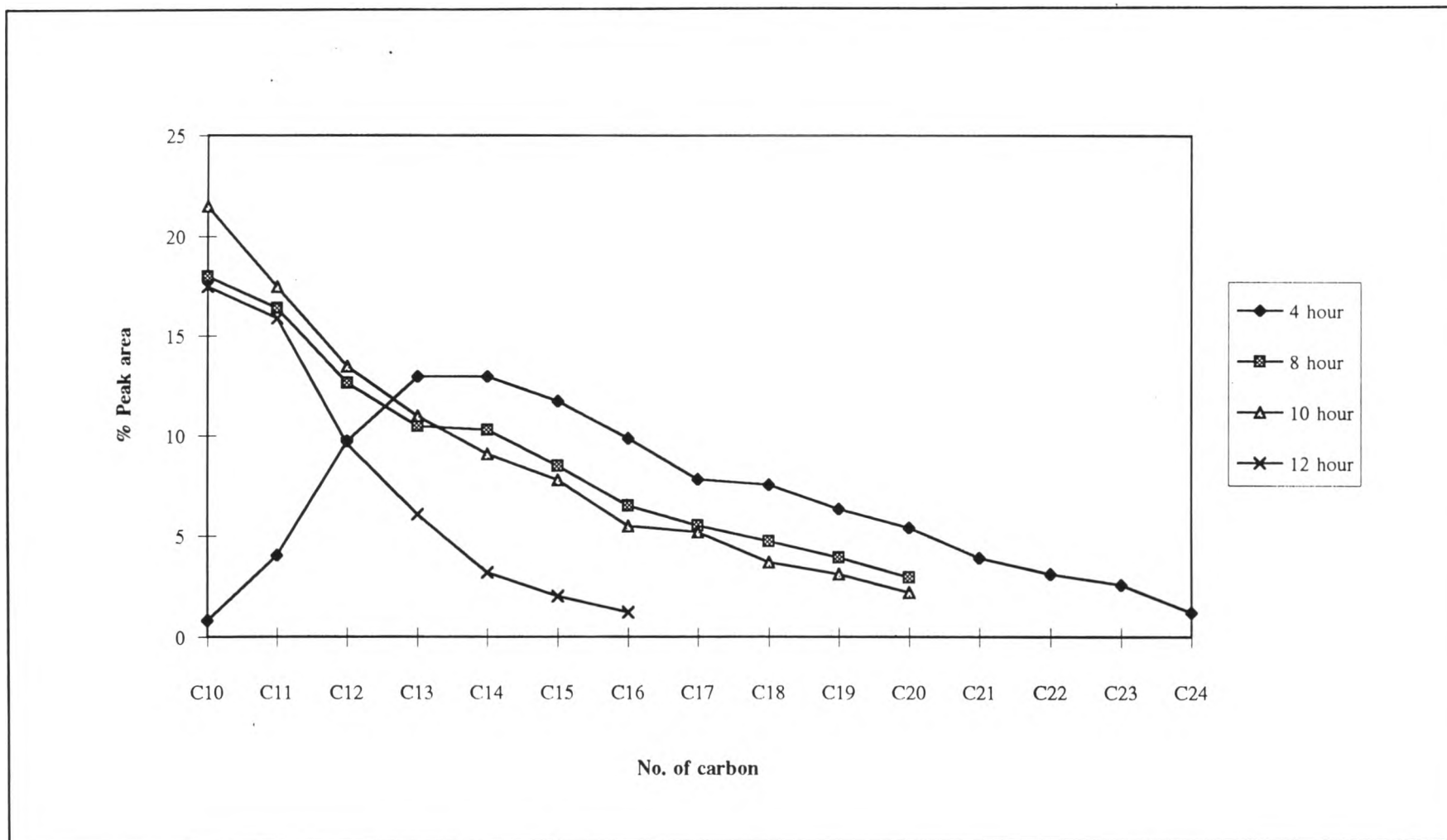


Figure 4.4 Composition trend of product from hydrocracking as a function of reaction time

4.2.5 Effect of Temperature

The study of the effect of temperature on the hydrocracking of used polyethylene was performed by operating at various reaction temperatures: 300, 350 and 400°C, using 40%wt of the Pt(0.6%)/Sn(0.15%)/Cl(1.21%)/F(0.5%) on Al₂O₃ catalyst under 600 psig of hydrogen pressure and the optimum reaction time (12 hours). The GC/MS chromatograms and composition of products from hydrocracking as a function of temperature, are shown in Figure B10 and Tables B9, B10 respectively. Used polyethylene conversion and composition as a function of temperature are shown in Table 4.5 and Figure 4.5

The composition of product from hydrocracking operated at 350°C was C₁₀-C₂₃ hydrocarbons with C₁₀-C₁₅ as the main components. The composition of product from hydrocracking operated at 400°C was C₁₀-C₁₆ hydrocarbon. Increasing temperature had a beneficial effect on increasing the yield of lower molecular weight component (C₁₀-C₁₂) and decreasing the number of carbon of hydrocracking product. The hydrocracking reaction could not occur at 300°C. A temperature of 400°C was found to be optimal. The best percentage yield was 94.8 %wt.

Table 4.5 Oil product yield from hydrocracking as a function of reaction temperature

Temperature (°C)	Oil product (%yield)
300	0.0
350	24.1
400	94.8

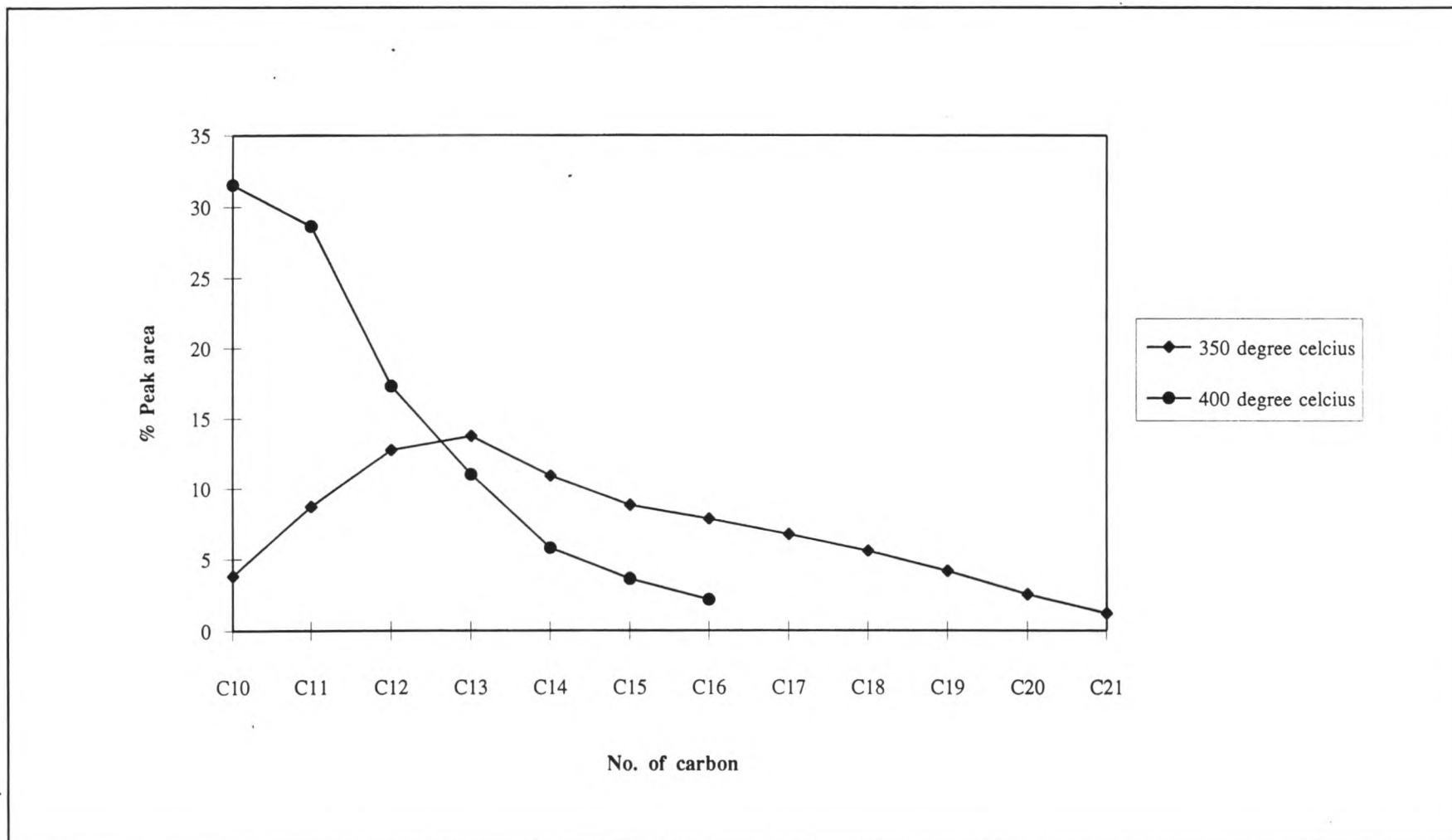


Figure 4.5 Composition trend of product from hydrocracking as a function of reaction temperature

4.2.6 Effect of Hydrogen Pressure

The study of the effect of hydrogen pressure was performed by varying hydrogen pressures, 400, 500 and 600 psig, at 400°C (the optimum reaction temperature), for 12 hours (the optimum reaction time) over 40%wt of the Pt(0.6%) / Sn(0.15%) / Cl(1.21%) / F(0.5%) on Al₂O₃ catalyst. The GC/MS chromatogram and composition of products from hydrocracking are shown in Figure B11 and Tables B11, B12 respectively. Used polyethylene conversion and the composition trend as a function of above processing valuables are shown in Table 4.6 and Figure 4.6

The product composition changed with changes in hydrogen pressure. The composition of products from hydrocracking operated at 500 psig consisted of C₁₀-C₂₁ hydrocarbons and C₁₀-C₁₄ were the main components. The composition of product from hydrocracking operated at 600 psig was C₁₀-C₁₆ hydrocarbons. In Figure 4.6, increasing the hydrogen pressure had a beneficial effect on decreasing the number of carbon of hydrocracking product. However, as seen in Table 4.6 the hydrogen pressure range of 400-600 psig was satisfactory. The hydrocracking reaction could not occur at 400 psig. In conclusion, the optimum hydrogen pressure was 600 psig. The best percentage yield was 94.8 % wt.

To study reproducibility of the reaction, the optimum condition was chosen. The percentage yields of the product for three experiments were 94.8, 93.2, 94.5%. No significant difference in product yields were found. It can be said that the results can be assumed that the reactions should be reproducible at any conditions.

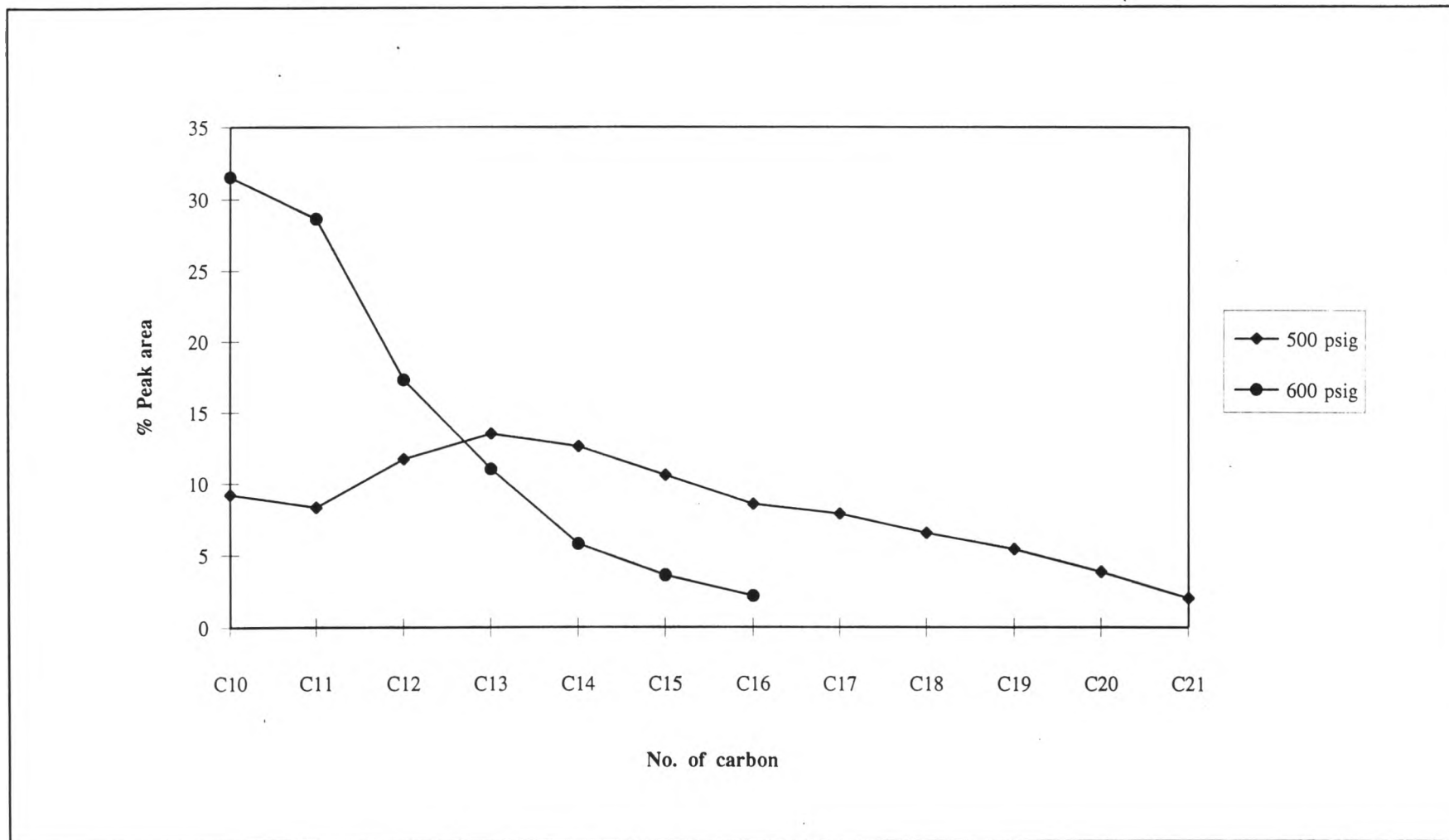


Figure 4.6 Composition trend of product from hydrocracking as a function of hydrogen pressure

Table 4.6 Oil product yield from hydrocracking as a function of hydrogen pressure

Hydrogen pressure (psig)	Oil product (%yield)
400	0.0
500	11.2
600	94.8

4.3 Determination of product properties

4.3.1 Spectroscopic properties

The ^{13}C NMR spectrum of the products from the optimum condition is shown in Figure B12. It indicates aliphatic carbons at 10-40 ppm. None of the olefinic and aromatic carbons were observed.

4.3.2 Physical properties

The physical properties of the product obtained under the optimum conditions are shown in Table 4.7. It is clear that the liquid hydrocarbon obtained could be used as gasoline base.

Table 4.7 Properties of optimum condition product

Properties	Method	Product	Gasoline base
API Gravity @ 60 °F	ASTM D 1298	51.3	59.3
Specific Gravity @ 60 / 60 °F	ASTM D 1298	0.7741	-
Color	ASTM D 1500	1.0	0.5-1.0
Distillation, °C	ASTM D 86	172	max. 200
Lead Content, g/l	ASTM D 3116	0.00	max. 0.013
Sulfur Content, %wt	ASTM D 129	0.00	-
Pour Point, °C	ASTM D 97	-24	-

On comparing the properties of the product with the specifications of base gasoline, it could be seen that the advantages of product are the absence of sulfur and lead which would cause air pollution.