CHAPTER IV

RESULT AND DISCUSSION

Iron, Cobalt and Nickel with tin and fluoride were impregnated on Al_2O_3 or molecular sieve to be catalysts for depolymerization of used PP from battery cases into fuel oil in high yield by hydrocracking. Tin and fluoride were impregnated with the metal to increase the conversion and decrease the amount of coke. The Al_2O_3 and molecular sieve were selected for comparison with each other because they are cheap and easily impregnated.

4.1 Characterization of the catalysts.

Characterization of the catalysts by XRFS is shown in Figures A1-A7 and Table A4.1. They confirm the impregnation of catalysts. Fluorine peaks were not detected because X-ray fluorescence cannot detect such light atoms. Normally, the catalysts should be prepared for characterization by a pelletizing powder method, but for this research they were prepared by a liquid method because there was no pelletizing powder instrument available. As a result, the errors in the amounts shown in Table A4.1 are considerable due to particle size and surface effect. However, it can be seen that the amount of the metal varies according to the amount of impregnated metal in a quantitative sense.

4.2 Hydrocracking Process

The study of hydrocracking reaction was divided into two parts, hydrocracking over Al_2O_3 supported catalyst, and hydrocracking over MS supported catalyst. The optimum conditions for both systems were obtained. Then, the optimum conditions for hydrocracking were studied for the best system as a function of processing variables. Fuel oils were characterized by GC-MS and by gas chromatography.

4.2.1 Hydrocracking Process over Alumina Catalysts

The comparison of oil product yields from hydrocracking of used PP at 360°C, 500 psig H_2 pressure over Fe(10%)-Sn(5%)-F(2%)/Al_2O_3, Co(10%)-Sn(5%)-F(2%)/Al_2O_3, Ni(5%)-Sn(5%)-F(2%)/Al_2O_3 and commercial catalyst under comparable conditions, reaction times and catalyst concentrations are shown in Figure 4.1 and Table 4.1. The optimum conditions of hydrocracking of used PP with an alumina supported catalyst were a concentration of 25-40%wt. for 6-8 hours. The best metal was nickel because the mildest conditions could be used. The yield from the nickel catalyst with a catalyst concentration of 25%wt. for 6 hours was reduced because the increased reaction times and higher catalyst concentrations cause the formation of the larger amounts of gas. On the other hand, the optimum yield from iron and cobalt catalysts were observed under more strenuous conditions: catalyst concentration of 35%wt. for 8 hours. The commercial catalyst is the least effective catalyst because the highest percentage of wax is observed, showing low efficiency in cracking.

Table 4.1 Oil product yield from Hydrocracking over Alumina catalysts

Catalyst Type	No.	Conc. (%wt.)	Time (hr.)	Yield (% wt.)		
				Oil	Wax	Total
Commercial catalyst	1	40	12	65.2	2.0	67.2
Fe(10%)-Sn(5%)-F(2%)	1	25	6	55.5	34.2	89.7
	2	30	8	82.6	1.0	83.6
	3	35	10	83.5	0.2	83.7
	4	40	12	78.3	0.0	78.3
Co(10%)-Sn(5%)-F(2%)	1	25	6	58.1	28.3	86.4
	2	30	8	80.8	0.7	81.5
	3	35	10	74.8	0.1	74.9
	4	40	12	71.6	0.0	71.6
Ni(5%)-Sn(5%)-F(2%)	1	25	6	76.5	11.5	88.0
	2	30	8	78.0	2.0	80.0
	3	35	10	72.6	0	72.6

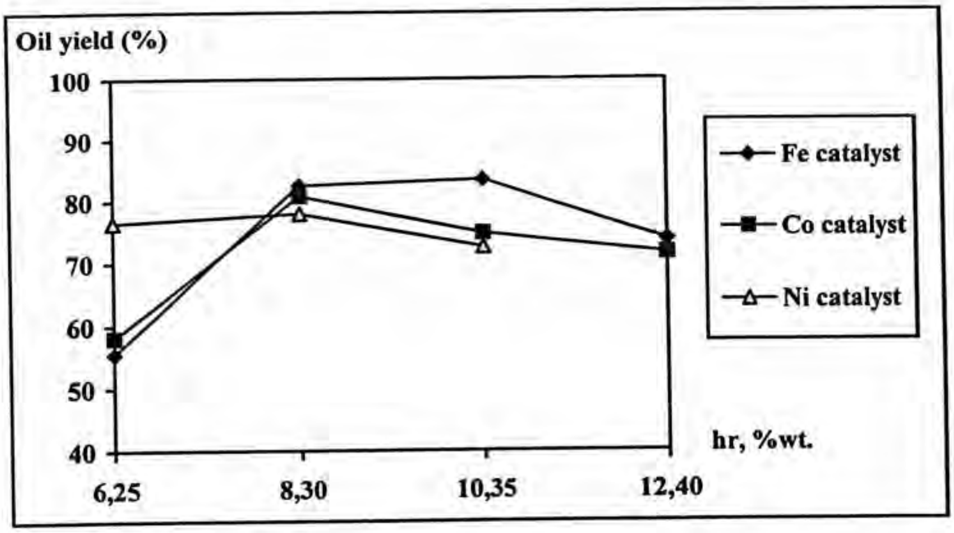


Figure 4.1 Comparison of oil product yield from hydrocracking as functions of catalyst types, catalyst concentrations and reaction time

The order of activity of catalysts was Ni(5%)-Sn(5%)-F(2%)/Al_2O_3, Co(10%)-Sn(5%)-F(2%)/Al_2O_3, Fe(10%)-Sn(5%)-F(2%)/Al_2O_3 and commercial catalyst. The GC chromatograms and the composition trend of all products except the product from commercial catalyst (on Figure B1-B3 and Figure 4.2) showed that the compositions are not different and all products consisted of many isomers of C_8-C_{20} hydrocarbons with C_8-C_{10} hydrocarbons found as the main components. As many isomers of hydrocarbons were present, many of them could not be detected and thus the precise MWD could not be calculated. The GC chromatogram of the product from commercial catalyst (Figure B1) showed higher selectivity and gave fewer components than the other catalysts. However, the efficiency of commercial catalyst is less than the prepared catalyst as seen from the amount of wax (2%wt.)

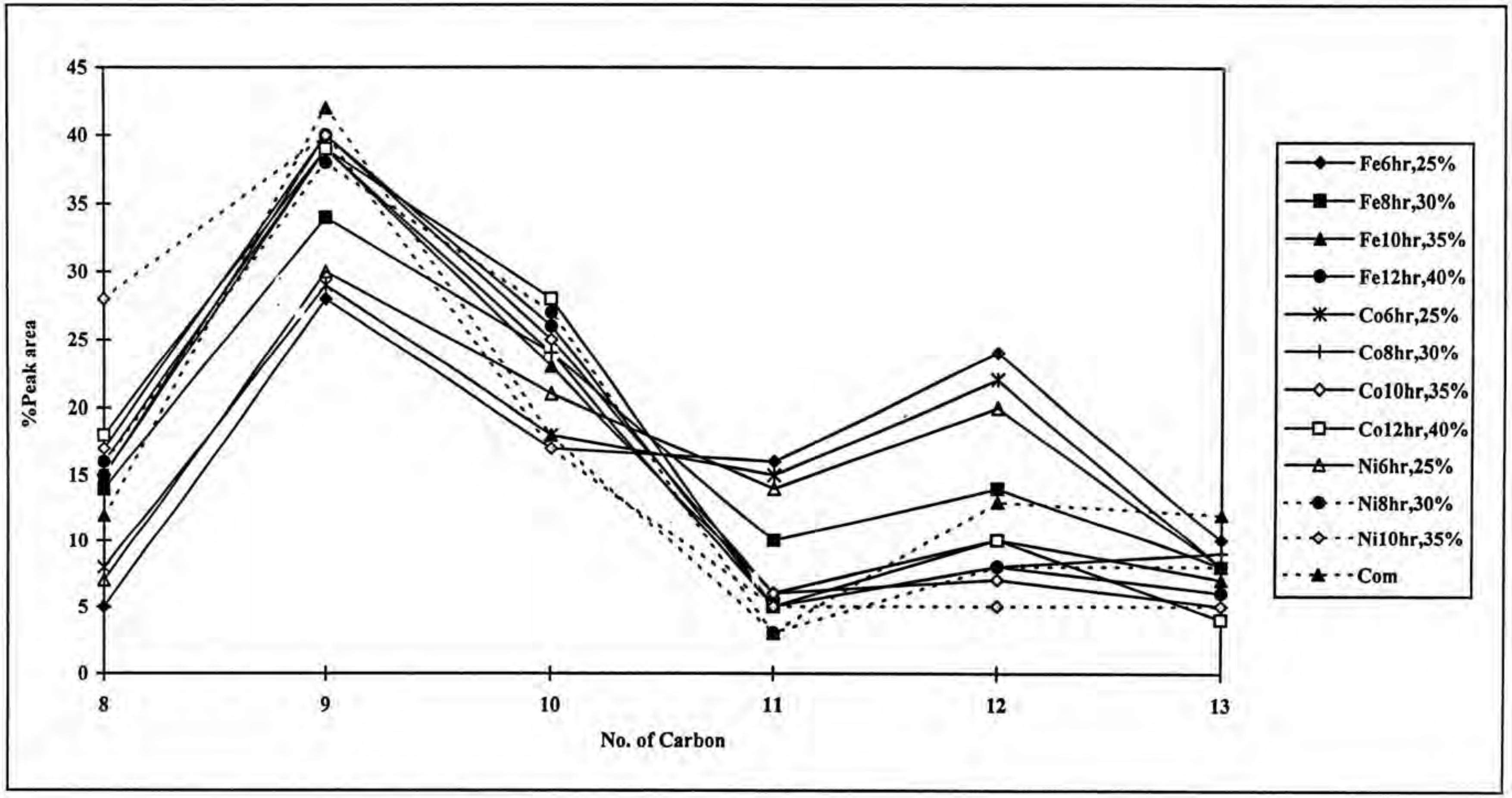


Figure 4.2 Composition trend of oil product from hydrocracking over alumina catalysts

4.2.2 Hydrocracking Process over Molecular Sieve Catalysts

To find a suitable hydrocracking catalyst, Fe(5%)-Sn(5%)-F(2%) Co(5%)-Sn(5%)-F(2%), Ni(5%)-Sn(5%)-F(2%) on Molecular sieve type 4A were employed to crack the used PP under fixed conditions of temperature, 360°C, hydrogen pressure, 500 psig, reaction time, 6 hours, catalyst concentration, 40%wt. of used PP, and agitation speed, 500 rpm. in a stirred autoclave to obtain the oil fraction and wax fraction.

It was found that Ni(5%)-Sn(5%)-F(2%)/MS was the best catalyst followed by Co(5%)-Sn(5%)-F(2%)/MS and Fe(5%)-Sn(5%)-F(2%)/MS. (Figure 4.3)

From the GC chromatograms and the composition trend (Figure B4 and Figure 4.4) of the oil products, it was found that the components were similar but the nickel catalyst gave the highest proportions of main components (C_8-C_{10} hydrocarbons) than the other catalysts while the iron catalyst gave the highest proportion of C_{11}-C_{15} hydrocarbons.

Therefore, the nickel catalyst was chosen to study the effect of variation of doping of the element on molecular sieve. The catalysts used were ; Ni(5%)-Sn(5%)-F(2%)/MS, Ni(2.5%)-Sn(5%)-F(2%)/MS, Ni(5%)-Sn(2.5%)-F(2%)/MS and Ni(5%)-Sn(5%)-F(1%)/MS under the above conditions. Comparison of the oil yields using these catalysts (Figure 4.3) showed the significance of the tin component. With nickel catalysts, the oil yield is high except when the lower amount of tin was used. Because SnF_2 and SnF_4 are lewis acids that act as a promoter in the cracking and the isomerization by inducing H^- and releasing H^+ to the surrounding. Similarly the effect of tin component, fluoride component complexing with aluminium enhances the Lewis acid of alumina as a result of the high potential of electronegativity of fluoride so the reduction of the amount of fluoride component reduces the catalyst efficiency.

The characterisation of the oil products (Figure B5 and Figure 4.4) showed that the compositions of the products of all experiments were similar with C_8-C_{10} as the main components, except the composition from the Ni(5%)-Sn(2.5%)-F(2%)/MS catalyst. In this case, high molecular weight (C_{12} and C_{15}) species were the main components consistent with the observation that reducing the amount of tin reduces the catalyst efficiency.

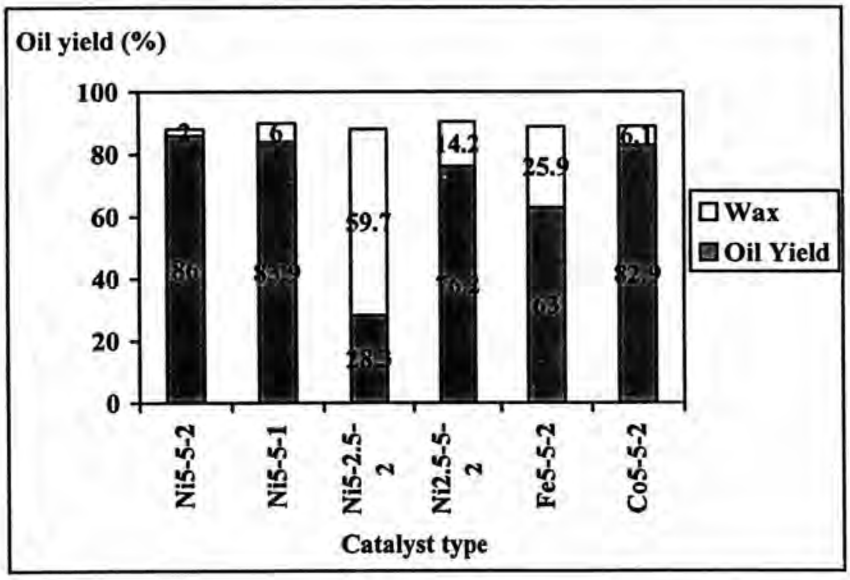


Figure 4.3 Comparison of oil yield from hydrocracking as functions of catalyst types and element compositions on molecular sieve

Ni5-5-2 = Ni(5%)-Sn(5%)-F(2%)/MS
Ni5-5-1 = Ni(5%)-Sn(5%)-F(1%)/MS
Ni5-2.5-2 = Ni(5%)-Sn(2.5%)-F(2%)/MS
Ni2.5-5-2 = Ni(2.5%)-Sn(5%)-F(2%)/MS
Fe5-5-2 = Fe(5%)-Sn(5%)-F(2%)/MS
Co5-5-2 = Co(5%)-Sn(5%)-F(2%)/MS

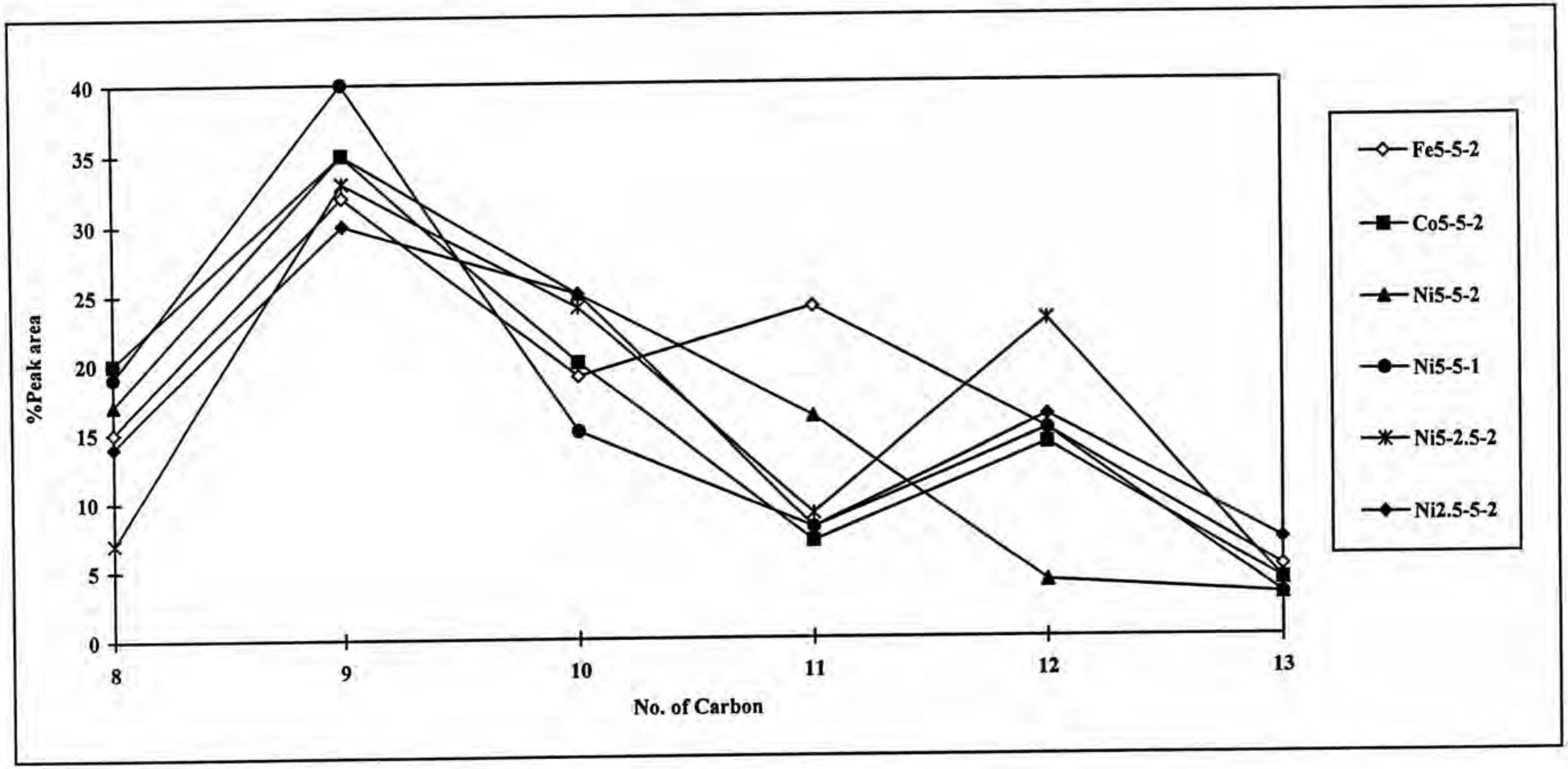


Figure 4.4 Composition trend of oil product from hydrocracking as functions of catalyst types and element compositions on molecular sieve

After the Ni(5%)-Sn(5%)-F(2%)/MS catalyst had been chosen, the optimum conditions for this catalyst were determined by varying the operating parameters : reaction time, catalyst concentration, hydrogen pressure and reaction temperature. The reaction time was the first parameter studied,operating at 360°C, a hydrogen pressure of 500 psig and a catalyst concentration 40%wt. The reaction times were at 3, 5, 6 and 12 hours.

Highest oil yield (86.0%wt.) was obtained with a reaction time of 6 hours (Figure 4.5). The yield decreased with a reaction time of 12 hours. The GC chromatograms and the composition trend (Figure B6 and Figure 4.6) show the increase of main component (C_8-C_{10} hydrocarbons) when the reaction time was increased. Thus, the optimum reaction time in this experiment was 6 hours.

Similar results were obtained using Fe(5%)-Sn(5%)-F(2%)/MS, (Figure 4.5, 4.6 and Figure B9), but the yields were consistently lower.

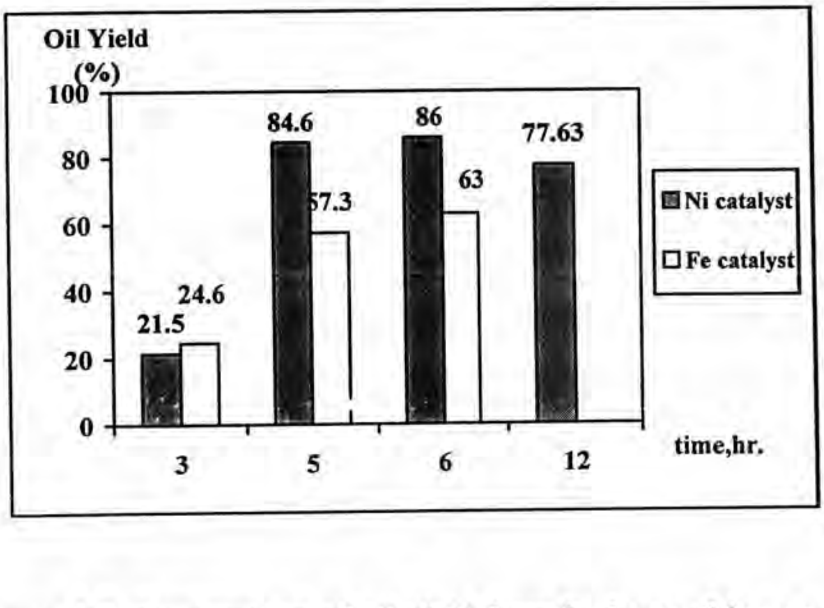
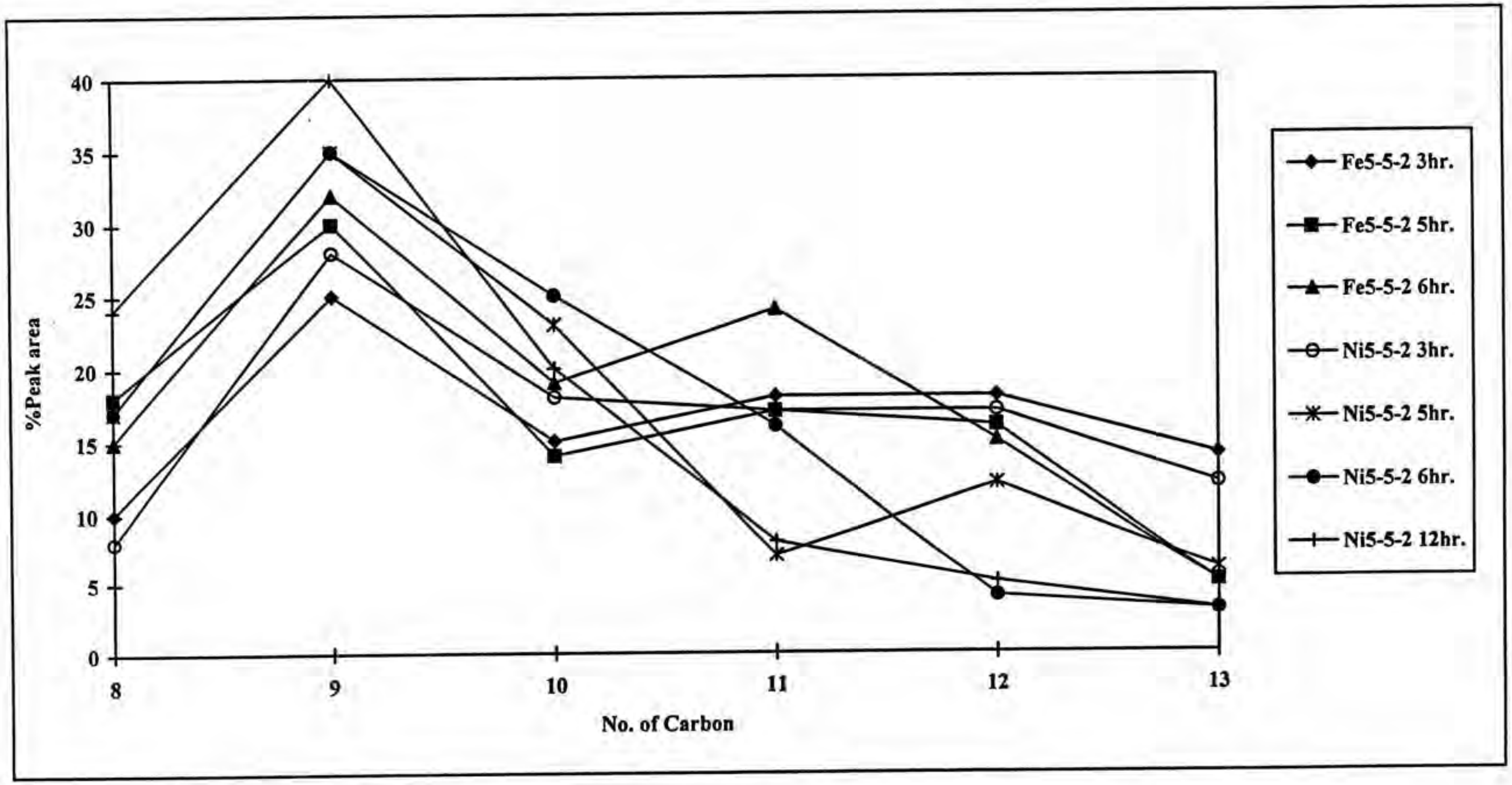


Figure 4.5 Comparison of oil yield from hydrocracking as a function of reaction time



<u>Figure 4.6</u> Composition trend of oil product over Ni(5%)-Sn(5%)-F(2%)/MS and Fe(5%)-Sn(5%)-F(2%)MS catalyst as a function of reaction time

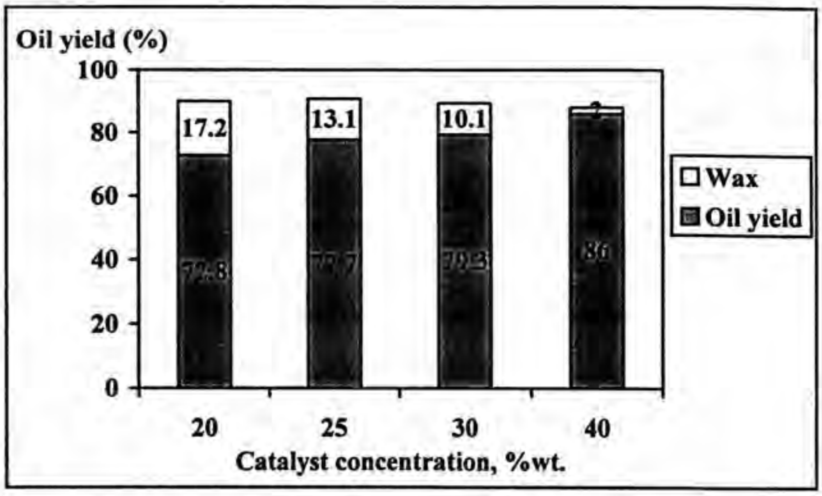
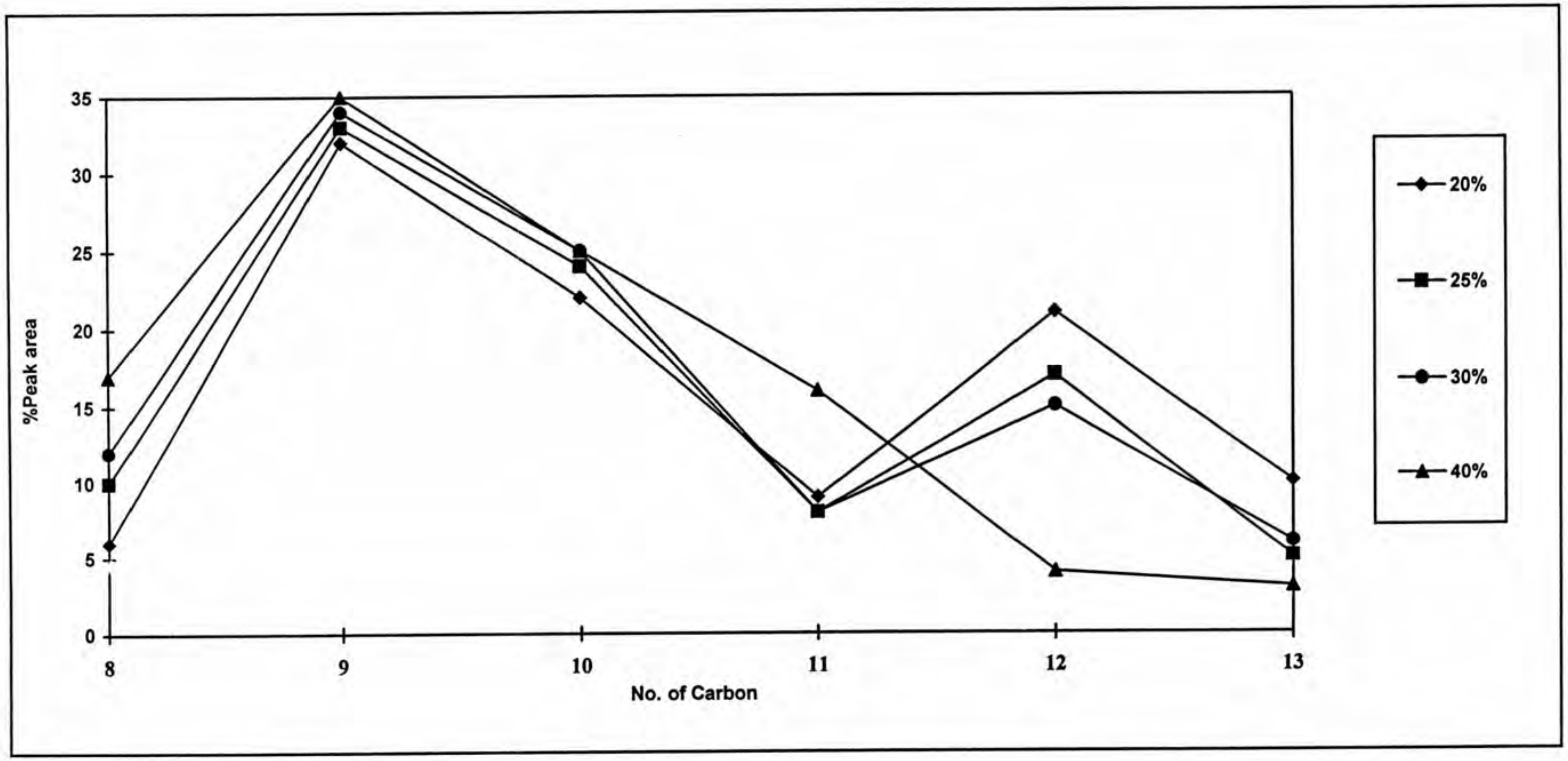


Figure 4.7 Comparison of oil yield from hydrocracking as a function of catalyst concentration

Considering the other parameters, a suitable catalyst concentration was sought. The catalyst concentration of Ni(5%)-Sn(5%)-F(2%)/MS was varied between 20, 25, 30 and 40%wt. at the optimum reaction time of 6 hours, a hydrogen pressure of 500 psig and a temperature of 360°C. The product yields, the GC chromatograms and the composition trend are shown in Figure 4.7, Figure B7 and Figure 4.8.

The oil yield varied according to the catalyst concentration. The highest oil yield was obtained from a catalyst concentration 40%wt.. The oil products from hydrocracking performed consisted of C_8-C_{16} hydrocarbons with C_8-C_{10} hydrocarbons as the main components. The best percentage yield (86.0%) and the highest composition of main components were obtained using 40%wt., the catalyst concentration 40%wt. can be considered optimal.



<u>Figure 4.8</u> Composition trend of oil product from hydrocracking as a function of catalyst concentration

The next parameter of interest was hydrogen pressure. It was varied between 300, 400 and 500 psig over 40%wt of Ni(2.5%)-Sn(5%)-F(2%)/MS at the optimum reaction time (6 hours) and a temperature of 360°C. The oil yield, the GC chromatogram and the composition trend are shown in Figure 4.9, Figure B8 and Figure 4.10.

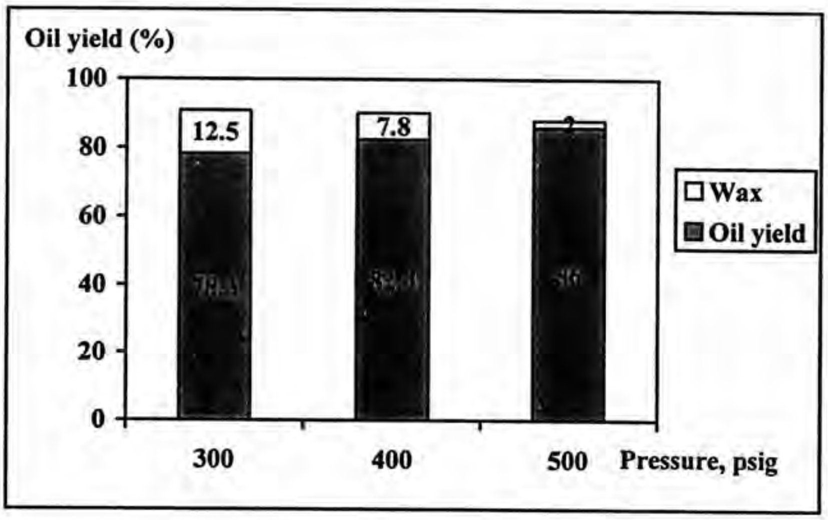


Figure 4.9 Comparison of oil yield from hydrocracking as a function of hydrogen pressure

There was no significant change in the composition of products, also consisted of C_8-C_{16} hydrocarbons with C_8-C_{10} hydrocarbons as the main components. The hydrogen pressure range at 300-500 psig was satisfactory but the optimum hydrogen pressure at 500 psig was chosen since it gives the highest oil yield.

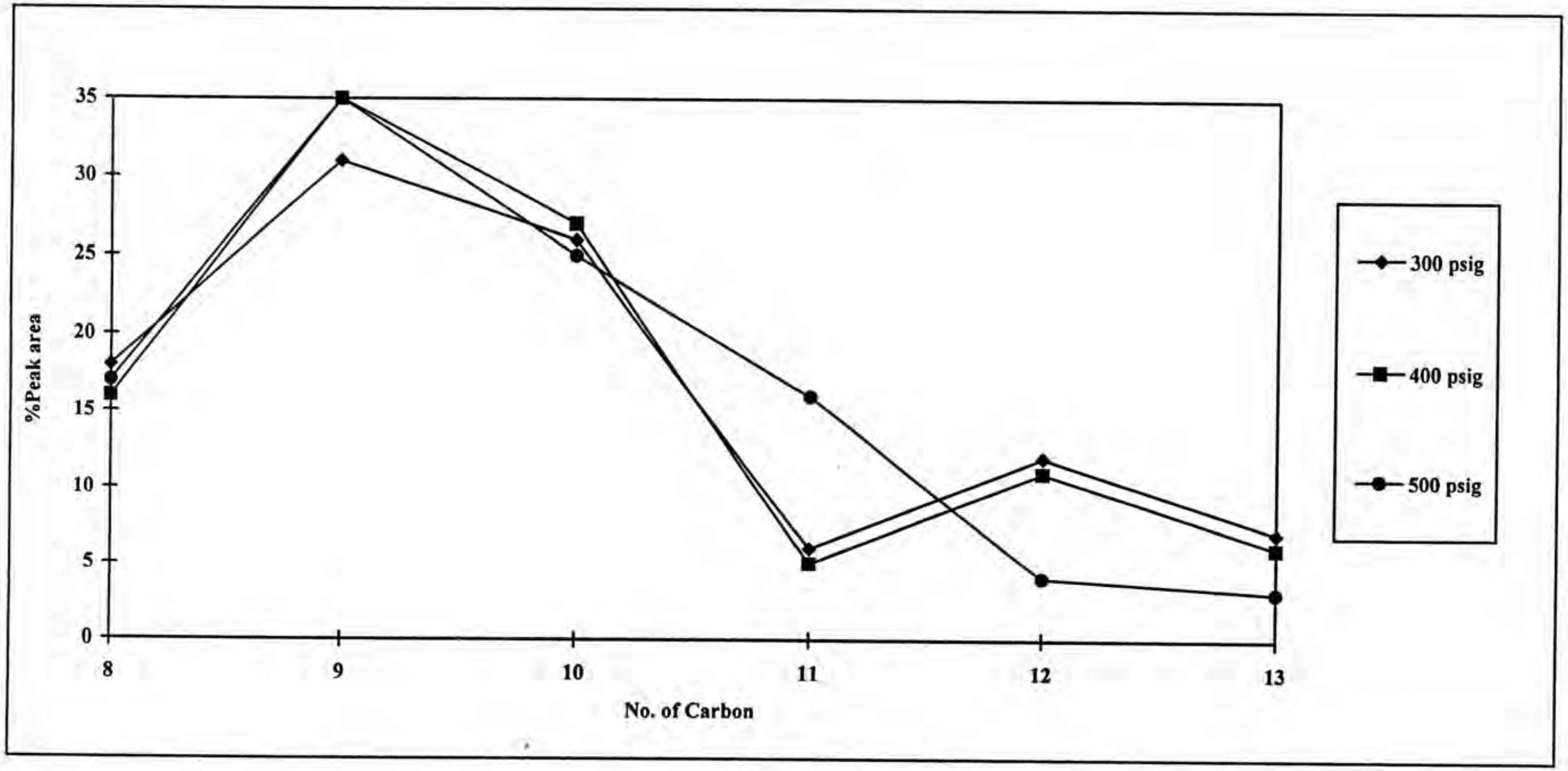


Figure 4.10 Composition trend of oil product from hydrocracking as a function of hydrogen pressure

The last variable to be studied for hydrocracking was reaction temperature. The condition of the hydrocracking reaction were constant (6 hours and 500 psig) and the reaction temperature was varied between 300, 330 and 360°C. The oil yields, the GC chromatograms and the composition trend are shown in Figure 4.11, Figure B8 and Figure 4.12.

The oil yield from hydrocracking is increased following the increase of temperature. The hydrocracking reaction did not occur at 300°C while a large increase in oil yield occurs on going from 330 to 360°C, 31.0 to 86.0%wt.. The C_8-C_{16} hydrocarbons are the main components of the oil products from both of these temperatures, with C_8-C_{10} hydrocarbons as the main components. Howere, proportion of the main components were larger at the higher temperature. A temperature of 360°C can be considered.

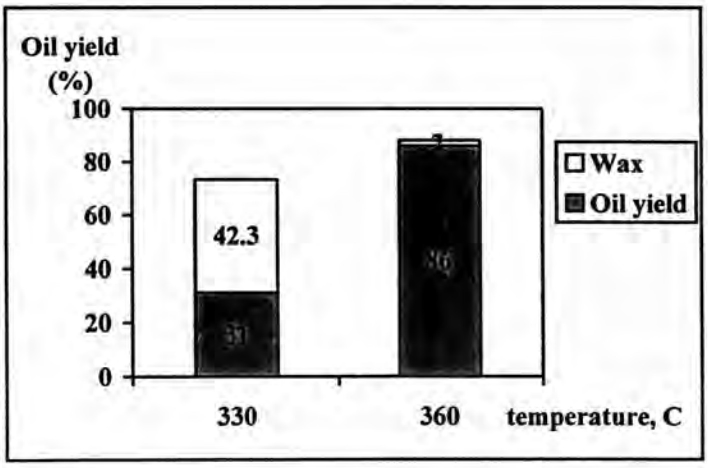


Figure 4.11 Comparison of oil yield from hydrocracking as a function of reaction temperature

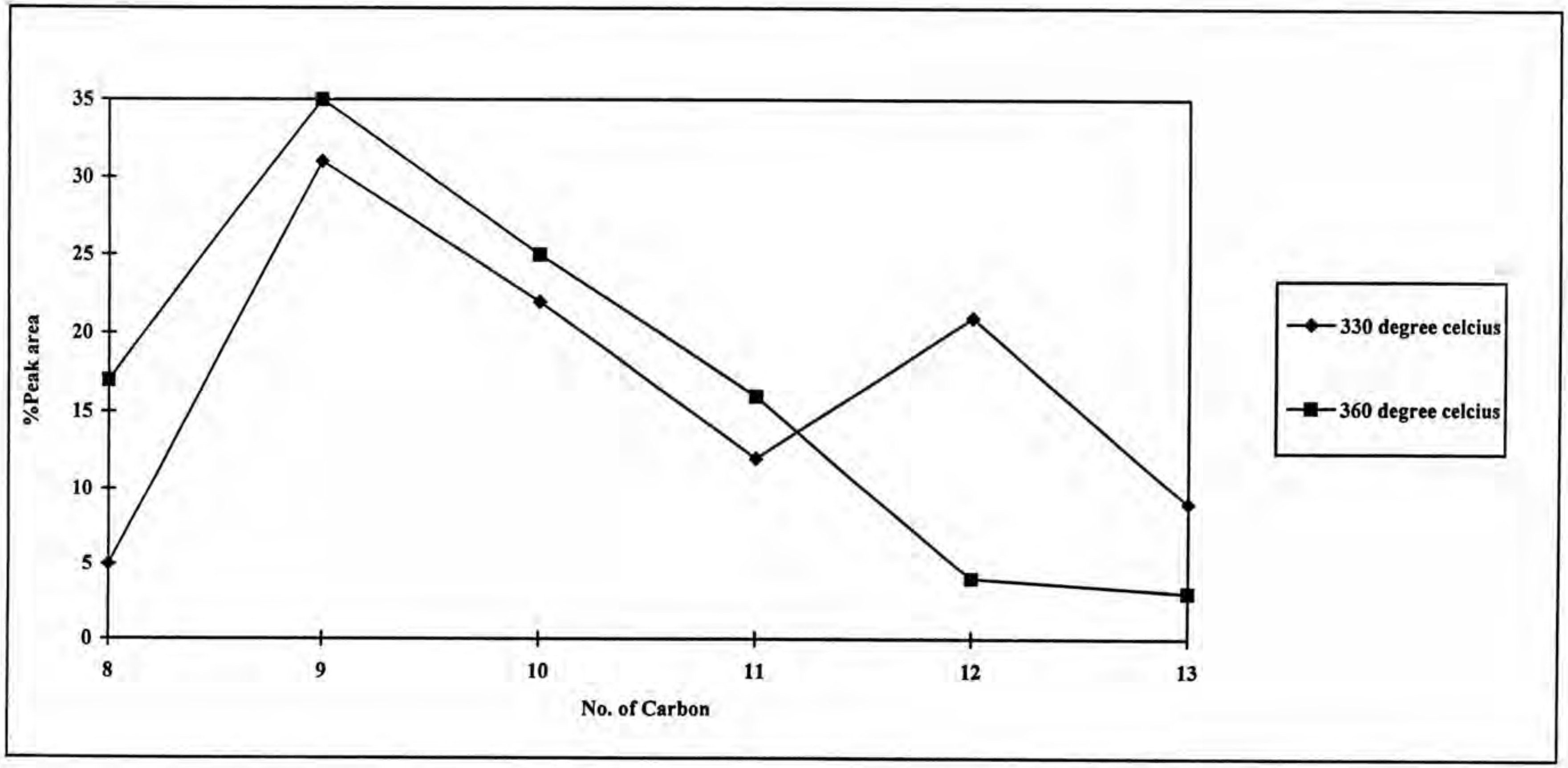


Figure 4.12 Composition trend of oil product from hydrocracking as a function of reaction temperature

Further Study of Activities of Used Catalysts

To study the activity of used catalysts, Ni(5%)-Sn(5%)-F(2%)/MS was chosen under the optimum conditions. This catalyst could be reused three times using the method in procedure 3.3.2.10. After three times, the catalyst could not used because the supports were broken. The oil yields from three experiments were 87.3, 86.2 and 81.6%wt. respectively. The GC chromatogram and the composition trend of the oil product (Figure B9 and Figure 4.13) were similar to those obtained previously. It can be concluded that the catalyst can be reused without losing efficiency for a limited number of times.

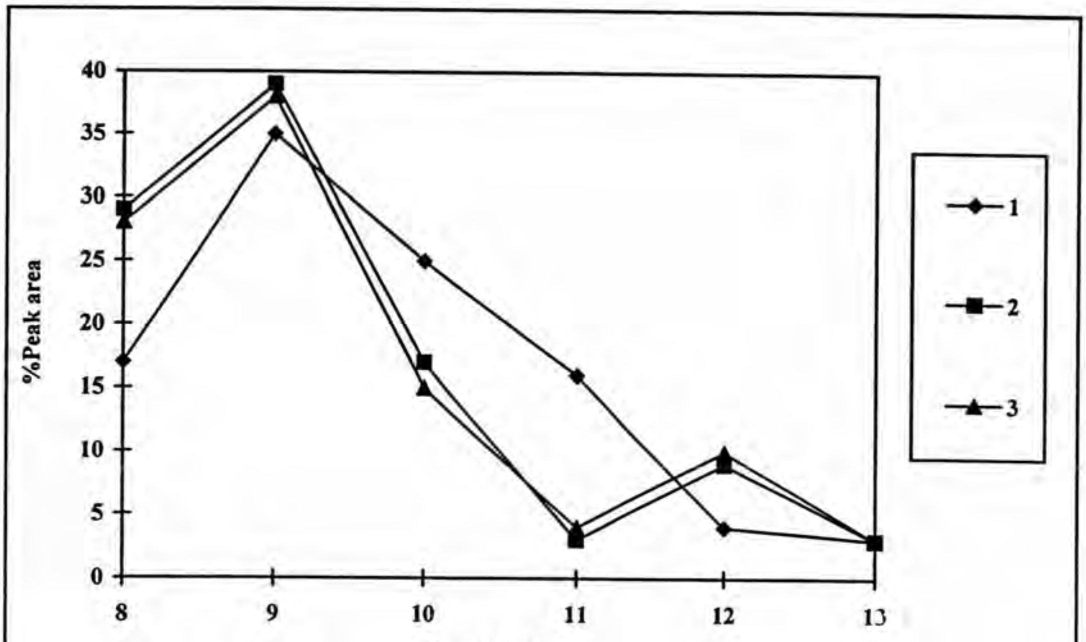


Figure 4.13 Composition trend of oil product from studying of used catalysts

Reproducibility of Hydrocracking

The reproducibility of the reaction using 40%wt. of Fe(5%)-Sn(5%)-F(2%)/MS and 40%wt. of Ni(5%)-Sn(5%)-F(2%)/MS were assessed under the optimum conditions. The oil yield with the nickel catalyst from three experiments were 84.2, 86.4 and 87.3%wt. respectively. The oil yield with the iron catalyst from two experiments were 62.8 and 63.1%wt. It can be seen that the oil yields are not outstandingly different.

The GC chromatograms and the composition trend (Figure B9,B10 and Figure 4.13) show the same compositions. From above results, it can be concluded that the reactions should be reproducible.

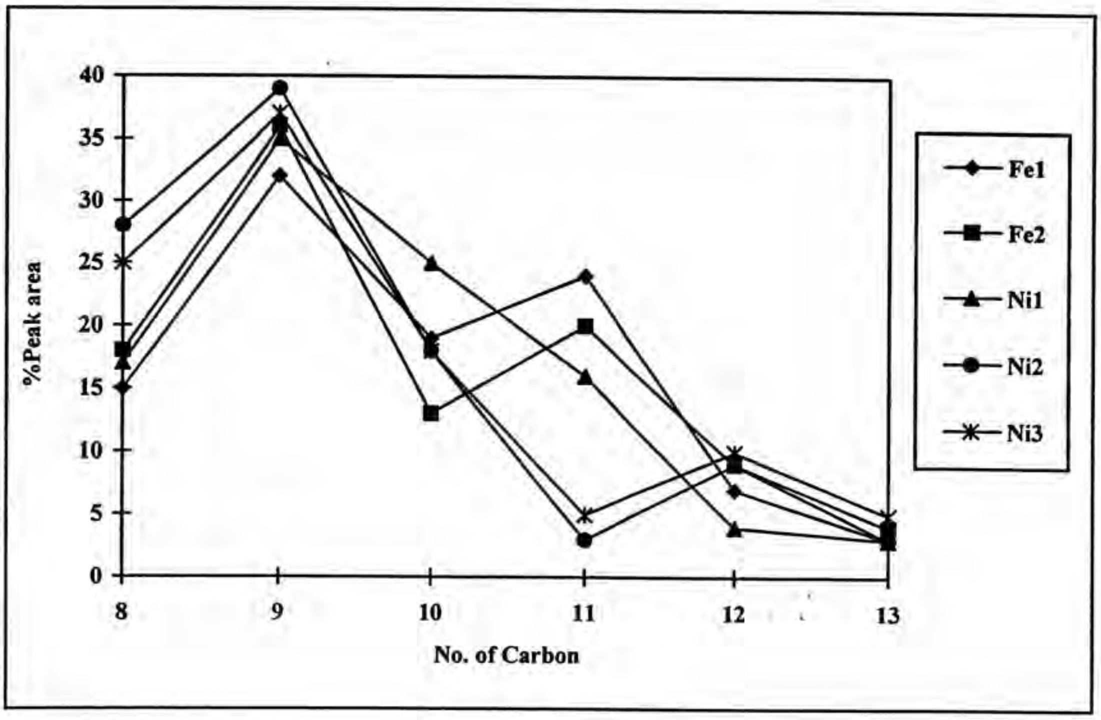


Figure 4.14 Composition trend of oil product from reproducibility of hydrocracking

4.2.3 Effect of the Type of Support on Hydrocracking

The fixed conditions for studying the hydrocracking as a function of support type were 360°C, 500 psig and 6 hours using 25%wt. of Ni(5%)-Sn(5%)-F(2%)/Al_2O_3 and 25%wt. of Ni(5%)-Sn(5%)-F(2%)/MS catalysts. The oil yield, the GC chromatogram and the composition trend are shown in Figures 4.1 and 4.7, Figure B1and B7 and Figure 4.15.

The oil yield from the alumina supported catalyst is less than the oil yield from the molecular sieve supported catalyst only by 1.8%wt. but the composition is outstandingly different. The main component of oil product from hydrocracking with the Ni(5%)-Sn(5%)-F(2%)/MS catalyst was C_8-C_{10} hydrocarbons with only traces of C_{11}-C_{16} hydrocarbons. On the other hand, the main components of the oil product from hydrocracking with the Ni(5%)-Sn(5%)-F(2%)/Al_2O_3 were also C_8-C_{10} hydrocarbons but with a larger proportion of C_{11}-C_{20} hydrocarbons.

A plausible explanation is that cracking with the alumina catalyst is random because it occurs on the surface of alumina. Cracking with the molecular sieve support is specific since the active surface is within the porous structure, and only those molecules that can diffuse through the pore can be absorbed and cracked resulting in size selectivity.

Thus, it can be concluded that the molecular sieve catalyst gives the better result of cracking, oil yield and size selectivity, than the alumina.

Besides the experimental parameters, the structure of the raw material also influences hydrocracking. Leesuksuan [13] studied the hydrocracking reaction of used polyethylene using Ni(5%)-Sn(5%)-F(2%)/Al_2O_3 and operating under severe conditions. The oil products were lower yield and consisted of higher molecular weight hydrocarbons. The cracking of polyethylene was more difficult than that of polypropylene because the straight chain of polyethylene causes close packing between the molecules. In addition, the formation of carbocations on polyethylene is more difficult than on polypropylene because the secondary carbocations of polyethylene are less stable, requiring higher energy to break the C-H bond. [34]

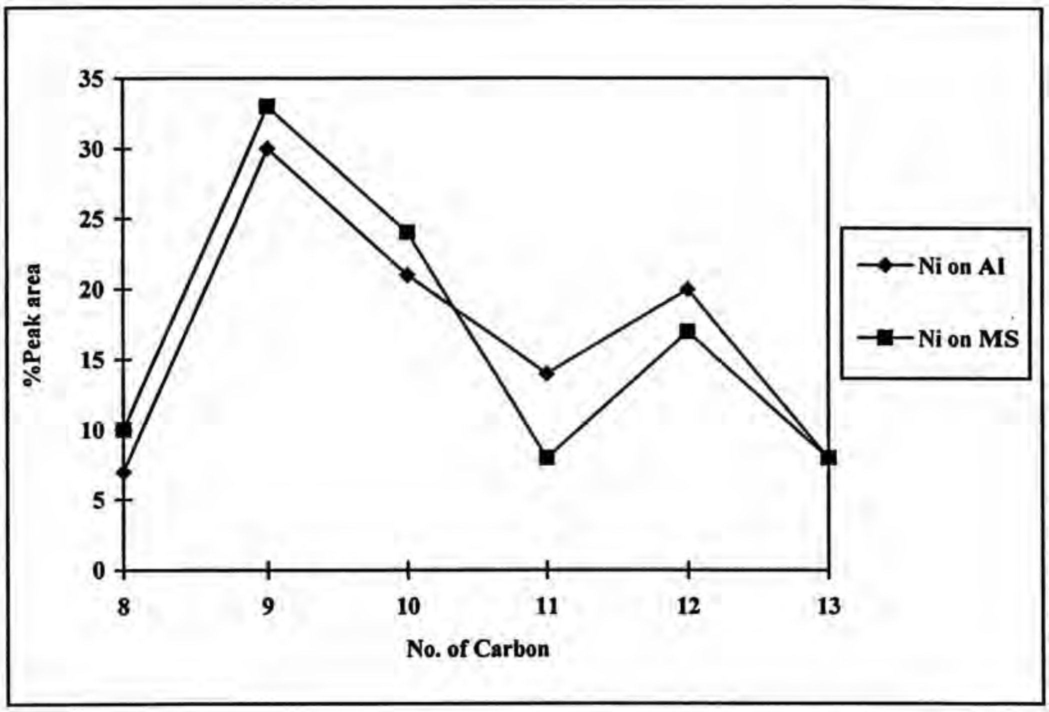


Figure 4.15 Composition trend of oil product from hydrocracking as a function of support type

4.3 Determination of Product Properties

4.3.1 Spectroscopic properties

The ^{13}C NMR spectrum and FTIR spectrum of the product from the optimum conditions are shown in Figures B22 and B23. The NMR spectrum shows aliphatic carbon between 10-50 ppm and the IR spectrum shows C-H stretching around 2,800-3,000 cm^{-1} and C-H bending around 1,300-1,500 cm^{-1}. No signals due to olefinic or aromatic groups were observed in either spectrum.

4.3.2 Physical properties

The physical properties of the products from hydrocracking under the optimum condition, the product from 40%wt. of Ni(5%)-Sn(5%)-F(2%)/MS operating at 500 psig for 6 hr., the product from reproducibility of the reaction using 40%wt. of Ni(5%)-Sn(5%)-F(2%)/MS , the product from Fe(5%)-Sn(5%)-F(2%)/MS and Co(5%)-Sn(5%)-F(2%)/MS operating at 500 psig for 6 hr., the product from 25%wt. of Ni(5%)-Sn(5%)-F(2%)/Al_2O_3 operating at 500 psig for 6 hours and the product from 35%wt. of Fe(10%)-Sn(5%)-F(2%)/Al_2O_3 and 35%wt. of Co(10%)-Sn(5%)-F(2%)/Al_2O_3 are shown in Table 4.2. From the Table 4.2. The result from ASTM D86 distillation are presented in Table B7, it is clear that the liquid hydrocarbon obtained could be used as high speed diesel oil.

Table 4.2 Properties of oil product

Product	Test Item						
	API Gravity @ 60°F ASTMD1298	Calculated Cetane index ASTM D 976	Flash Point °C ASTM D 93	Distillation 90% rec., °C ASTM D 86	Color ASTM D 1500	Sulfur Content , %wt. ASTM D 4294	Kinematic Viscosity, cSt ASTM D 445
HSD		47 min	52 min	357 max	2.0 max	0.05 max	1.8-4.1
Ni on MS (1)	43.8	57.2	40	348.1	< 0.5	0	1.8
Ni on MS (2)	47.3	53.4	43	347.0	< 0.5	0	1.8
Fe on MS	43.0	67.0	44	317.8	< 0.5	0	NT
Co on MS	44.2	NT	49	NT	< 0.5	NT	NT
Fe on Al_2O_3	45.3	NT	46	NT	< 0.5	NT	NT
Co on Al_2O_3	46.3	NT	41	NT	0.5	NT	NT
Ni on Al_2O_3	47.4	NT	38	NT	0.5	NT	NT

NT = not tested

HSD = High Speed Diesel

The oil product from hydrocracking over Ni(5%)-Sn(5%)-F(2%)/MS under optimum conditions, gave the nearest result in all physical properties that affirms the reproducibility of the reaction. On comparing the products with the specifications of base diesel, it can be seen that the advantage of these products is the absence of sulfur and lead which would lead to air pollution. Moreover, this oil has a high calculated cetane index (57.2 and 53.4), a consequence of high branching of the hydrocarbons, low color (<0.5) and kinematic viscosity index in the required range. The off-specification of flash point can be solved by distillation of product to increase boiling point. The calculated cetane index of oil from iron catalyst is higher than from the nickel catalyst because it has higher temperature at 50% distillation than the oil from nickel catalyst.

The oil product from hydrocracking of used polypropylene over Ni(5%)-Sn(5%)-F(2%)/MS can be used instead of high speed diesel oil from refinery oil because of good physical properties