CHAPTER IV

RESULTS AND DISCUSSION

This research was to determine the suitable condition for depolymerization of used polyethylene to fuel in high %yield by catalytic hydrocracking reaction. The noble group metals (e.g. Fe, Co, Ni), tin and fluoride were impregnated on various types of molecular sieve support (4A-DG, 3A-EPG and 13xPG) to be catalyst for this study.

4.1 Measuring Pore Volume of Molecular Sieve Support

Table 4.1 Pore volume of molecular sieve support

Molecular sieve type	Pore volume (cc/g)
4A-DG	0.0261
3A-EPG	0.0977
13xPG	0.3880

The pore volume of molecular sieve support 4A-DG, 3A-EPG and 13xPG types were characterized by Micro Pore Sizer as shown in table 4.1.

It can be seen that the pore volume of molecular sieve 4A-DG, 3A-EPG and 13xPG types were 0.0261, 0.0977 and 0.3880 cc/g respectively.

4.2 Characterization of Catalysts

The prepared catalysts were characterized by X-ray fluorescence (XRFS) as shown in Figure A1-A8 and Table A1. It can be seen that %fluoride, %tin and %transition metals (e.g. nickel, iron or cobalt) were impregnated on the molecular sieve support as desired.

For example, the Fe(10%)-Sn(5%)-F(2%) on molecular sieve (4A-DG type) catalyst had 10.2%wt of iron, 4.3%wt of tin and 1.8%wt of fluoride and other catalysts were the same.

4.3 Hydrocracking Process

In this research, the hydrocracking reactions were studied as a function of the processing variables, i.e. catalyst type, catalyst concentration, reaction time, reaction temperature, hydrogen pressure and pore size of molecular sieve support. The products were characterized by GC compared with the retention times of the standard C_9-C_{14}-C_{16} hydrocarbons. The change in product as a function of the above variables allowed several options for suitable conditions.

4.3.1 Effect of Catalyst Type

Hydrocracking of used PE was performed using three catalyst types, Fe(10%)-Sn(5%)-F(2%), Co(10%)-Sn(5%)-F(2%) and Ni(10%)-Sn(5%)-F(2%) on molecular sieve (4A-DG type) catalysts under fixed conditions at 390 °C, a hydrogen pressure of 600 psig, a reaction time of 4 hours and catalyst concentration 40% wt of used PE.

Table 4.2 Oil product yield from hydrocracking on molecular sieve (4A-DG type) catalyst as functions of catalyst type and element composition

Catalyst Type	Yield (%wt)		
	Oil	Wax	Total
Fe10-5-2/MS(4A-DG)	61.6	25.1	86.7
Co10-5-2/MS(4A-DG)	49.4	37.9	87.3
Ni10-5-2/MS(4A-DG)	86.4	1.5	87.9
Ni10-5-1/MS(4A-DG)	68.3	17.7	86.0
Ni10-2.5-2/MS(4A-DG)	63.4	21.0	84.4
Ni 5-5-2/MS(4A-DG)	64.3	18.7	83.0

(conditions : 40%wt of catalyst , 390 °C , 600 psig , 4 hours)

Fe10-5-2/MS = Fe(10%)-Sn(5%)-F(2%) on molecular sieve
Co10-5-2/MS = Co(10%)-Sn(5%)-F(2%) on molecular sieve
Ni10-5-2/MS = Ni(10%)-Sn(5%)-F(2%) on molecular sieve
Ni10-5-1/MS = Ni(10%)-Sn(5%)-F(1%) on molecular sieve
Ni10-2.5-2/MS = Ni(10%)-Sn(2.5%)-F(2%) on molecular sieve
Ni 5-5-2/MS = Ni(5%)-Sn(5%)-F(2%) on molecular sieve

The results are shown in Table 4.2 and Figure 4.1. It can be seen that the oil of the hydrocracking reaction using Ni(10%)-Sn(5%)-F(2%) on molecular sieve (4A-DG type) catalyst gave the highest oil yield (86.4%wt) compared with other catalysts. Nickel is more effective for the hydrogenative stabilization of free radical fragments than cobalt and iron. So, the products of hydrocracking reaction using Co and Fe catalysts had less yield than the product of hydrocracking reaction using Ni catalyst.

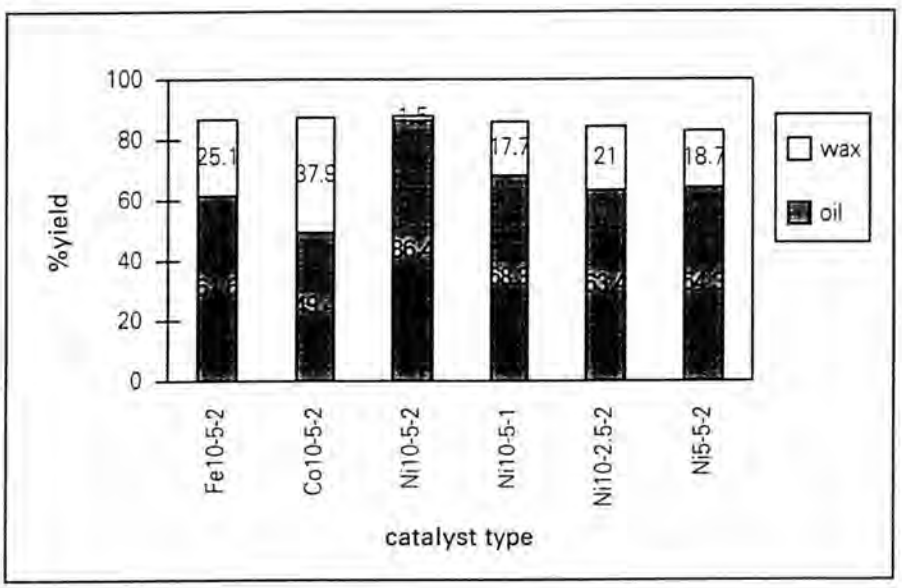

Figure 4.1 Comparison of oil yield from hydrocracking on molecular sieve (4A-DG type) catalyst as functions of catalyst type and element composition

From GC chromatograms and composition trend (Figure B1 and Figure 4.2) of oil products compared with the standard C_9-C_{14}-C_{16} hydrocarbons (Figure B12), the oil products were C_6-C_{25} hydrocarbons. The iron catalyst gave the highest proportions of main compositions (C_8-C_{12} hydrocarbons) while the cobalt and nickel catalysts gave the highest proportions of C_{12}-C_{16} hydrocarbons.

Consequently, nickel catalysis was chosen for studying the other effects because it gave the highest oil yield.

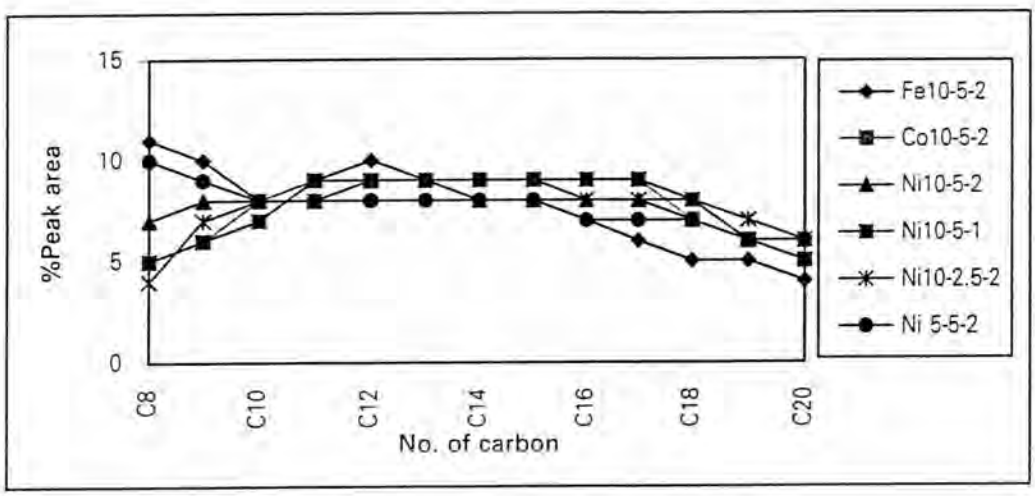

Figure 4.2 Composition trend of oil product from hydrocracking on molecular sieve (4A-DG type) catalyst as functions of catalyst type and element composition

4.3.2 Effect of Element Composition of Ni/Sn/F Catalyst

Studying the effect of element composition of catalyst was performed by varying %component of nickel, tin and fluoride ; Ni(10%)-Sn(5%)-F(2%), Ni(10%)-Sn(5%)-F(1%), Ni(10%)-Sn(2.5%)-F(2%) and Ni(5%)-Sn(5%)-F(2%) on molecular sieve (4A-DG type) catalysts. The reaction used 40%wt catalyst concentration, 390 °C temperature, and 600 psig hydrogen pressure for 4 hours.

The results are shown in Table 4.2 and Figure 4.1. The oil yield was increased following the increasing of %nickel because it increased the hydrogenation / dehydrogenation sites. In the same way the oil yield was increased following the increasing of %tin and %fluoride because the impregnation with NH_4F enhances acidic activities of SnO and SnO_2 by forming SnF_2 and SnF_4. The SnF_2 and SnF_4 act as a promoter in the cracking and the isomerization by inducing H^- and releasing H^+ to the surrounding. Besides, NH_4F enhances acidic activity of alumina by inductively withdrawing electrons from the aluminium atom as a result of the fluoride has higher electronegativity than oxygen, the residual hydrogen atom on the surface becomes more acidic. Thus, the increasing of the amount of tin and fluoride components increases the catalyst efficiency. [23]

GC chromatograms (Figure B2 and Figure 4.2) of oil products from these reactions were compared with the standard C_9-C_{14}-C_{16} (Figure B12).

The oil products consisted of C_6-C_{25} hydrocarbons with C_8-C_{20} as the main components.

Therefore, Ni(10%)-Sn(5%)-F(2%) / MS (4A-DG) could be considered optimal because it gave the highest oil yield.

4.3.3 Effect of Reaction Time

The effect of reaction time was studied by varying the reaction time between 30 minutes, 2 and 4 hours and using 40%wt of the Ni(10%)-Sn(5%)-F(2%) / MS (4A-DG) catalyst, 390 °C temperature and 600 psig hydrogen pressure. The yield of oil product is shown in Table 4.3 and Figure 4.3.

Table 4.3 Oil product yield from hydrocracking over Ni(10%)-Sn(5%)-F(2%) on molecular sieve (4A-DG type) catalyst as a function of reaction time

Reaction time	Yield(%wt)		
	Oil	Wax	Total
30 min.	57.6	27.9	85.5
2 hr.	64.0	20.5	84.5
4 hr.	86.4	1.5	87.9

(conditions : 40%wt of catalyst , 390 °C , 600 psig)

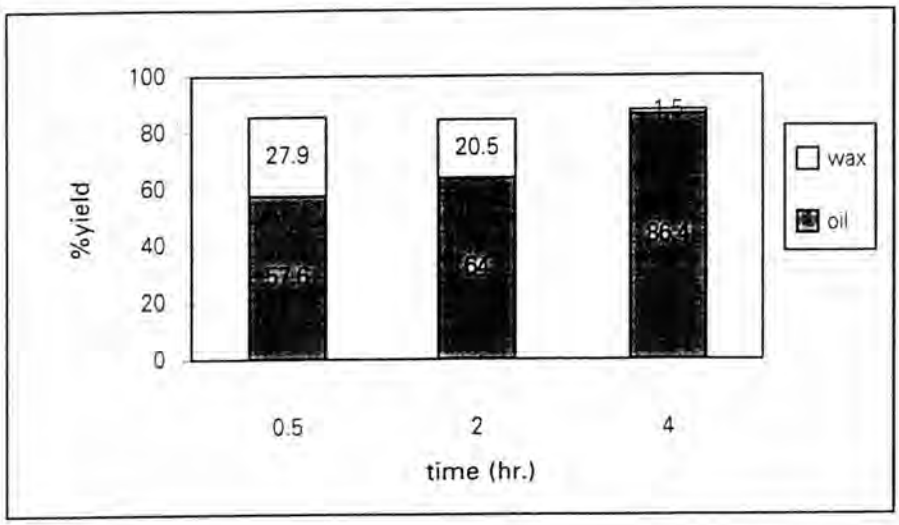

Figure 4.3 Comparison of oil yield from hydrocracking over Ni(10%)-Sn(5%)-F(2%) on molecular sieve(4A-DG type) catalyst as a function of reaction time

The results showed that the highest oil yield (86.4%wt) was obtained from a reaction time of 4 hours, because increasing reaction time had a beneficial effect on increasing the hydrocracking reaction. From GC chromatograms (Figure B3 and Figure 4.4) compared with the standard C_9-C_{14}-C_{16} (Figure B12), the composition of oil product from hydrocracking operated at 30 minutes, 2 and 4 hours consisted of C_6-C_{25} hydrocarbons with C_8-C_{20} as the main components.

Thus, the reaction time 4 hours should be considered optimal.

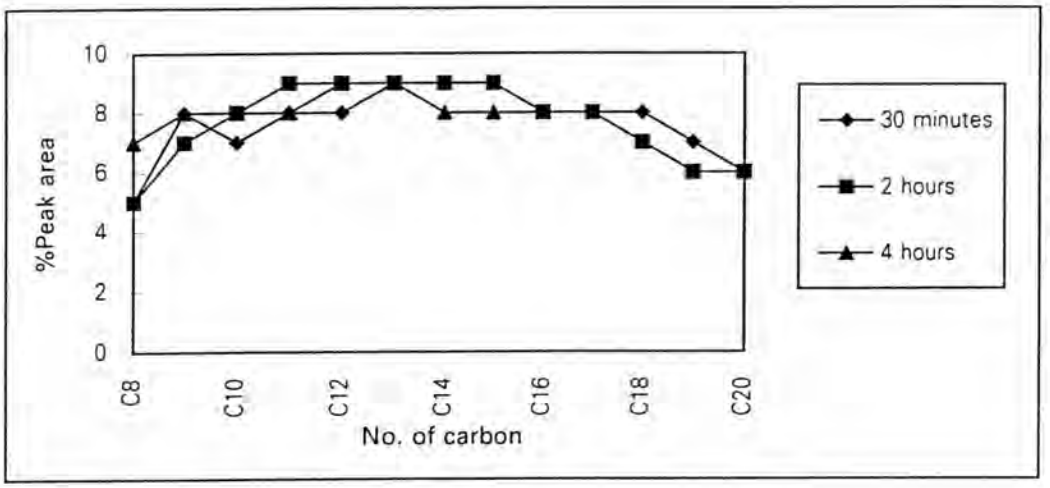

Figure 4.4 Composition trend of oil product from hydrocracking over Ni(10%)-Sn(5%)-F(2%) on molecular sieve (4A-DG type) catalyst as a function of reaction time

4.3.4 Effect of Reaction Temperature

Effect of temperature on the hydrocracking of used PE was studied by varying the temperature at 350 °C, 370 °C and 390°C. The catalyst used in this study was 40%wt of the Ni(10%)-Sn(5%)-F(2%) / MS(4A-DG) under hydrogen pressure at 600 psig for 4 hours.

Table 4.4 Oil product yield from hydrocracking over Ni(10%)-Sn(5%)-F(2%) on molecular sieve (4A-DG type) catalyst as a function of reaction temperature

Reaction temperature (°C)	Yield(%wt)		
	Oil	Wax	Total
350	27.0	62.6	89.6
370	46.7	42.7	89.4
390	86.4	1.5	87.9

(conditions : 40%wt of catalyst , 600 psig , 4 hours)

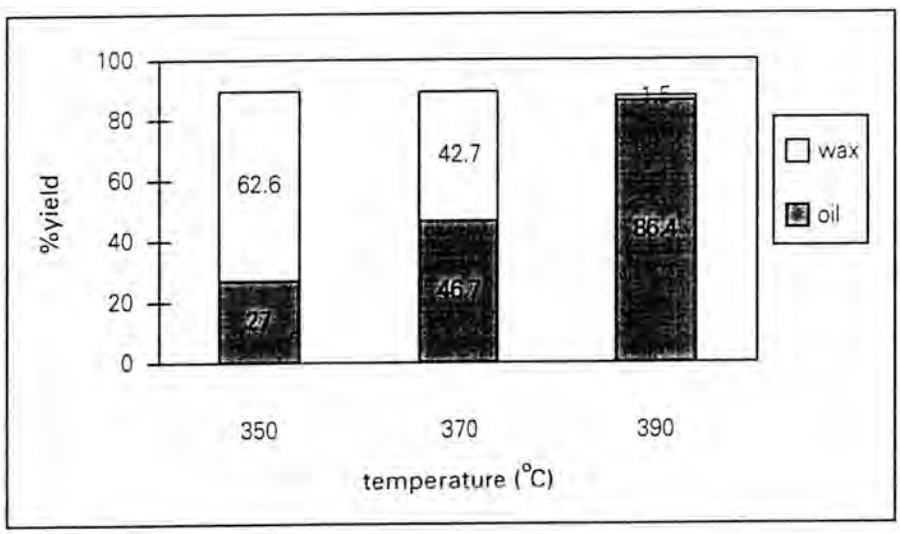

Figure 4.5 Comparison of oil yield from hydrocracking over Ni(10%)-Sn(5%)-F(2%) on molecular sieve (4A-DG type) catalyst as a function of reaction temperature

The results of hydrocracking using the various reaction temperatures shown in Table 4.4 and Figure 4.5 demonstrate that operating at 390 °C

provided the highest oil yield (86.4%wt) because the high temperature allowed the more cracking. The GC chromatograms (Figure B4 and Figure 4.6) compared with the standard C_9-C_{14}-C_{16} (Figure B12) display that the products were C_6-C_{25} hydrocarbons with C_8-C_{20} as the main components.

Hence, a temperature of 390 °C could be considered optimal.

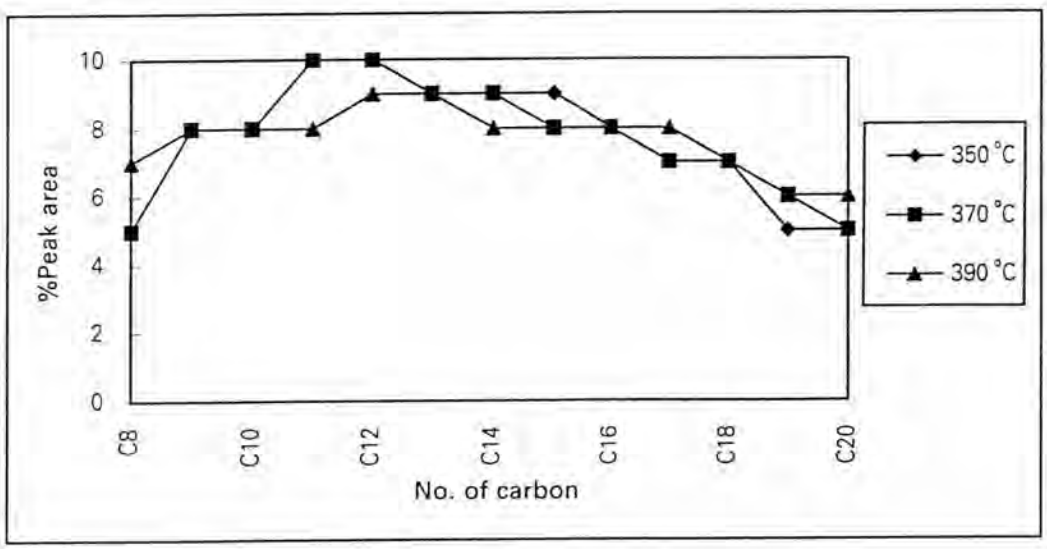

Figure 4.6 Composition trend of oil product from hydrocracking over Ni(10%)-Sn(5%)-F(2%) on molecular sieve (4A-DG type) catalyst as a function of reaction temperature

4.3.5 Effect of Hydrogen Pressure

The effect of hydrogen pressure was studied by varying hydrogen pressure at 400, 500 and 600 psig, using 40%wt of the Ni(10%)-Sn(5%)-F(2%) / MS (4A-DG) and 390 °C temperature for 4 hours.

Table 4.5 Oil product yield from hydrocracking over Ni(10%)-Sn(5%)-F(2%) on molecular sieve (4A-DG type) catalyst as a function of hydrogen pressure

Hydrogen pressure (psig)	Yield(%wt)		
	Oil	Wax	Total
400	75.9	9.9	85.8
500	84.0	1.9	85.9
600	86.4	1.5	87.9

(conditions : 40%wt of catalyst , 390 °C , 4 hours)

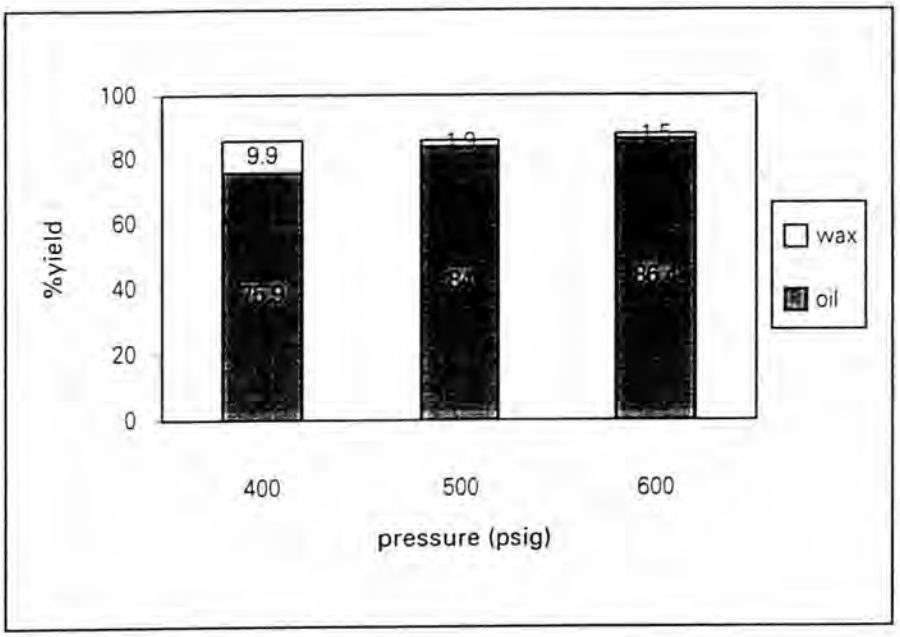

Figure 4.7 Comparison of oil yield from hydrocracking over Ni(10%)-Sn(5%)-F(2%) on molecular sieve (4A-DG type) catalyst as a function of hydrogen pressure

The comparison of the oil yield from these conditions (Table 4.5 and Figure 4.7) showed that the hydrogen pressure range of 500-600 psig was satisfactory. The economic considerations dicate the use of minimum hydrogen pressure. In conclusion, a pressure in the vicinity of 500 psig could be considered optimal.

As seen in Figure B5 and Figure 4.8 compared with the standard C_9-C_{14}-C_{16} (Figure B12), the oil products consisted of C_6-C_{25} hydrocarbons with C_8-C_{20} as the main components.

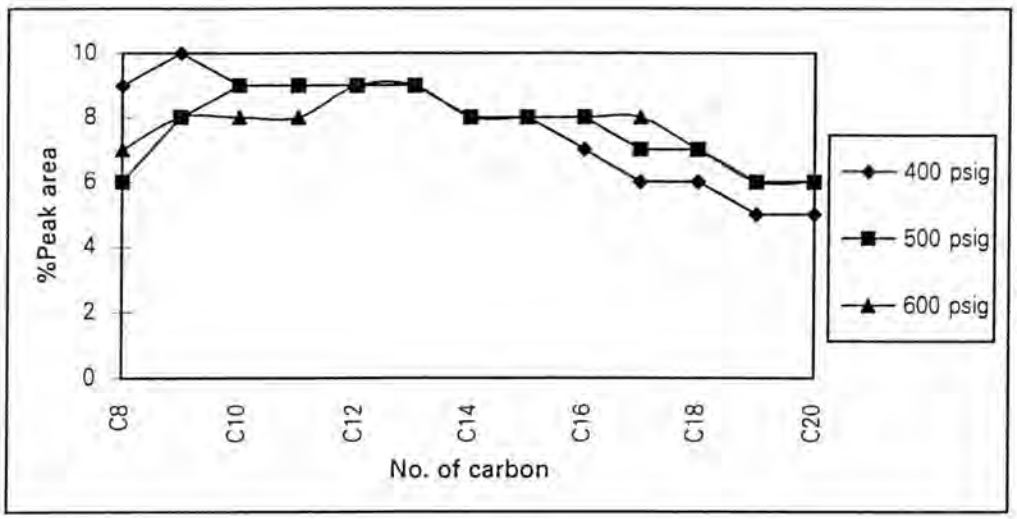

Figure 4.8 Composition trend of oil product from hydrocracking over Ni(10%)-Sn(5%)-F(2%) on molecular sieve (4A-DG type) catalyst as a function of hydrogen pressure

4.3.6 Effect of Catalyst Concentration

The effect of catalyst concentration was studied by varying catalyst concentration between 20, 30 and 40%wt of Ni(10%)-Sn(%)-F(2%) / MS (4A-DG) catalyst. This process in this study used 390 °C temperature, 500 psig hydrogen pressure for 4 hours.

Table 4.6 Oil product yield from hydrocracking over Ni(10%)-Sn(5%)-F(2%) on molecular sieve (4A-DG type) catalyst as a function of catalyst concentration

Catalyst concentration (%wt)	Yield(%wt)		
	Oil	Wax	Total
20	29.4	63.5	92.9
30	57.6	28.8	86.4
40	84.0	1.9	85.9

(conditions: 390 °C , 500 psig , 4 hours)

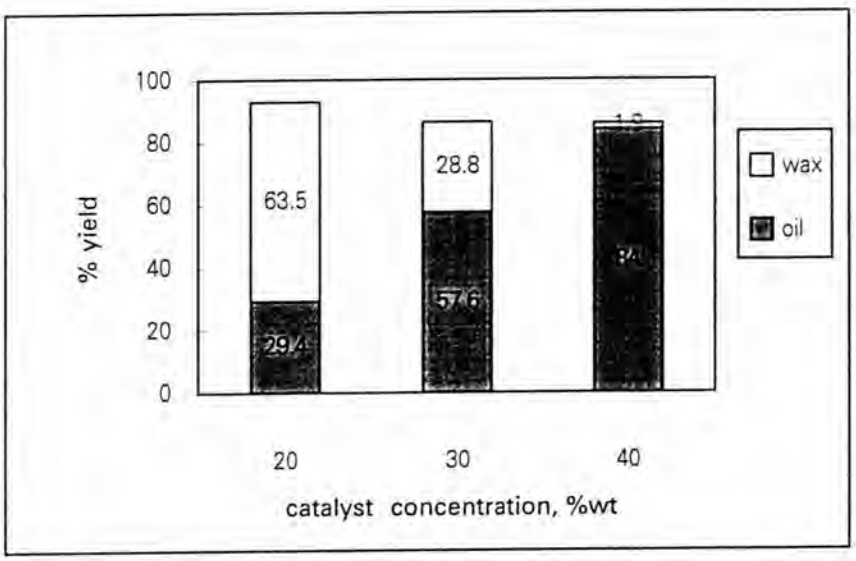

Figure 4.9 Comparison of oil yield from hydrocracking over Ni(10%)-Sn(5%)-F(2%) on molecular sieve (4A-DG type) catalyst as a function of catalyst concentration

As seen in Table 4.6 and Figure 4.9, the oil yield was varied according to the catalyst concentration. When the catalyst concentration was increased, the oil yield was increased too. The highest oil yield (84.0%wt) was obtained from 40%wt of catalyst.

The GC analysis of the oil products is shown in Figure B6 and Fingure 4.10 compared with the standard C_9-C_{14}-C_{16} (Figure B12). The oil products were C_6-C_{25} hydrocarbons with C_8-C_{20} as the main components.

The results of %yield oil showed that the catalyst concentration 40%wt could be considered optimal.

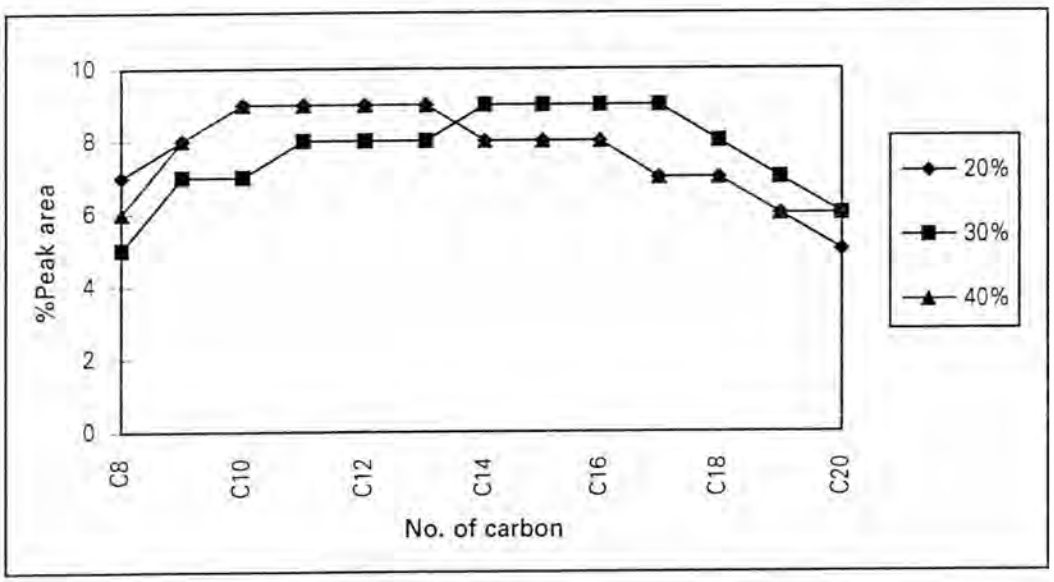

Figure 4.10 Composition trend of oil product from hydrocracking over Ni(10%)-Sn(5%)-F(2%) on molecular sieve (4A-DG type) catalyst as a function of catalyst concentration

4.3.7 Effect of Molecular Sieve Support Type

Studying the effect of type of molecular sieve support was performed by using three molecular sieve support types ; 4A-DG, 3A-EPG and 13xPG, with 40%wt of Ni(10%)-Sn(5%)-F(2%) on these molecular sieve supports under optimum conditions (390 °C, 500 psig and 4 hours).

Table 4.7 Oil product yield from hydrocracking over Ni(10%)-Sn(5%)-F(2%) on molecular sieve catalyst as a function of molecular sieve type

Molecular sieve type	Yield(%wt)		
	Oil	Wax	Total
4A-DG	84.0	1.9	85.9
3A-EPG	77.7	5.0	82.7
13xPG	68.4	8.9	77.3

(conditios : 40 %wt of catalyst , 390 °C , 500 psig , 4 hours)

The yield of oil product is shown in Table 4.7 and Figure 4.11. The results showed that the highest oil yield (84.0%wt) was obtained from the molecular sieve support 4A-DG type.

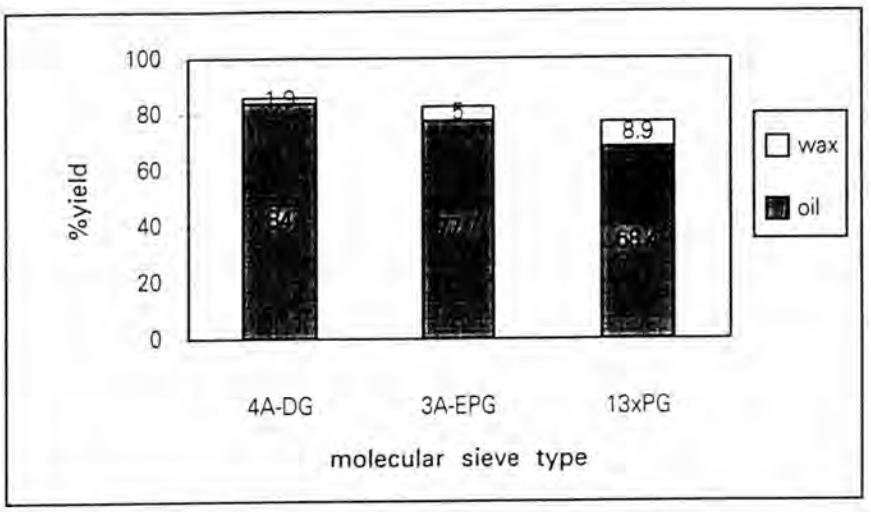

Figure 4.11 Comparison of oil yield from hydrocracking over Ni(10%)-Sn(5%)-F(2%) on molecular sieve catalyst as a function of molecular sieve type

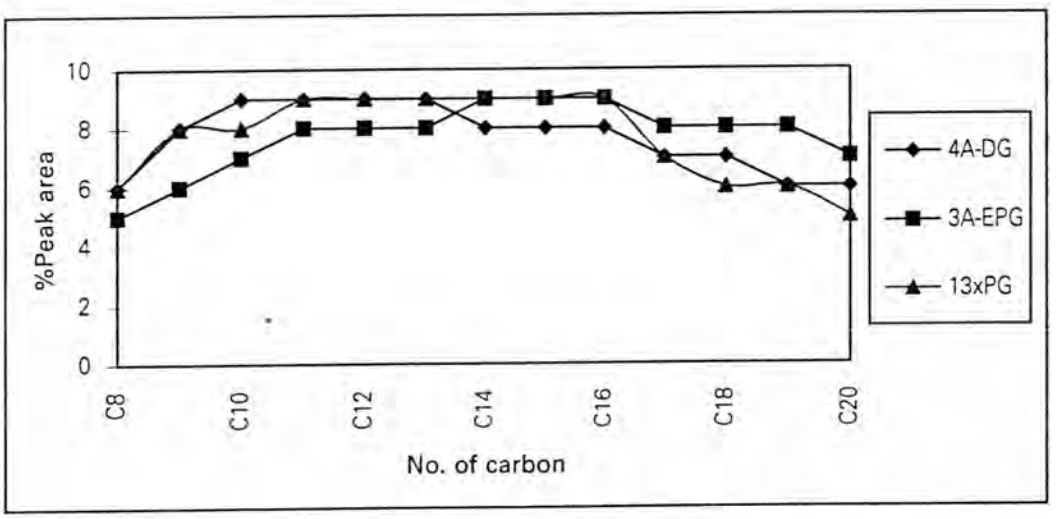

Figure 4.12 Composition trend of oil product from hydrocracking over Ni(10%)-Sn(5%)-F(2%)on molecular sieve catalyst as a function of molecular sieve type

From GC chromatograms (Figure B7 and Figure 4.12) compared with the standard C_9-C_{14}-C_{16} (Figure B12), the compositions of them were C_6-C_{25} hydrocarbons with C_8-C_{20} as the main components. It could be concluded that the molecular sieve support type had not influence to the molecular weight distribution of oil product because the pore sizes of these molecular sieve supports were larger than the molecules of PE reactants to obtain the same composition trends of oil products.

4.3.8 Activity of Used Catalyst of Hydrocracking

The activity of used catalysts, Ni(10%)-Sn(5%)-F(2%) on molecular sieve support 4A-DG, 3A-EPG and 13xPG types, were studied under the optimum conditions. The yield of oil product is shown in Table 4.8 and Figure 4.13 - 4.15. It can be seen that these catalysts could not be reused because the activity of used catalysts was reduced .

Table 4.8 Oil product yield from hydrocracking over used Ni(10%)-Sn(5%)-F(2%) on three molecular sieve support types (4A-DG, 3A-EPG and 13xPG)

Molecular sieve type	Yield(%wt)		
	Oil	Wax	Total
Ni / 4A-DG	84.0	1.9	85.9
Ni / 4A-DG (reused #1)	65.2	19.1	82.7
Ni / 4A-DG (reused #2)	47.3	35.6	77.3
Ni / 3A-EPG	77.7	5.0	82.7
Ni / 3A-EPG (reused #1)	54.6	30.9	85.5
Ni / 13xPG	68.4	8.9	77.3
Ni / 13xPG (reused #1)	43.7	36.8	80.5

(conditions : 40 %wt of catalyst , 390 °C , 500 psig , 4 hours)

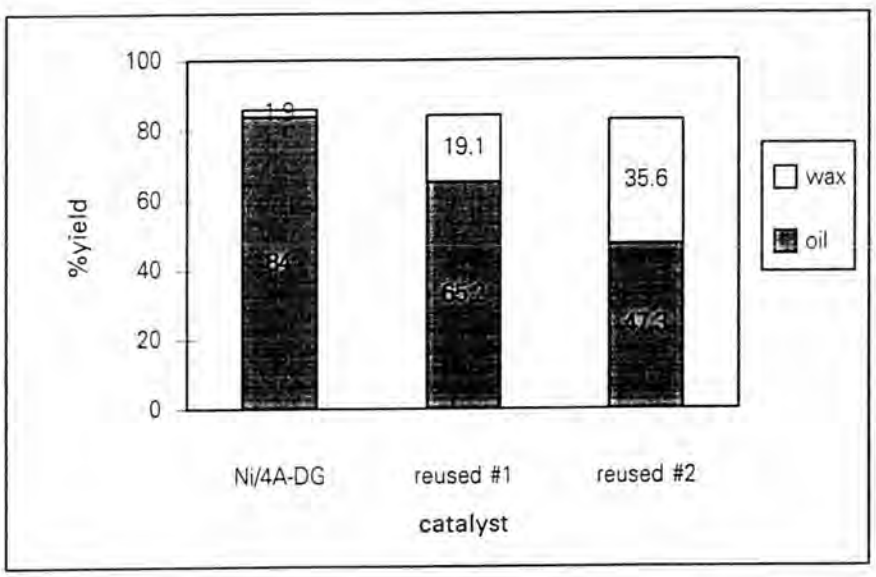

Figure 4.13 Comparison of oil yield from hydrocracking over used Ni(10%)-Sn(5%)-F(2%) on molecular sieve (4A-DG type) catalyst

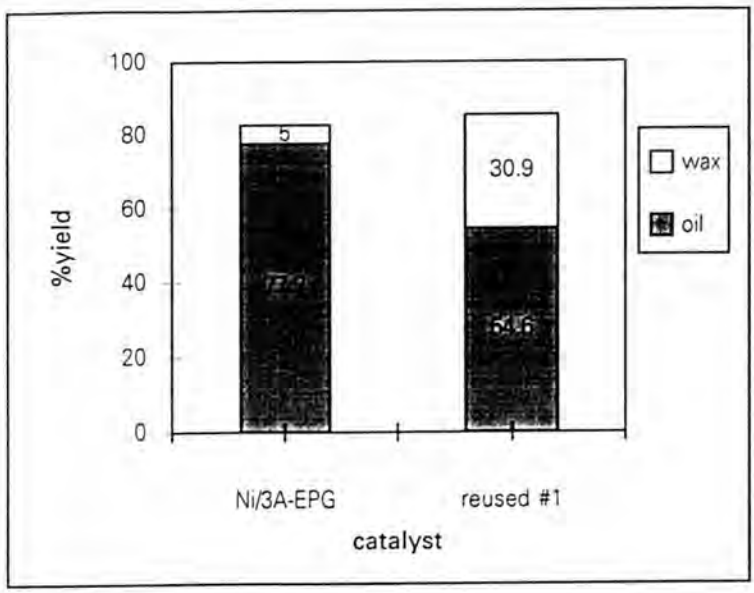

Figure 4.14 Comparison of oil yield from hydrocracking over used Ni(10%)-Sn(5%)-F(2%) on molecular sieve (3A-EPG type) catalyst

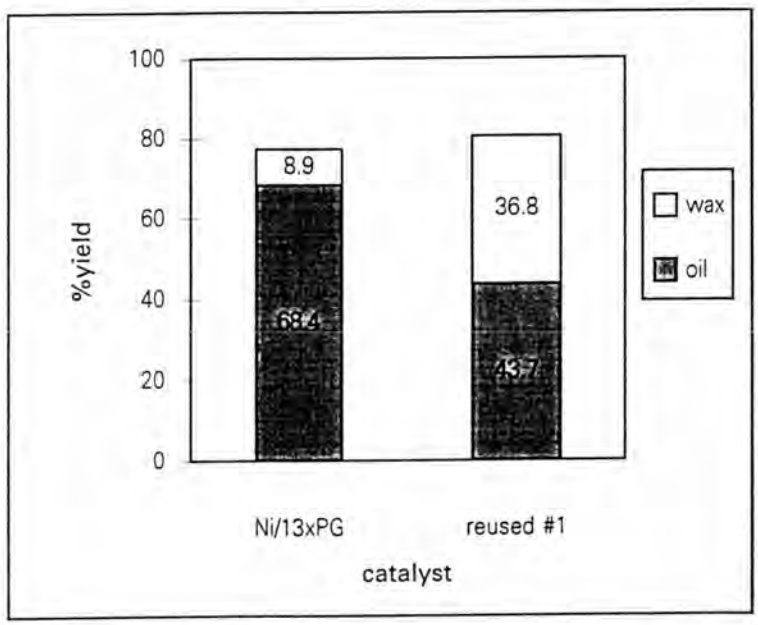

Figure 4.15 Comparison of oil yield from hydrocracking over used Ni(10%)-Sn(5%)-F(2%) on molecular sieve (13xPG type) catalyst

The GC chromatograms and the composition trend of oil product (Figure B8 - B10 and Figure 4.16 - 4.18) compared with the standard C_9-C_{14}-C_{16} (Figure B12) were similar.

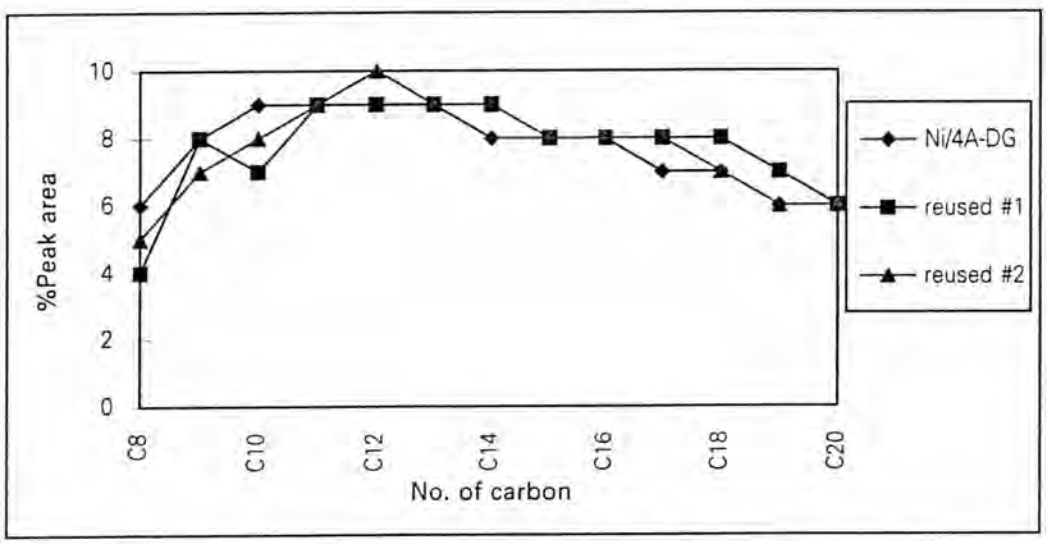

Figure 4.16 Composition trend of oil product from hydrocracking over used Ni(10%)-Sn(5%)-F(2%) on molecular sieve (4A-DG type) catalyst

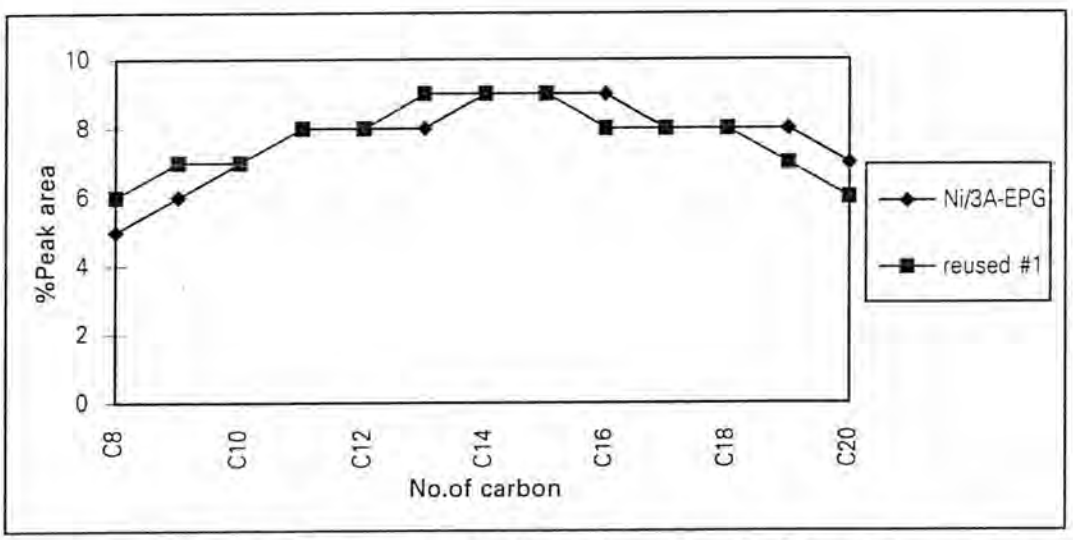

Figure 4.17 Composition trend of oil product from hydrocracking over used Ni(10%)-Sn(5%)-F(2%) on molecular sieve (3A-EPG type) catalyst

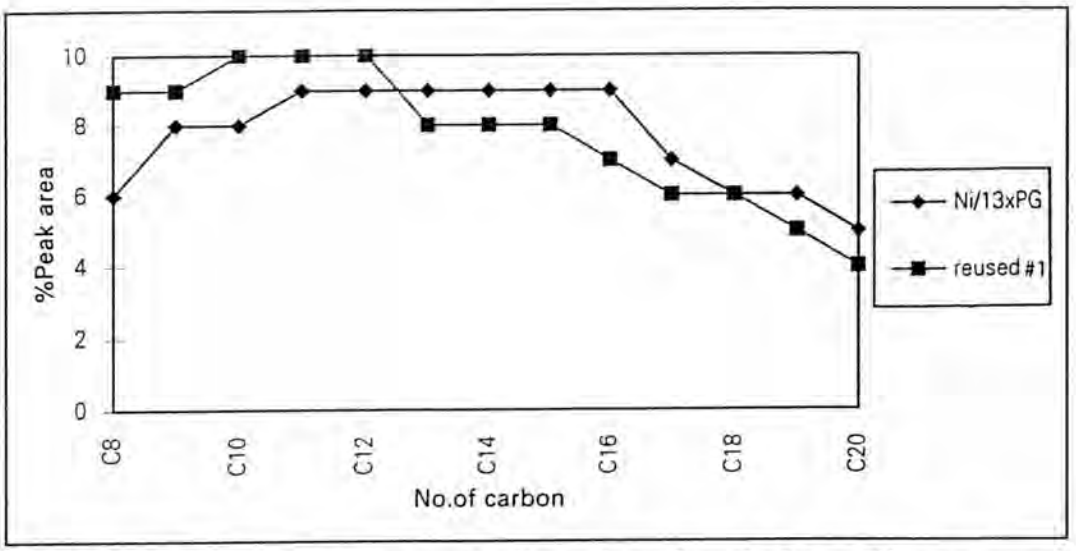

Figure 4.18 Composition trend of oil product from hydrocracking over used Ni(10%)-Sn(5%)-F(2%) on molecular sieve (13xPG type) catalyst

4.3.9 Reproducibility of Hydrocracking

To study the reproducibility of hydrocracking using the same Ni(10%)-Sn(5%)-F(2%) / MS(4A-DG) catalysts were performed under the optimum conditions. The oil yields from two experiments were 84.9 and 83.0%wt (Table 4.9 and Figure 4.19). It can be seen that the oil yields are similar.

Table 4.9 Oil product yield from reproducibility of hydrocracking over Ni(10%)-Sn(5%)-F(2%) on molecular sieve (4A-DG type) catalyst

Molecular sieve type	Yield(%wt)		
	Oil	Wax	Total
4A-DG	84.9	1.4	86.3
reproduced #1	83.0	2.4	85.4

(conditions : 40 %wt of catalyst , 390 °C , 500 psig , 4 hours)

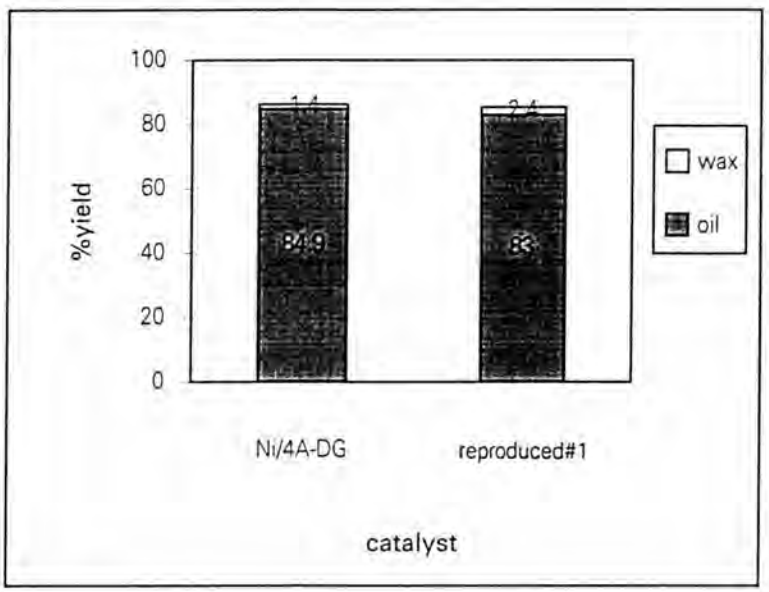

Figure 4.19 Comparison of oil yield from reproducibility of hydrocracking over Ni(10%)- Sn(5%)-F(2%) on molecular sieve (4A-DG type) catalyst

The GC chromatograms and the composition trend (Figure B11 and Figure 4.20) of oil product compared with the standard C_9-C_{14}-C_{16} (Figure B12) show the same compositions. So, it can be concluded that the reactions could be reproducible at any conditions.

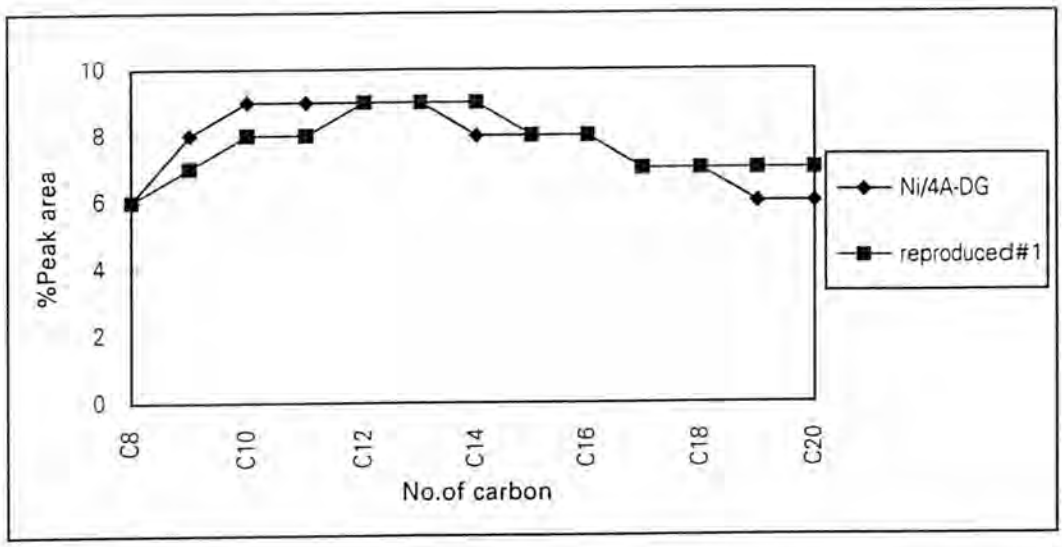

Figure 4.20 Composition trend of oil product from reproducibility of hydrocracking over Ni(10%)-Sn(5%)-F(2%) on molecular sieve (4A-DG type) catalyst

4.4 Determination of Product Properties

The physical properties of the products from hydrocracking under the optimum conditions , the products from 40%wt of Ni(10%)-Sn(5%)-F(2%) on molecular sieve support 4A-DG, 3A-EPG and 13xPG types are shown in Table 4.10 and Figure C1 - C3.

Table4.10 Properties of oil products

Properties	Method	Ni(10%)-Sn(5%)-F(2%)		
		4A-DG	3A-EPG	13xPG
API Gravity @ 60 °F	ASTM D 1298	46.2	44.5	44.1
Specific Gravity @60/60°F	ASTM D 1298	0.7963	0.8040	0.8058
Kinetic Viscosity, cSt 40 °C	ASTM D 445	1.571	1.839	1.711
Flash Point , °C	ASTM D 93	T_{room}	T_{room}	T_{room}
Pour Point , °C	ASTM D 97	-8	-8	-8
Distillation , °C	ASTM D 86	393.0	392.4	394.0
Color	ASTM D 1500	6	6	7.5
Sulfur Content , %wt	ASTM D 4294	0	0	0

T_{room} = room temperature

It can be seen that the physical properties of these oil products were the same and could not be classified by oil type (e.g. gasoline, diesel and jet) because their physical properties were wide ranging. They must be distilled before they are utilized.