

## CHAPTER IV

### RESULT AND DISCUSSION

The main purpose of the study was to determine suitable conditions for obtaining a high yield of product from used polystyrene. A hydrocracking process with bifunctional catalyst was used. Fe/Sn/F on  $\text{Al}_2\text{O}_3$  catalyst, Fe/Sn/F on molecular sieve catalyst, Ni/Sn/F on molecular sieve catalyst and Co/Sn/F on molecular sieve catalyst were selected for these experiments, because iron, tin, nickel and cobalt are active components in hydrocracking and hydrogenation reaction. In addition, fluorine acts as a promoter by enhancing the activity of the acidic function. Finally, molecular sieve was chosen because it is inexpensive and is easily impregnated with iron, tin, nickel and cobalt, and helps to maintain a high metal dispersion.

#### 4.1 Characterization of Catalysts

The plots of x-ray fluorescence data, element concentration of molecular sieve, alumina and catalysts are shown in Figures A1, A2, A3, A4, A5 and Tables A1, A2, A3, A4, A5, respectively. The molecular sieve showed peak characteristic of aluminium, chlorine, calcium, titanium, chromium, manganese, iron, cobalt, nickel, copper, zinc and molybdenum.

The Fe(5%)/Sn(5%)/F(2%) on molecular sieve catalyst showed peak characteristic of aluminium, silicon, chlorine, calcium, titanium,

chromium, manganese, iron, nickel, copper, zinc, molybdenum and tin. The Fe(2.5%)/Sn(5%)/F(2%) on molecular sieve catalyst showed peak characteristic of aluminium, silicon, chlorine, calcium, titanium, chromium, manganese, iron, nickel, copper, zinc, molybdenum and tin. The Fe(5%)/Sn(2.5%)/F(2%) on molecular sieve catalyst showed peak characteristic of aluminium, chlorine, calcium, titanium, chromium, manganese, iron, nickel, copper, zinc, molybdenum and tin.

The concentrations of iron and tin in Fe(2.5%)/Sn(2.5%) catalyst were lower than those found in the Fe(5%)/Sn(5%) catalyst, but higher than those found in the molecular sieve alone. This confirmed that impregnation was successful.

The Co(5%)/Sn(5%)/F(2%) on molecular sieve catalyst showed peak characteristic of aluminium, silicon, chlorine, calcium, titanium, chromium, manganese, iron, cobalt, nickel, copper, zinc, molybdenum and tin. The Ni(5%)/Sn(5%)/F(2%) on molecular sieve catalyst showed peak characteristic of aluminium, silicon, chlorine, calcium, titanium, chromium, manganese, iron, cobalt, nickel, copper, zinc, molybdenum and tin. Both the Co(5%)/Sn(5%)/F(2%) and the Ni(5%)/Sn(5%)/F(2%) on molecular sieve catalysts had higher concentrations of Ni/Sn and Co/Sn than the molecular sieve and it can be concluded that Ni/Sn and Co/Sn can impregnate the molecular sieve.

The commercial catalyst from United Catalyst showed peak characteristic of aluminium, silicon, chlorine, calcium, titanium, chromium, manganese, iron, cobalt, nickel and molybdenum. The commercial catalyst from Thai Oil showed peak characteristic of aluminium, silicon, chlorine, calcium, titanium, chromium, manganese, iron, cobalt, nickel, copper, zinc, molybdenum, tin and platinum.

The alumina catalyst showed peak characteristic of aluminium, silicon, chlorine, calcium, titanium, chromium, manganese, iron, cobalt, nickel, copper, zinc, molybdenum and platinum. The Fe(5%)/Sn(5%)/F(2%) on alumina catalyst showed peak characteristic of aluminium, chlorine, calcium, titanium, chromium, manganese, iron, nickel, copper, zinc, molybdenum and tin. The concentration of Fe/Sn from Fe(5%)/Sn(5%)/F(2%) on alumina catalyst was clearly much higher than that of alumina alone and this indicated that Fe/Sn can impregnate alumina. There was no fluorine peak observed because X-ray fluorescence cannot detect it.

#### 4.2 Hydrocracking Process

The hydrocracking reactions were studied as a function of the processing variables, i.e. catalyst type, %component of catalyst, time, catalyst concentration, temperature and pressure. The products were identified and analyzed by GC. The change in product as a function of the above variables allowed several options for suitable conditions.

#### 4.2.1 Effect of Catalyst Types

The comparison between five catalyst types (two commercial catalysts, Fe/Sn/F on molecular sieve catalyst, Co/Sn/F on molecular sieve catalyst and Ni/Sn/F on molecular sieve catalyst) for hydrocracking of used polystyrene used, 40%wt of catalyst concentration, 325°C temperature and 500 psig hydrogen pressure for 3 hours. The results of GC analysis of the products using different catalysts, keeping other processing conditions constant, are shown in Figures B1, B7 and Tables B1, B2, B17, B18. The percentage yields are shown in Table 4.1.

The products consisted of C6-C9 hydrocarbons and Polynaphthene in Type I Catalyst and C6-C11 hydrocarbons and polynaphthene in Type 4 and 5 Catalyst. For all catalyst types, the main components were toluene, ethylbenzene and iso-propylbenzene. As seen in Table 4.1, the results with Type 4 and 5 catalysts were satisfactory. However, economic considerations dictate the use of the Type 5 catalyst. Hence, the Fe(5%)/Sn(5%)/F(2%) on molecular sieve of Type 5 catalyst can be considered optimal.

**Table 4.1** %Yield of hydrocarbon product from hydrocracking as a function of catalyst type

| Catalyst Type                  | Hydrocarbon Product (%yield) |
|--------------------------------|------------------------------|
| Type 1 : Commercial catalyst I | viscous material             |
| Type 2 : Commercial catalyst I | 58.7                         |
| Type 3 : Ni(5%)/Sn(5%)/F(2%)   | viscous material             |
| Type 4 : Co(5%)/Sn(5%)/F(2%)   | 72.4                         |
| Type 5 : Fe(5%)/Sn(5%)/F(2%)   | 87.3                         |

#### 4.2.2 Effect of % Component of Fe/Sn/F on Molecular Sieve

The effect of Fe/Sn/F composition on molecular sieve catalyst was studied by varying the amount in these catalysts; Fe(5%)/Sn(5%)/F(2%), Fe(2.5%)/Sn(5%)/F(2%), Fe(5%)/Sn(2.5%)/F(2%) and Fe(5%)/Sn(5%)/F(1%). The reaction used 40% wt catalyst concentration, 325°C temperature and 500 psig hydrogen pressure for 3 hours. GC chromatograms and composition of products from these reactions are shown in Figures B2, B8 and Tables B3, B4, B19, B20. The percentage yield of hydrocracking product is shown in Table 4.2.

The products were C6-C11 hydrocarbons and polynaphthene using catalyst components A, B and C. Toluene, ethylbenzene and iso-propylbenzene were the main components. The catalysis with highest amounts of Fe/Sn/F gave the highest yield. This showed that Fe, Sn and F all had an effect on hydrocracking polystyrene. In conclusion, Fe(5%)/Sn(5%)/F(2%), on molecular sieve could be considered optimal.

Table 4.2 %Yield of hydrocarbon product from hydrocracking as a %component of Fe/Sn/F on molecular sieve catalyst

| Catalyst Type                       | Hydrocarbon Product<br>(%yield) |
|-------------------------------------|---------------------------------|
| component A : Fe(5%)/Sn(5%)/F(2%)   | 87.3                            |
| component B : Fe(2.5%)/Sn(5%)/F(2%) | 71.4                            |
| component C : Fe(5%)/Sn(2.5%)/F(2%) | 69.5                            |
| component D : Fe(5%)/Sn(5%)/F(1%)   | viscous material                |

#### 4.2.3 Effect of Reaction Time

The effect of reaction time was studied by varying the reaction time between at 1, 1.5 and 2 hours and using 40% wt of the Fe(5%)/Sn(5%)/F(2%) on molecular sieve catalyst, 350°C temperature and 500 psig hydrogen pressure. The GC chromatograms and composition of the products are shown in Figures B3, B9 and Tables B5, B6, B21, B22. The percentage yield values are shown in Table 4.3.

As shown in Figures 4.5 and 4.6, the products were C6-C11 hydrocarbons and polynaphthene. They all had toluene, ethylbenzene and iso-propylbenzene as their main components. It was found that the reaction time at 1.5 hours provided a lower percentage yield and smaller amount of ethylbenzene than that at 2 hours. However, the difference was small. The optimal reaction time is 1.5 hours.



**Table 4.3** %Yield of hydrocarbon product from hydrocracking as a function of reaction time

| Reaction Time<br>(hours) | Hydrocarbon Product<br>(%yield) |
|--------------------------|---------------------------------|
| 1                        | viscous material                |
| 1.5                      | 84.2                            |
| 2                        | 85.9                            |

#### 4.2.4 Effect of Catalyst Concentration

The study of catalyst concentration was performed by varying catalyst concentration between 10%, 15%, 20% and 40 % wt. The catalyst used in this study was Fe(5%)/Sn(5%)/F(2%) on molecular sieve catalyst, with a temperature of 350°C and 500 psig hydrogen pressure for 1.5 hours. GC analysis of the products are shown in Figures B4, B10 and Tables B7, B8, B23, B24. The percentage yields are in Table 4.4.

It was found that all products consisted of C5-C11 hydrocarbons and polynaphthene. Toluene, ethylbenzene and iso-propylbenzene were the main components. The main trend observed was that an increase in catalyst concentration had a beneficial effect in decreasing the amount of ethylbenzene, while the percentage yield was unchanged except for the run using 10% catalyst. As the differences in yields were marginal, a catalyst concentration of 15% by wt should be considered optimal.

Table 4.4 %Yield of hydrocarbon product from hydrocracking as a function of catalyst concentration

| Catalyst Concentration<br>(%wt) | Hydrocarbon Product<br>(%yield) |
|---------------------------------|---------------------------------|
| 10                              | viscous material                |
| 15                              | 84.8                            |
| 20                              | 85.2                            |
| 40                              | 85.9                            |

#### 4.2.5 Effect of Temperature

Effect of temperature study on the hydrocracking of used polystyrene was performed by operating at two reaction temperatures; 325°C and 350°C; using 15%wt of the Fe(5%)/Sn(5%)/F(2%) on molecular sieve catalyst, 500 psig hydrogen pressure for 1.5 hours reaction time. The percentage yields are shown in Table 4.5.

The result of %yield showed clearly that the optimal temperature was at 350°C



Table 4.5 %Yield of hydrocarbon product from hydrocracking as a function of reaction temperature

| Temperature<br>(°C) | Hydrocarbon Product<br>(%yield) |
|---------------------|---------------------------------|
| 325                 | viscous material                |
| 350                 | 84.8                            |

#### 4.2.6 Effect of Hydrogen Pressure

The effect of hydrogen pressure was studied by varying hydrogen pressures between 300, 350, 400 and 500 psig, using 15% wt of the Fe(5%)/Sn(5%)/F(2%) on molecular sieve catalyst and 350°C temperature (the optimum reaction temperature) for 1.5 hours (the optimum reaction time). The GC chromatograms and the composition of products are shown in Figures B4, B10 and Tables B9, B10, B25, B26. The percentage yields are shown in Table 4.6.

As seen in Figures 4.11 and 4.12, the products consisted of C8-C11 hydrocarbons and polynaphthene for hydrogen pressure at 350-400 psig and C6-C11 hydrocarbons and Polynaphthene for hydrogen pressure at 500 psig. They all had toluene, ethylbenzene and iso-propylbenzene as the main components. The main trend observed was that an increase in hydrogen pressure had a beneficial effect on the percentage yield of ethylbenzene. Hence, a pressure in the vicinity of 400 psig could be considered optimal.

Table 4.6 %Yield of hydrocarbon product from hydrocracking as a function of hydrogen pressure

| Hydrogen Pressure<br>(psig) | Hydrocarbon Product<br>(%yield) |
|-----------------------------|---------------------------------|
| 300                         | viscous material                |
| 350                         | viscous material                |
| 400                         | 85.6                            |
| 500                         | 84.8                            |

#### 4.2.7 Effect of Support

The effect of changing the support from molecular sieve to alumina support was tested. The reaction used a 15% wt of the Fe(5%)/Sn(5%)/F(2%) catalyst, 350°C temperature and 400 psig hydrogen pressure for 1.5 hours. The percentage yields are shown in Table 4.7.

It is obvious that the molecular sieve should be considered the optimal support. Moreover, it is cheaper than alumina support.

Table 4.7 %Yield of hydrocarbon product from hydrocracking as a function of support

| Support         | Hydrocarbon Product<br>(%yield) |
|-----------------|---------------------------------|
| molecular sieve | 85.6                            |
| alumina support | viscous material                |

### 4.3 Cracking Process under Nitrogen Pressure

The yield of hydrocarbon products from cracking under nitrogen are shown in Tables 4.8-4.11. The cracking was studied as a function of processing variables, i.e. reaction time, catalyst concentration, temperature and nitrogen pressure. Products were identified by GC.

#### 4.3.1 Effect of Reaction Time

The effect of reaction time was studied by varying reaction time between 5, 5.5 and 6 hours, operating at 350°C temperature, 40% wt of the Fe(5%)/Sn(5%)/F(2%) on molecular sieve catalyst and 150 psig nitrogen pressure. The GC chromatograms and composition of products are shown in Figures B5, B11 and Table B11, B12, B27, B28. The percentage yields are shown in Table 4.8.

It can be seen that the products consisted of C6-C11 hydrocarbons and polynaphthene after 6 hours and C6-C9 after 5.5 hours. The main components were toluene, ethylbenzene and iso-propylbenzene. The results showed clearly in both of the percentage yield and GC

chromatogram that the reaction time of 6 hours should be considered optimal.

**Table 4.8** %Yield of hydrocarbon product from cracking under nitrogen pressure as a function of reaction time

| Reaction Time<br>(hours) | Hydrocarbon Product<br>(%yield) |
|--------------------------|---------------------------------|
| 5                        | viscous material                |
| 5.5                      | 12.1                            |
| 6                        | 87.5                            |

#### 4.3.2 Effect of Catalyst Concentration

The effect of catalyst concentration was studied by varying catalyst concentration between 5%, 10%, 20% and 40 % wt. The process in this study used 350°C temperature, Fe(5%)/Sn(5%)/F(2%) on molecular sieve catalyst and 150 psig nitrogen pressure for 6 hours. The GC analysis of the products are shown in Figures B6, B12 and Tables B13, B14, B29, B30. The percentage yields are shown in Table 4.9.

The products were C6-C11 hydrocarbons and polynaphthene for 10%, 20% and 40 % wt, and C6-C9 hydrocarbons and polynaphthene for 5% wt while toluene, ethylbenzene and iso-propylbenzene were the main components. The yields were virtually the same using 10, 20 and 40 %wt of catalysts. Thus, due to the economic considerations, a catalyst concentration of 10% wt is considered optimal.

Table 4.9 %Yield of hydrocarbon product from cracking under nitrogen pressure as a function of catalyst concentration

| Catalyst Concentration<br>(% wt) | Hydrocarbon Product<br>(%yield) |
|----------------------------------|---------------------------------|
| 5                                | 25.1                            |
| 10                               | 85.1                            |
| 20                               | 85.5                            |
| 40                               | 87.5                            |

#### 4.3.3 Effect of Temperature

This was studied by using two different reaction temperatures, 325°C and 350°C, with 10%wt of the Fe(5%)/Sn(5%)/F(2%) on molecular sieve catalyst and 150 psig of nitrogen pressure for the optimum reaction time of 6 hours. The percentage yields are shown in Table 4.10.

The result of %yield showed clearly that the optimal temperature was 350°C.

Table 4.10 %Yield of hydrocarbon product from cracking under nitrogen pressure as a function of temperature

| Temperature<br>(°C) | Hydrocarbon Product<br>(%yield) |
|---------------------|---------------------------------|
| 325                 | viscous material                |
| 350                 | 87.5                            |

#### 4.3.4 Effect of Nitrogen Pressure

The effect of nitrogen pressure was studied by varying nitrogen pressures at 0, 50, 100 and 150 psig with operating conditions of 350°C (the optimum reaction temperature) and over 10% wt of the Fe(5%)/Sn(5%)/F(2%) on molecular sieve catalyst for 6 hours (the optimum reaction time). The GC chromatograms and composition of the products are shown in Figures B6, B12 and Tables B15, B16, B31, B32. The percentage yields are shown in Table 4.11.

The compositions of products was C6-C11 hydrocarbons and polynaphthene. They all had toluene, ethylbenzene and isopropylbenzene as the main components. Although, a 150 psig nitrogen pressure had a beneficial effect on the percentage yield due to economic considerations, nitrogen pressure at 100 psig should be considered optimal.



Table 4.11 %Yield of hydrocarbon product from cracking under nitrogen pressure as a function of temperature

| Nitrogen Pressure<br>(psig) | Hydrocarbon Product<br>(%yield) |
|-----------------------------|---------------------------------|
| 0                           | viscous material                |
| 50                          | viscous material                |
| 100                         | 84.3                            |
| 150                         | 87.5                            |

#### 4.4 Determination of Product Properties

The  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra of the products are shown in Figures B13 and B14. They indicate the presence paraffins and aromatic hydrocarbons.