

## **CHAPTER IV**

### **RESULT AND DISCUSSION**

The purpose of this research was to study catalytic effect of new catalyst type for depolymerization of polystyrene. A cracking process under hydrogen or nitrogen atmosphere used a bifunctional catalyst. Iron, nickel or cobalt was impregnated with tin and fluoride on molecular sieve. Zinc, lead or aluminium was impregnated with iron and fluoride on molecular sieve. The transition metals are active component in hydrocracking and hydrogenation reaction. Fluoride acts as a promoter by enhancing the activity of the acidic function. Molecular sieve was chosen as an acidic component because of its inexpensive and easy availability.

#### **4.1 Characterization of Catalysts**

The catalyst characterization data by X-ray fluorescence are shown in Figure A1-A8 and Table A1. It can be seen that the element concentrations vary were similar to the concentrations of the impregnated elements in a quantitative sense. They confirmed the impregnation of catalysts.

## 4.2 Hydrocracking Process

The hydrocracking reactions were studied as a function of the processing variables, i.e. catalyst type, temperature and pressure. The products were identified by GC. The main compositions of products were ethylbenzene, toluene, iso-propylbenzene and xylenes. Therefore, the suitable conditions were chosen to study the catalyst activity.

### 4.2.1 Effect of Catalyst Type

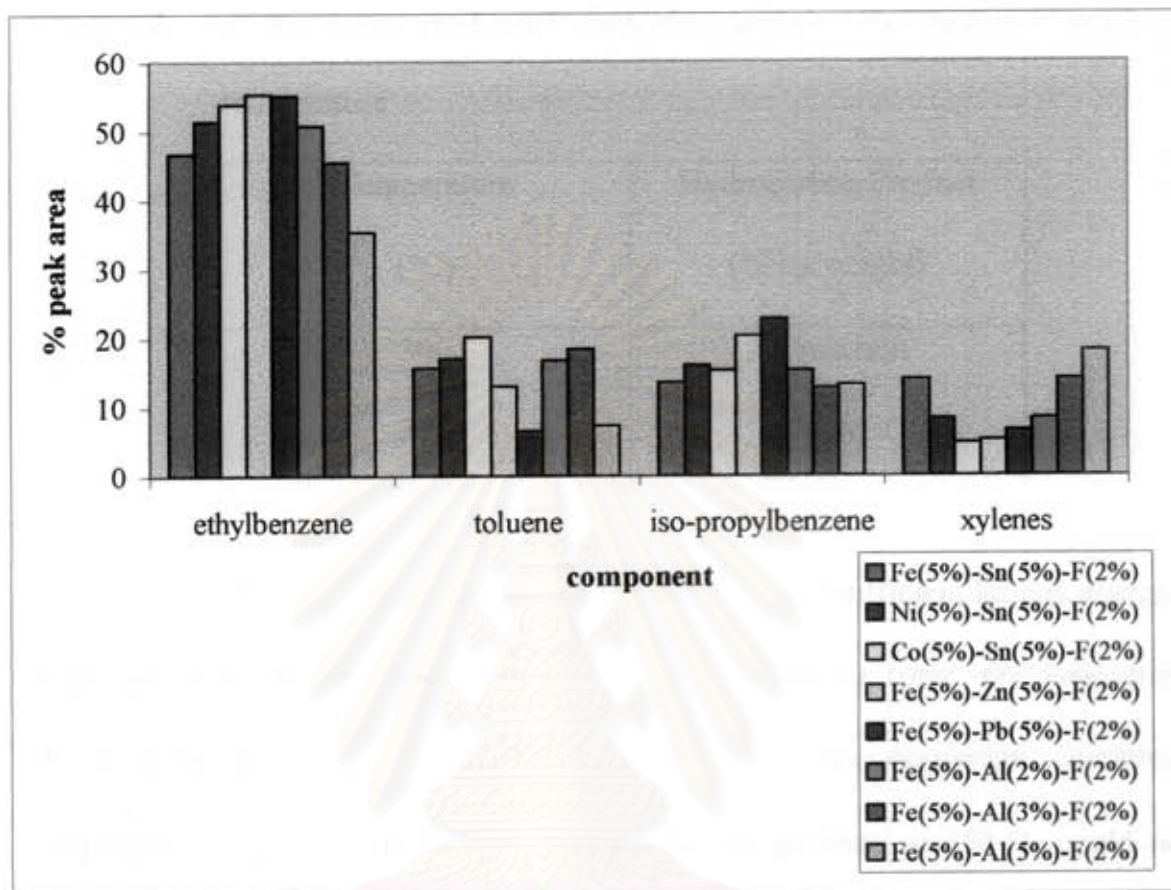
The effect of catalyst type on hydrocracking of used polystyrene was studied by using 15% by weight of Fe(5%)-Sn(5%)-F(2%), Ni(5%)-Sn(5%)-F(2%), Co(5%)-Sn(5%)-F(2%), Fe(5%)-Zn(5%)-F(2%), Fe(5%)-Pb(5%)-F(2%), Fe(5%)-Al(2%)-F(2%), Fe(5%)-Al(3%)-F(2%) or Fe(5%)-Al(5%)-F(2%) catalyst, initial hydrogen pressure of 400 psig at 350 °C for 90 minutes. The average percentage yields are shown in Table 4.1. The GC chromatograms and product compositions are shown in Figure C1-C8 and Table C1-C8. The comparison of main components of product of each catalyst is shown in Figure 4.1.

For all catalysts, the products were consisted of C<sub>6</sub>-C<sub>11</sub> hydrocarbons and polynaphthene, the major component was ethylbenzene. It was found that Ni(5%)-Sn(5%)-F(2%) gave the highest percentage yield followed by Co(5%)-Sn(5%)-F(2%) and Fe(5%)-Sn(5%)-F(2%). The comparison of the percentage

yields showed the significance of the tin component because  $\text{SnF}_2$  and  $\text{SnF}_4$  are Lewis acid that act as a promoter in the cracking and the isomerization by inducing  $\text{H}^-$  and releasing  $\text{H}^+$  to the surrounding.  $\text{Fe}(5\%)\text{-Zn}(5\%)\text{-F}(2\%)$  gave the lowest percentage yield because no tin was impregnated to enhance the acidity. It had the combination of Fe and Zn as a metallic component. In tin series, nickel was more effective than cobalt and iron catalyst, due to economic considerations,  $\text{Fe}(5\%)\text{-Sn}(5\%)\text{-F}(2\%)$  would be considered suitable to depolymerize polystyrene.

**Table 4.1** Hydrocarbon products from hydrocracking as a function of catalyst type

Catalyst Type	Hydrocarbon Product (% by weight)
$\text{Fe}(5\%)\text{-Sn}(5\%)\text{-F}(2\%)$	76.36
$\text{Ni}(5\%)\text{-Sn}(5\%)\text{-F}(2\%)$	77.46
$\text{Co}(5\%)\text{-Sn}(5\%)\text{-F}(2\%)$	77.18
$\text{Fe}(5\%)\text{-Zn}(5\%)\text{-F}(2\%)$	35.56
$\text{Fe}(5\%)\text{-Pb}(5\%)\text{-F}(2\%)$	58.24
$\text{Fe}(5\%)\text{-Al}(2\%)\text{-F}(2\%)$	67.58
$\text{Fe}(5\%)\text{-Al}(3\%)\text{-F}(2\%)$	60.44
$\text{Fe}(5\%)\text{-Al}(5\%)\text{-F}(2\%)$	42.00



**Figure 4.1** · Comparison of main components of products from hydrocracking as a function of catalyst type

#### 4.2.2 Effect of Temperature

The effect of temperature was studied by operating at temperature between 300 and 350 °C, using 15% by weight of Fe(5%)-Sn(5%)-F(2%) catalyst, 400 psig initial hydrogen pressure for 90 minutes. The average percentage yields are shown in Table 4.2.

**Table 4.2** Hydrocarbon products from hydrocracking as a function of reaction temperature

Temperature (°C)	Hydrocarbon Product (% by weight)
300	No reaction
350	76.36

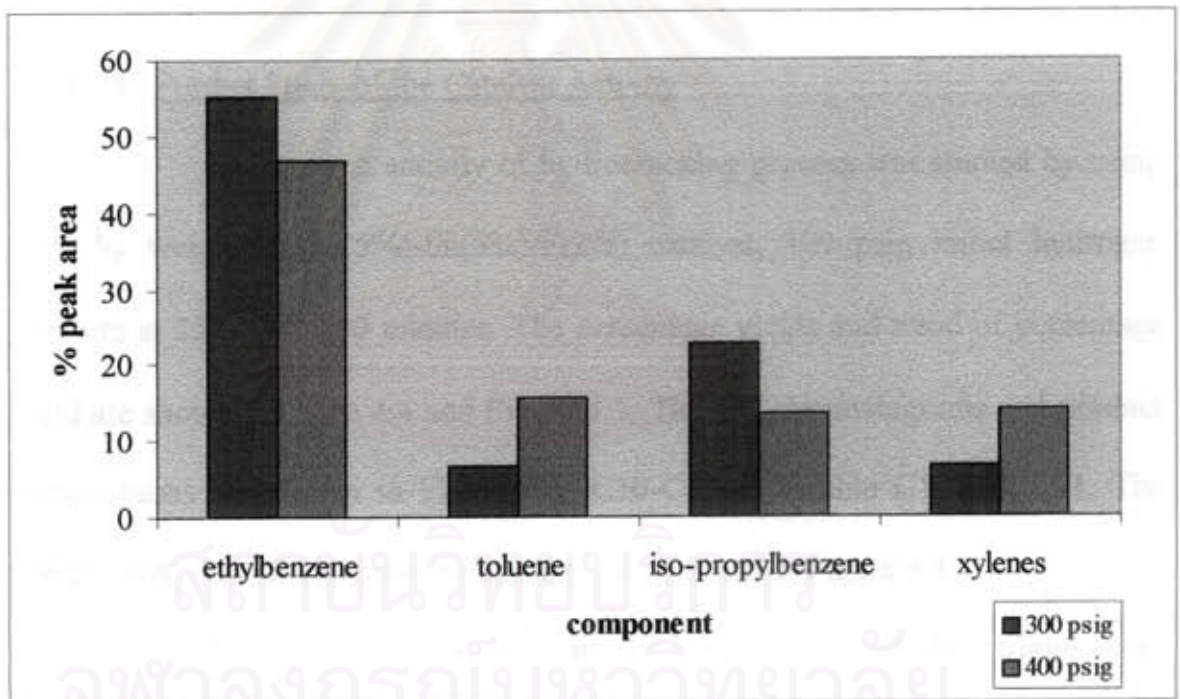
At 300 °C, polystyrene molecules have not sufficient kinetic energy, their collisions cannot cause chemical bonds to break or form, not producing chemical reaction. The temperature of 350 °C is the maximum operating temperature of the reactor. In this research, the temperature of 350 °C could be considered optimal.

#### 4.2.3 Effect of Hydrogen Pressure

The effect of hydrogen pressure was studied by varying initial hydrogen pressure between 300 and 400 psig, using 15% by weight of Fe(5%)-Sn (5%)-F(2%) catalyst and at 350 °C for 90 minutes. The average percentage yields are shown in Table 4.3. The GC chromatograms and product compositions are shown in Figure C1, C9 and Table C1, C9. The comparison of main components of product is shown in Figure 4.2.

**Table 4.3** Hydrocarbon products from hydrocracking as a function of hydrogen pressure

Hydrogen Pressure (psig)	Hydrocarbon Product (% by weight)
300	64.66
400	76.36



**Figure 4.2** Comparison of main components of products from hydrocracking as a function of hydrogen pressure

The products were consisted of C<sub>6</sub>-C<sub>11</sub> hydrocarbons and polynaphthene. The major component was ethylbenzene. Table 4.3 and Figure 4.2 showed that the initial hydrogen pressure at 400 psig gave higher percentage yield than the pressure at 300 psig. From Khomentrakarn's research [18] the initial hydrogen pressure at 400 psig was the optimum pressure for hydrocracking polystyrene. Hence, the initial hydrogen pressure of 400 psig was indicated the satisfaction and could be considered optimal.

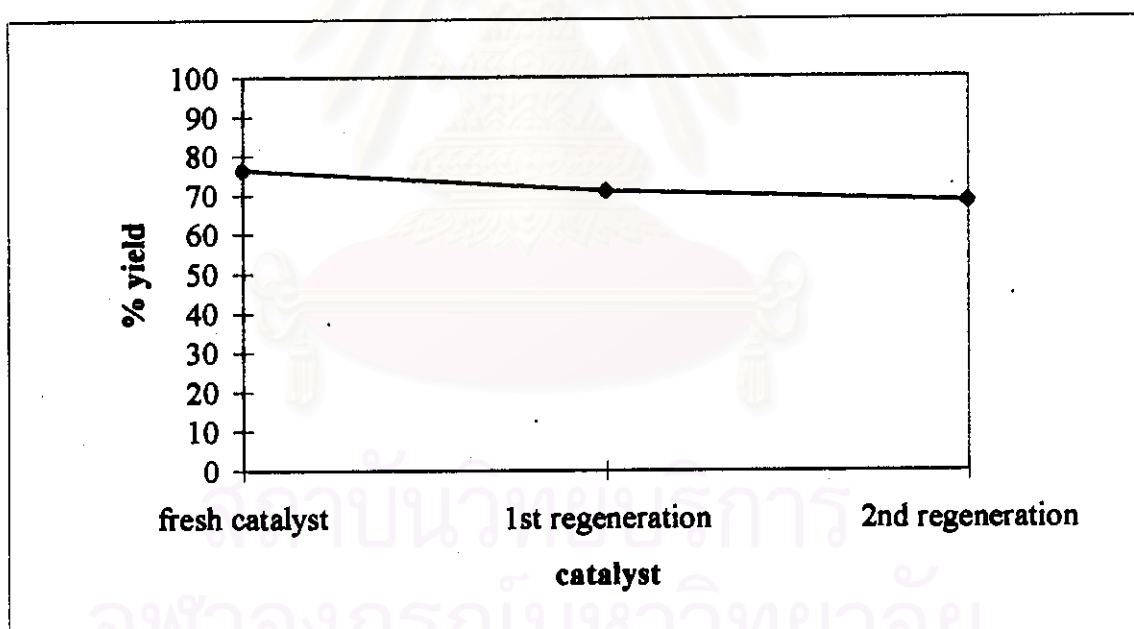
#### 4.2.4 Further Study of the Catalyst Activity

The catalyst activity of hydrocracking process was studied by using 15% by weight of Fe(5%)-Sn(5%)-F(2%) catalyst, 400 psig initial hydrogen pressure at 350 °C for 90 minutes. The percentage yields and trend of percentage yield are shown in Table 4.4 and Figure 4.3. The GC chromatograms and product compositions are shown in Figure C1, C10-C11 and Table C1, C10-C11. The comparison of main components of products is shown in Figure 4.4.

The products were consisted of C<sub>6</sub>-C<sub>11</sub> hydrocarbons and polynaphthene. Ethylbenzene was a major component. As seen in Figure 4.3 and 4.4, the percentage yield decreased gradually and it was no significant change in the composition of the products. Thus, it could be concluded that the catalyst could be reused without losing efficiency for a limited number of times.

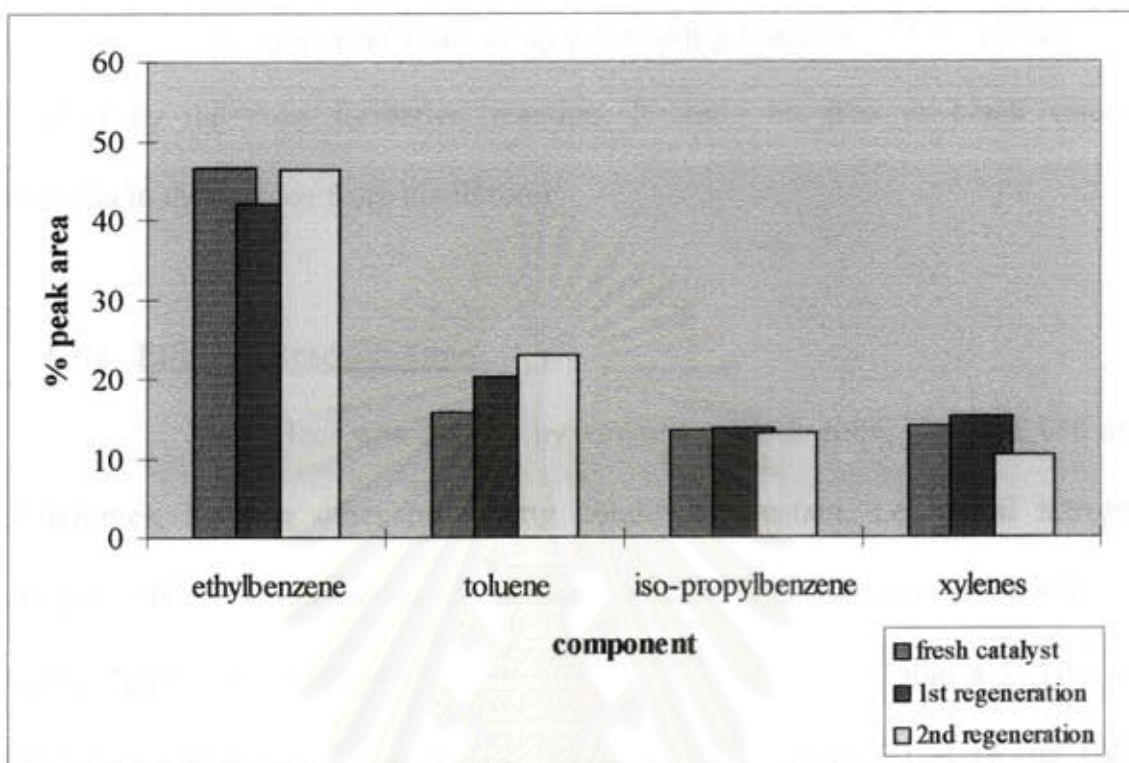
**Table 4.4** Hydrocarbon products from studying the catalyst activity of hydrocracking process

Catalyst	Hydrocarbon Product (% by weight)
fresh catalyst	76.36
1 <sup>st</sup> regeneration	70.90
2 <sup>nd</sup> regeneration	68.39



**Figure 4.3** Trend of percentage yield of hydrocarbon products from studying the catalyst activity of hydrocracking process





**Figure 4.4** Comparison of main components of products from studying the catalyst activity of hydrocracking process

### 4.3 Cracking Process under Nitrogen Pressure

The cracking process was studied as a function of processing variables, i.e. reaction time, nitrogen pressure, reaction temperature, catalyst type and catalyst concentration. The products were identified by GC. The main components of products were ethylbenzene, toluene, iso-propylbenzene and xylenes. The suitable conditions were chosen to study the catalyst activity.

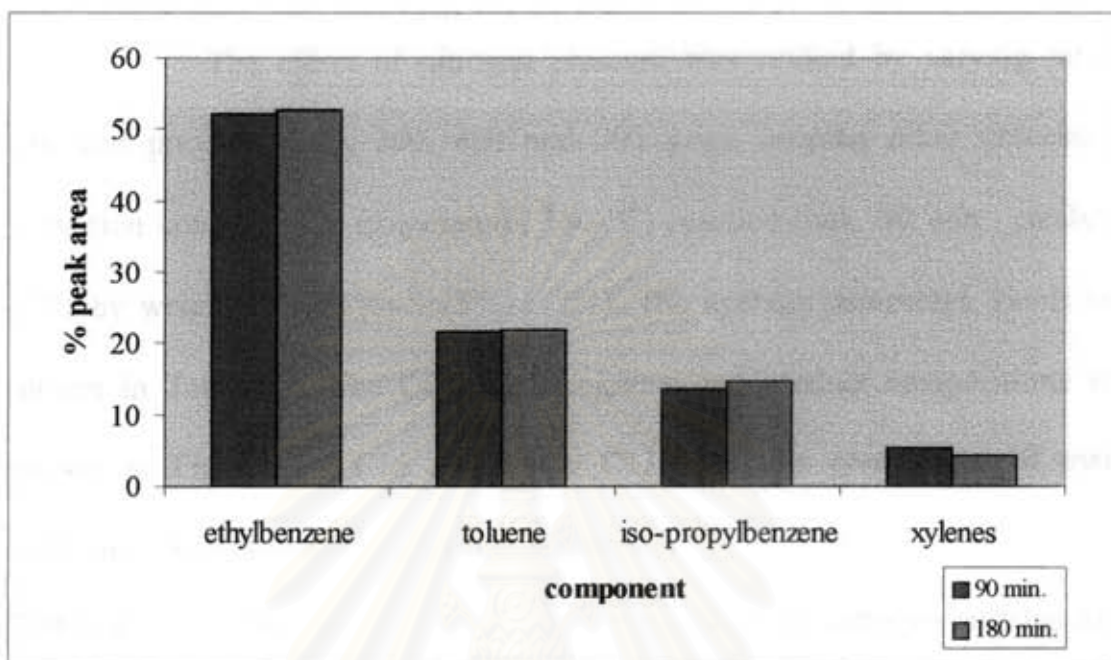
The hydrogen atom in hydrocracking reaction of this process was supplied by the coke formation reaction. It could be seen as black viscous materials in the residue from distillation.

#### 4.3.1 Effect of Reaction Time

This effect was studied by varying reaction time, between 180 and 90 minutes, keeping other processing condition constant, i.e. initial nitrogen pressure, 500 psig; temperature, 350 °C; catalyst, 15% by weight of Fe(5%)-Sn(5%)-F(2%). The average percentage yields are shown in Table 4.5. The GC chromatograms and product compositions are shown in Figure C12-C13 and Table C12-C13. The comparison of main components of products is shown in Figure 4.5.

**Table 4.5** Hydrocarbon products from cracking under nitrogen pressure as a function of reaction time

Reaction Time (min.)	Hydrocarbon Product (% by weight)
90	78.12
180	81.76



**Figure 4.5** Comparison of main components of products from cracking under nitrogen pressure as a function of reaction time

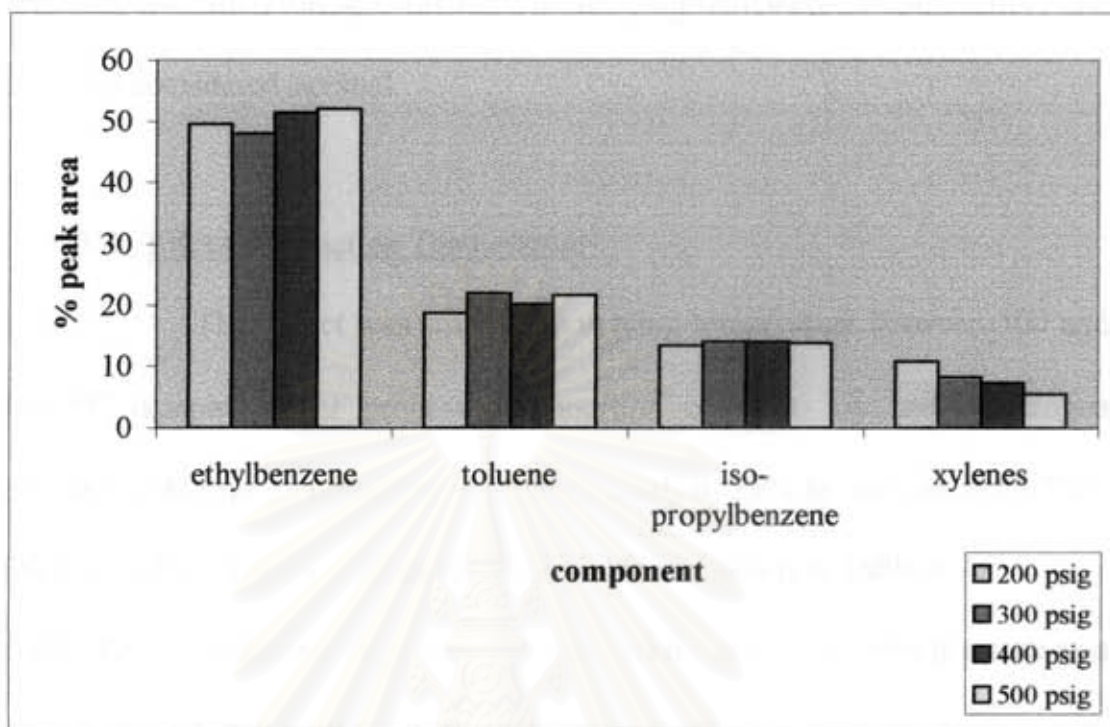
The products were consisted of  $C_6$ - $C_{11}$  hydrocarbons and polynaphthene. The major component was ethylbenzene. As seen in Table 4.5 and Figure 4.5, the percentage yields and the main components of the products from the reaction times of 180 and 90 minutes are not outstandingly different. It could be concluded that the reaction time of 90 minutes could be considered optimal.

### 4.3.2 Effect of Nitrogen Pressure

The effect of nitrogen pressure was studied by varying initial nitrogen pressure (200, 300, 400 and 500 psig), keeping other processing condition constant, i.e. temperature, 350 °C; reaction time, 90 min.; catalyst, 15% by weight of Fe(5%)-Sn(5%)-F(2%). The average percentage yields are shown in Table 4.6. The GC chromatograms and product compositions are shown in Figure C13-C16 and Table C13-C16. The comparison of main components of products is shown in Figure 4.6.

**Table 4.6** Hydrocarbon products from cracking under nitrogen pressure as a function of nitrogen pressure

Nitrogen Pressure (psig)	Hydrocarbon Product (% by weight)
200	59.38
300	75.48
400	75.60
500	78.12



**Figure 4.6** Comparison of main components of products from cracking under nitrogen pressure as a function of nitrogen pressure

The products were comprised of  $C_6$ - $C_{11}$  hydrocarbons and polynaphthene. Ethylbenzene was the major component. As seen in Table 4.6, the increase in nitrogen pressure has a beneficial effect on increasing the yield of depolymerized product because the nitrogen pressure probably enforced the liquid polystyrene into the pore of molecular sieve. At high pressure, the liquid polystyrene can diffuse into the pore of molecular sieve and can be absorbed at the active sites more than low pressure. Due to the percentage yields from the initial nitrogen pressure of 300, 400 and 500 psig are not outstandingly

different, the initial nitrogen pressure of 300 psig indicated the satisfaction, and could be considered optimal.

#### 4.3.3 Effect of Reaction Temperature

This effect was studied by varying temperature between 300 and 350 °C, keeping other processing condition constant, i.e. initial nitrogen pressure, 300 psig; reaction time, 90 min.; catalyst, 15% by weight of Fe(5%)-Sn(5%)-(F2%). The average percentage yields are shown in Table 4.7.

**Table 4.7** Hydrocarbon products from cracking under nitrogen pressure as a function of reaction temperature

Temperature (°C)	Hydrocarbon Product (% by weight)
300	No reaction
350	75.48

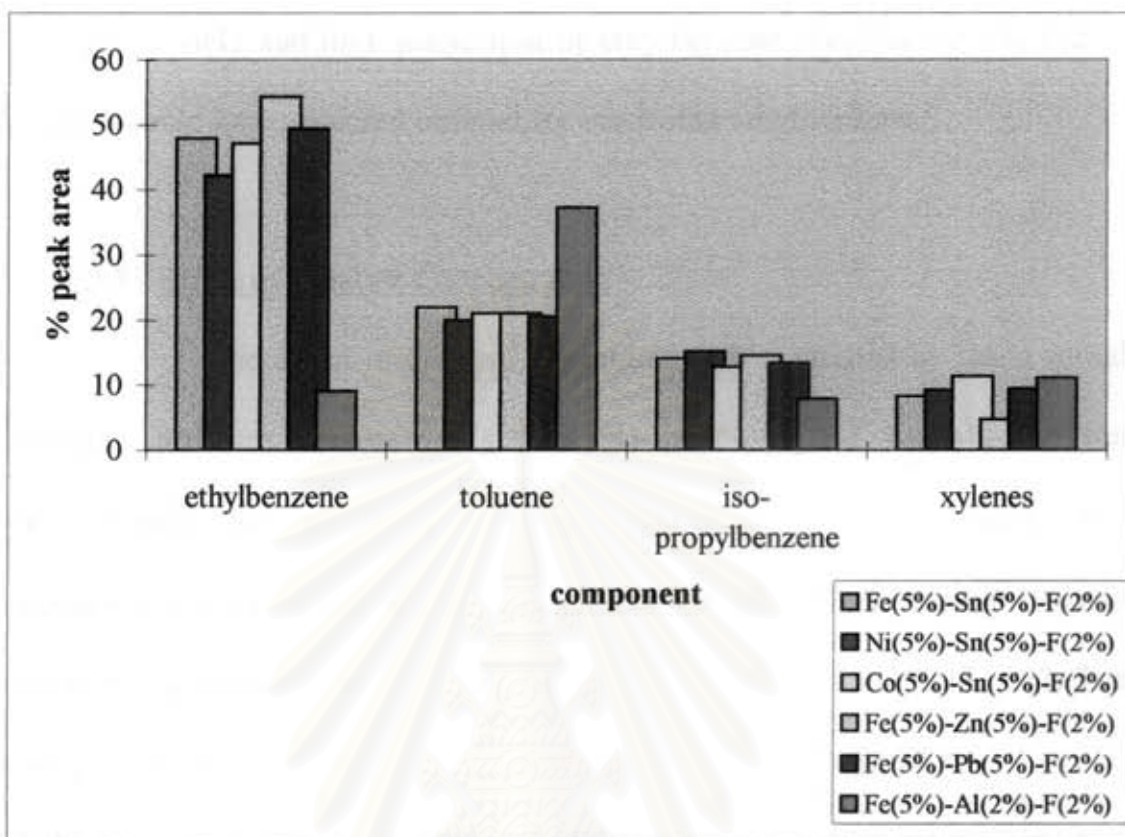
At 300 °C, polystyrene molecules have not sufficient kinetic energy, their collisions cannot cause chemical bonds to break or form, not producing a chemical reaction. The temperature of 350 °C is the maximum operating temperature of the high pressure reactor. In this research, the temperature of 350°C could be considered optimal.

#### 4.3.4 Effect of Catalyst Type

The effect of catalyst type was studied by using 15% by weight of various catalyst types (Fe(5%)-Sn(5%)-F(2%), Ni(5%)-Sn(5%)-F(2%), Co(5%)-Sn(5%)-F(2%), Fe(5%)-Zn(5%)-F(2%), Fe(5%)-Pb(5%)-F(2%) and Fe(5%)-Al(2%)-F(2%)) and keeping other processing condition constant, i.e. temperature, 350 °C; initial nitrogen pressure, 300 psig; reaction time, 90 min. The average percentage yields are shown in Table 4.8. The GC chromatograms and product compositions are shown in Figure C13, C17-C21 and Table C13, C17-C21. The comparison of main components of products is shown in Figure 4.7.

**Table 4.8** Hydrocarbon products from cracking under nitrogen pressure as a function of catalyst type

Catalyst Type	Hydrocarbon Product (% by weight)
Fe(5%)-Sn(5%)-F(2%)	75.48
Ni(5%)-Sn(5%)-F(2%)	69.44
Co(5%)-Sn(5%)-F(2%)	68.56
Fe(5%)-Zn(5%)-F(2%)	74.58
Fe(5%)-Pb(5%)-F(2%)	71.22
Fe(5%)-Al(2%)-F(2%)	73.98



**Figure 4.7** Comparison of main components of products from cracking under nitrogen pressure as a function of catalyst type

It was found that Fe(5%)-Sn(5%)-F(2%) gave the highest percentage yield. For all catalysts, the product were comprised of C<sub>6</sub>-C<sub>11</sub> hydrocarbons and polynaphthene. As seen in Figure 4.7, ethylbenzene was the major component for Fe(5%)-Sn(5%)-F(2%), Ni(5%)-Sn(5%)-F(2%), Co(5%)-Sn(5%)-F(2%), Fe(5%)-Zn(5%)-F(2%) and Fe(5%)-Pb(5%)-F(2%), while toluene was the major component for Fe(5%)-Al(2%)-F(2%). Fe(5%)-Zn(5%)-F(2%) gave the highest proportions of ethylbenzene. Due to the highest



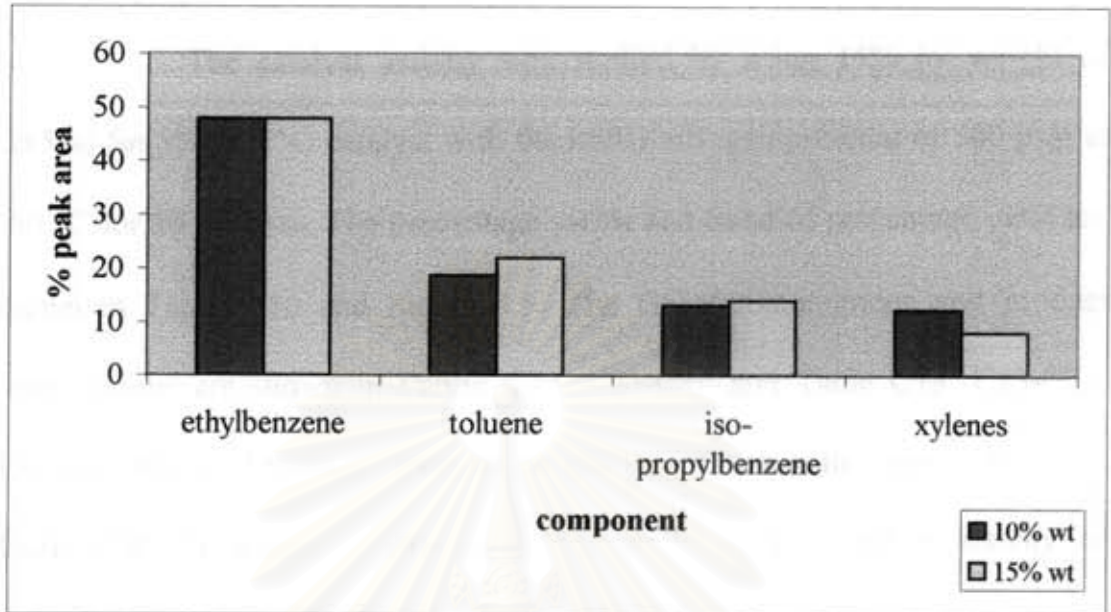
percentage yield and high proportion of ethylbenzene, Fe(5%)-Sn(5%)-F(2%) catalyst could be considered optimal for producing ethylbenzene.

#### 4.3.5 Effect of Catalyst Concentration

The effect of catalyst concentration was studied by using initial nitrogen pressure of 300 psig, Fe(5%)-Sn(5%)-F(2%) catalyst varying concentrations between 10 and 15% by weight at 350 °C for 90 minutes. The average percentage yields are shown in Table 4.9. The GC chromatograms and product compositions are shown in Figure C13, C22 and Table C13, C22. The comparison of main components of products is shown in Figure 4.8.

**Table 4.9** Hydrocarbon products from cracking under nitrogen pressure as a function of catalyst concentration

Catalyst Concentration (% by weight)	Hydrocarbon Product (% by weight)
10	60.64
15	75.48



**Figure 4.8** Comparison of main components of products from cracking under nitrogen pressure as a function of catalyst concentration

The products were  $C_5$ - $C_{11}$  hydrocarbons and polynaphthene for 10% by weight and  $C_6$ - $C_{11}$  hydrocarbons and polynaphthene for 15% by weight. The major component was ethylbenzene. Toluene, iso-propylbenzene and xylenes were the second, the third and the fourth major components, respectively. As seen in Table 4.9, the increase in catalyst concentration had an effect on increasing the percentage yield. Figure 4.8 show that the main components of the products are not outstandingly different. Therefore, the catalyst concentration of 15% by weight could be considered optimal.

#### 4.3.6 Further Study of the Catalyst Activity

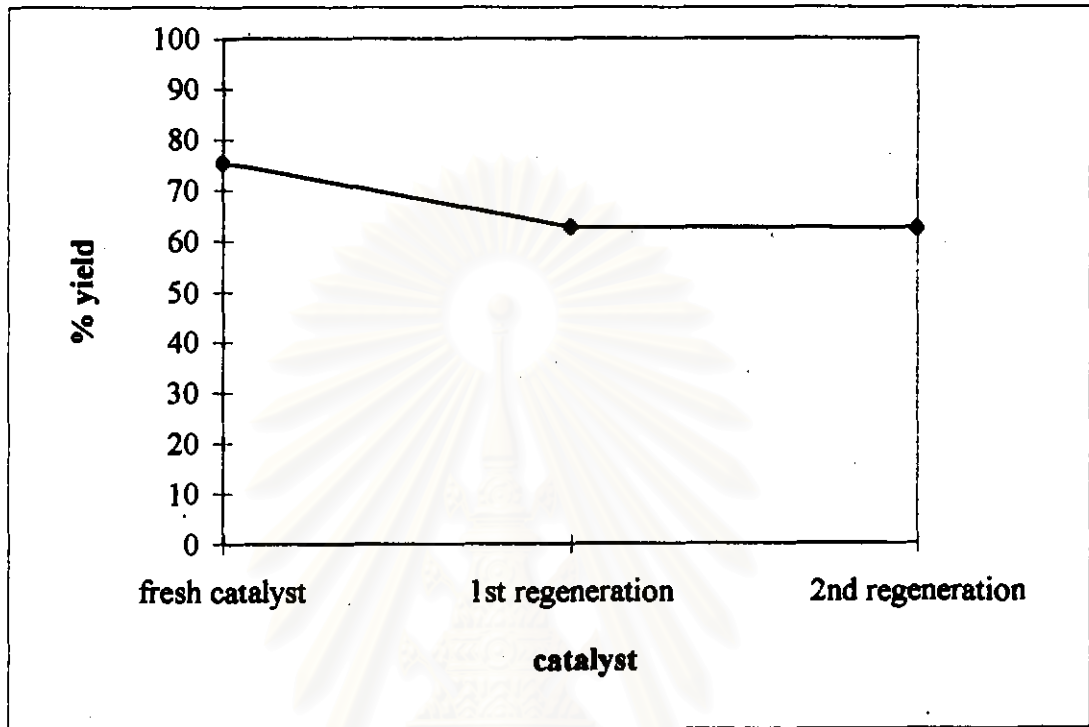
The catalyst activity was studied by using 15% by weight of Fe(5%)-Sn(5%)-F(2%) catalyst with the initial nitrogen pressure of 300 psig at 350 °C for 90 minutes. The percentage yields and trend of percentage yield are shown in Table 4.10 and Figure 4.9. The GC chromatograms and product compositions are shown in Figure C13, C23-C24 and Table C13, C23-C24. The comparison of main components of products is shown in Figure 4.10.

**Table 4.10** Hydrocarbon products from studying the catalyst activity of cracking under nitrogen pressure

Catalyst	Hydrocarbon Product (% by weight)
fresh catalyst	75.48
1 <sup>st</sup> regeneration	62.71
2 <sup>nd</sup> regeneration	62.50

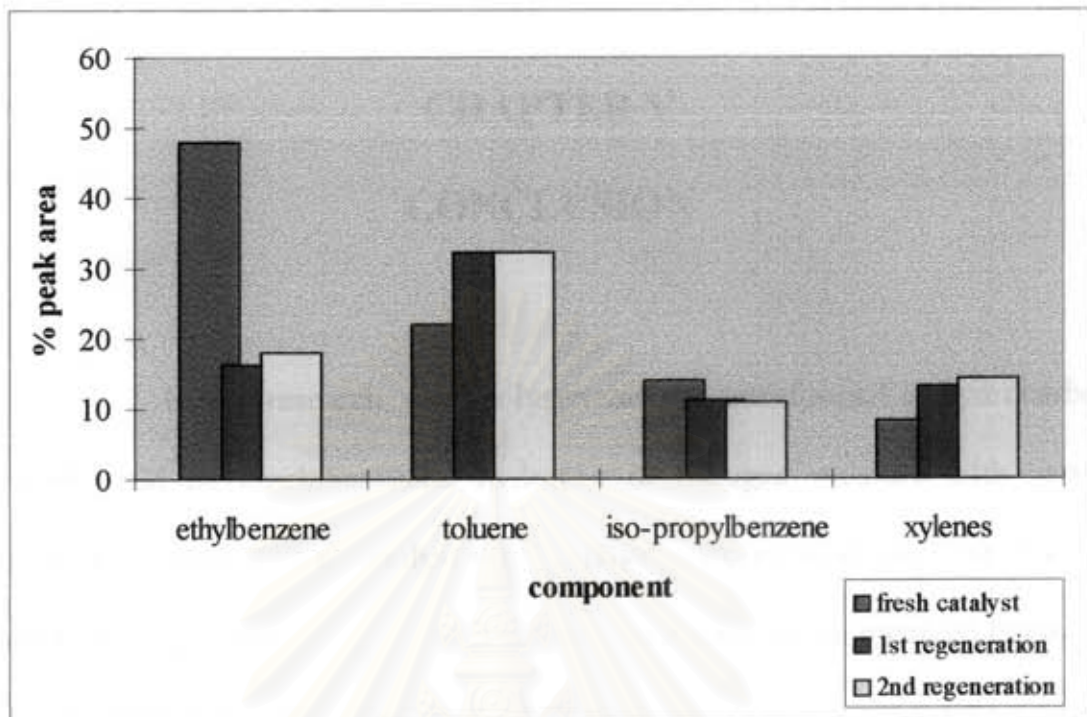
The products were C<sub>6</sub>-C<sub>11</sub> hydrocarbons and polynaphthene. From Table 4.10 and Figure 4.9, the percentage yield between fresh catalyst and the 1<sup>st</sup> regeneration catalyst decreased steeply because of the coke formation on the catalyst surface. From Figure 4.10, ethylbenzene was the major component for fresh catalyst. For the 1<sup>st</sup> and the 2<sup>nd</sup> regenerated catalyst, ethylbenzene and iso-propylbenzene decreased, while toluene was found to be the major component because the catalyst surface was attached by coke. It

reduced pore size of molecular sieve and changed product selectivity of the catalyst.



**Figure 4.9** Trend of percentage yield of hydrocarbon products from studying the catalyst activity of cracking under nitrogen pressure

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**Figure 4.10** Comparison of main components of products from studying catalyst activity of cracking under nitrogen pressure

#### 4.4 Reproducibility of Cracking Process

All experiments except the experiments for further study of the catalyst activity were repeated twice. The percentage yields of the first and the second experiments should not differ more than approximately 5%. If they differ more than 5%, the third experiment was done. The two experiments that have nearly percentage yields were chosen. The percentage yields and the average percentage yields are shown in Table B1-B6. It can be seen that the percentage yields are not outstandingly different. It could be assumed that the processes were reproducible.