

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Investigation of Continuous Aromatization Reaction

The continuous aromatization reaction of *n*-hexane under various reaction temperatures at different feeding rates of reactant and the catalyst concentration was performed. In this study, a homemade continuous reactor was designed and invented for aromatization reaction. The most important part of the reactor is a “packed catalyst column”. All studies in this research had been using this column (120 cm. long with 1/4 inches O.D., 15.75 cm³). This column can be packed with 10 grams of catalysts.

The continuous aromatization reactor was tested using the optimum catalyst from P. Prommart's research (0.6% Pt and 0.5% F/Al₂O₃). The column inventions are related to a process for converting hexane to aromatic hydrocarbons. The temperature was controlled at 400°C and 450°C and feeding rates are varied between 0.2 to 1.0 ml/min. The products of each reaction were characterized by gas chromatographic technique

The results of the variation of feeding rates are shown in Tables B1 and B2 in appendix, and are plotted as curves in Figures 4.1 and 4.2, respectively.

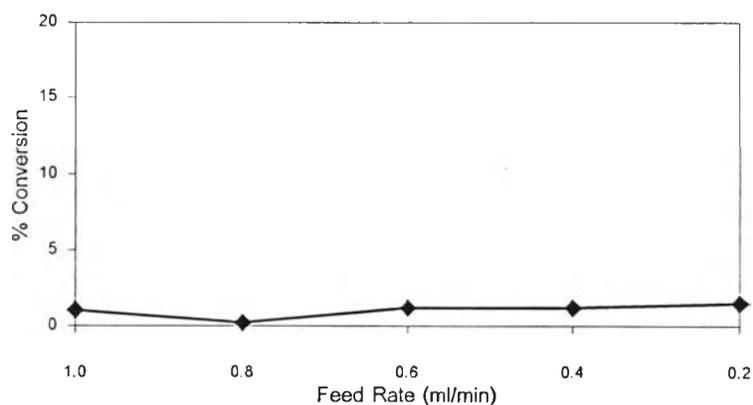


Figure 4.1 The efficiency test of the continuous reactor using 0.6% Pt - 0.5% F/Al₂O₃ under various feeding rates at 400°C

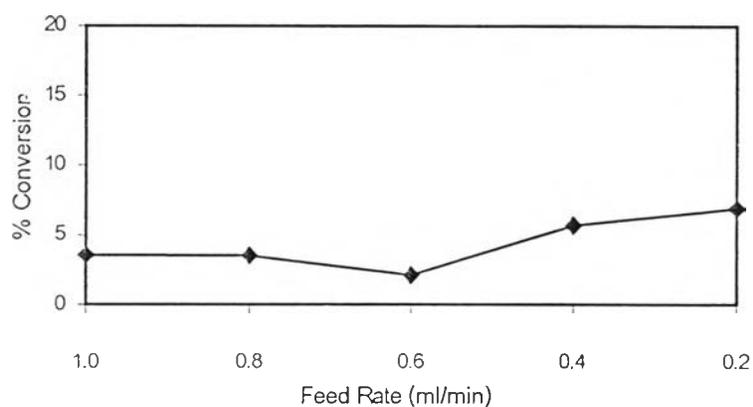


Figure 4.2 The efficiency test of the continuous reactor using 0.6% Pt - 0.5% F/Al₂O₃ under various feeding rates at 450°C

From the percentage of conversion, detected in the variation of temperatures and feeding rates, the results showed that the continuous aromatization could be controlled. In Figure 4.1 and Figure 4.2, the hexane could be converted to other compounds. The products were unstable and decomposed

immediately. The reaction activity at 400°C was lower than 450°C, due to the reaction energy. It could be seen that, in both reaction temperatures, Pt-F/Al₂O₃ catalyst could not aromatize *n*-hexane effectively. The high reaction temperature may increase the rate of aromatization but it was not recommended because it needed very high energy.

4.2 Synthesis of Zn/ZSM-5 by Ion Exchange Method

1) Preparation of Fully Hydrated Zeolite

Fully hydrated zeolite ZSM-5 was prepared by stored in saturated ammonium chloride solution in a desicator for certain time. The result was shown in Table 4.1.

Table 4.1. The results showing weight of hydrated Na/ZSM-5 at various storage times.

Storage time (hours)	Weight (g)
0	10.0219
24	10.1787
48	10.2107
60	10.2135
72	10.2151
86	10.2158
96	10.2155
108	10.2159

The variations of times are shown in Table 4.1. The result of this experiment showed that between 86-108 hours, the difference of the hydrated zeolite weight are too small ($\pm 0.0005\%$). Therefore, the recommendation time for fully hydration is about at least 4 days (96 hours).

2) Ion exchange Na/ZSM-5 by $ZnCl_2$

Normal zeolite can be subjected to cation exchanged by transition metal. Zeolite Na/ZSM-5 was cation exchanged with $ZnCl_2$ to produce Zn/ZSM-5. The reaction equation was shown below.



$ZnCl_2$ was used to prepared 10% Zn/ZSM-5. To find out the optimal time of ion exchanging, Na/ZSiM-5 was suspended into the $ZnCl_2$ solution and the mixture was stirred at $100^\circ C$. Ion-exchanged ZSM-5 was collected at 8, 12 and 15 hrs of stirring. The exchanged ZSM-5 was then measured for the concentration of Zn by XRF technique.

The result of variations was shown in Table 4.2.

Table 4.2. Relationship between concentration of zinc in ZSM-5 and various ion exchange times.

Time (hours)	% Zn
8	7.1
12	7.6
15	8.0

From the results in Table 4.2, it shows that the ion exchange time at 15 hours give the maximum concentration. This optimum condition was also used for palladium ion exchange.

3) Ion exchange Na/ZSM-5 by PdCl₂

3%Pd/ZSM-5 exchange was prepared using ion exchange reaction of PdCl₂ in the same manner for the preparation of Zn/ZSM-5 (15 hrs. and 100°C). Then the Pd content in Pd/ZSM-5 was investigated by XRF.

The results indicated that Pd/ZSM-5 prepared under this condition contained 2.28% of Pd by weight. Furthermore, the catalysts with 2%Pd/ZSM-5, 1%Pd/ZSM-5, and 0.5%Pd/ZSM-5 were prepared in the same manner.

4.3 The Efficiency of Zn/ZSM-5 Catalyst

The efficiency of continuous aromatization using 8% Zn/ZSM-5 catalyst was shown in Table B3, Table B4 in appendix and in Figure 4.3 and Figure 4.4.

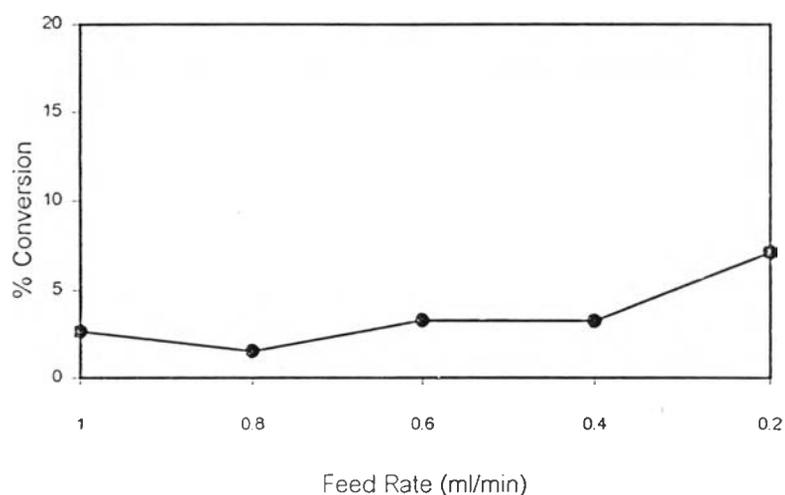


Figure 4.3 The efficiency of continuous aromatization using 8% Zn/ZSM-5 catalyst under various feeding rates at 400°C

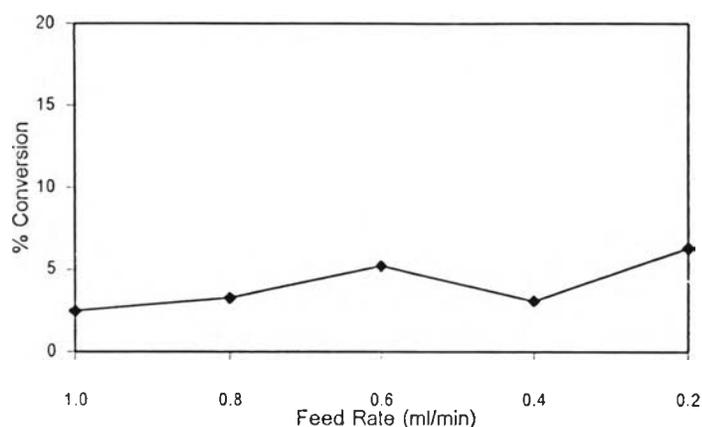


Figure 4.4 The efficiency of continuous aromatization using 8% Zn/ZSM-5 catalyst under various feeding rates at 450°C

These results showed that *n*-hexane was converted to other products, however the aromatic products were not observed. These results indicated that the activity and acidic properties of Zn/ZSM-5 may not be high enough and could cleave *n*-hexane to give C₂, C₃, and C₄ hydrocarbons, which were too volatile to be trapped in the cooling reservoir [18].

4.4 The Efficiency of Pd/ZSM-5 Catalysts

4.4.1 Effect of Temperatures and Feeding Rates

The study of the effects of temperatures and feeding rates in aromatization of *n*-hexane was performed by using various reaction temperatures (200, 250, 300, 350, 400, and 450 °C) on 2%Pd/ZSM-5 catalyst under the various feeding rates.

The results are given in Table B5, B6, B7, B8, B9 and B10 in appendix, and are shown in Figure 4.5, 4.6, 4.7, 4.8, 4.9 and 4.10, respectively.

The results of *n*-hexane aromatization over 2%Pd/ZSM-5 under reaction temperatures at 200 and 250 °C are presented (Figure 4.5 and 4.6). These results show that the aromatization of *n*-hexane requires more severe condition. The temperature at 250°C was not high enough to convert *n*-hexane in this continuous reactor.

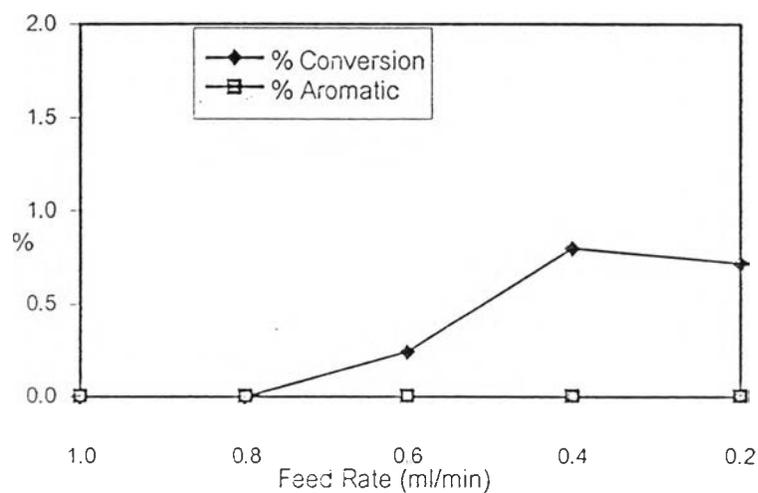


Figure 4.5 The percentage of conversion and aromatics from *n*-hexane aromatization using 2%Pd/ZSM-5 as catalyst under various feeding rates at 200°C

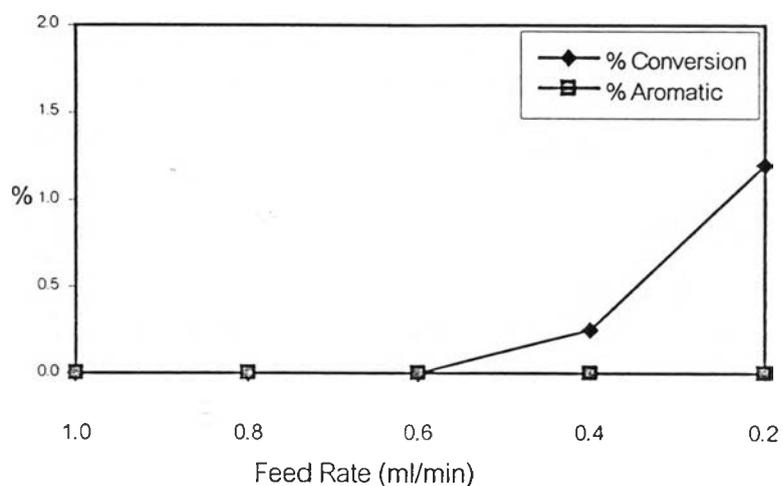


Figure 4.6 The percentage of conversion and aromatics from *n*-hexane aromatization using 2%Pd/ZSM-5 as catalyst under various feeding rates at 250°C

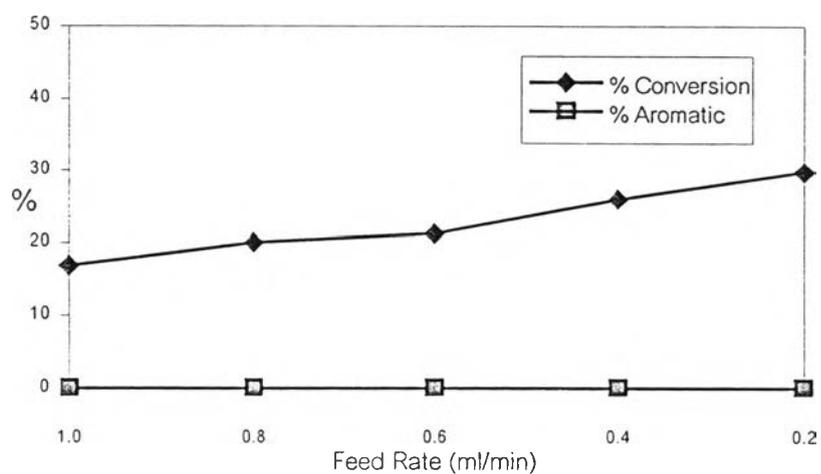


Figure 4.7 The percentage of conversion and aromatics from *n*-hexane aromatization using 2%Pd/ZSM-5 as catalyst under various feeding rates at 300°C

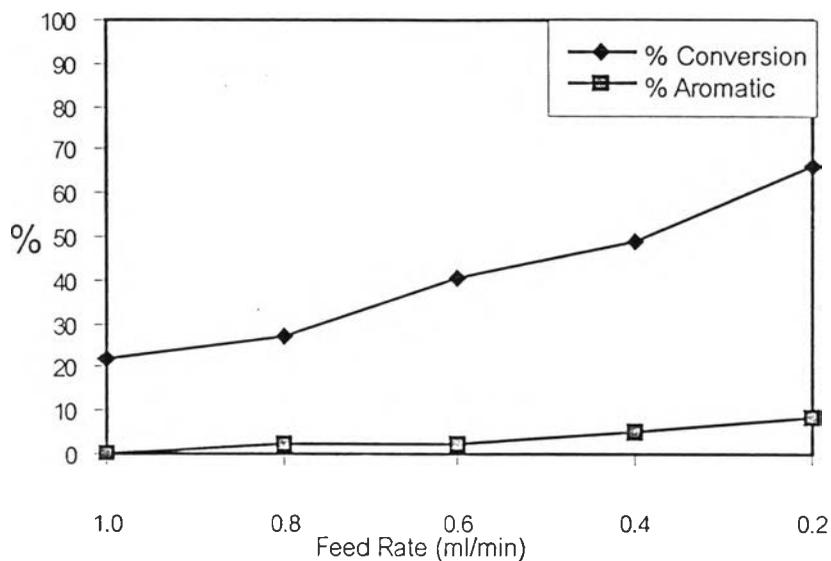


Figure 4.8 The percentage of conversion and aromatics from *n*-hexane aromatization using 2%Pd/ZSM-5 as catalyst under various feeding rates at 350°C

The results from *n*-hexane aromatization using 2% Pd/ZSM-5 as catalyst at 300 and 350°C under various feeding rates indicated that the reaction temperature at 350°C was minimum for *n*-hexane aromatization. Nevertheless, at 300°C *n*-hexane was converted to other products with low conversion.

The results of *n*-hexane aromatization at 400 and 450°C are shown in Table B9 and B10 and also presented in Figure 4.9 and Figure 4.10.

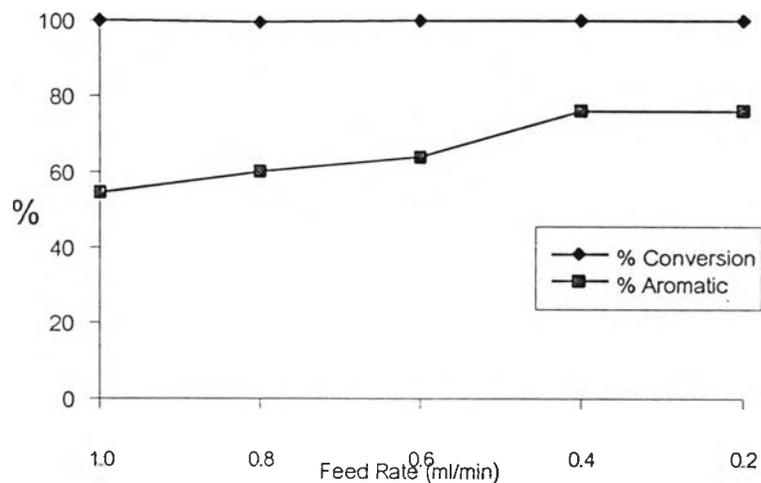


Figure 4.9 The percentage of conversion and aromatics from *n*-hexane aromatization using 2%Pd/ZSM-5 as catalyst under various feeding rates at 400°C

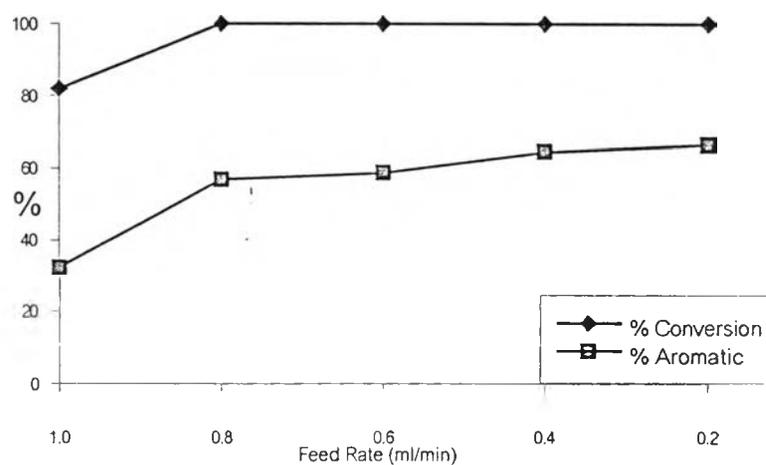


Figure 4.10 The percentage of conversion and aromatics from *n*-hexane aromatization using 2%Pd/ZSM-5 as catalyst under various feeding rates at 450°C

The results in Figure 4.9 indicate that at 400°C the aromatic products could be formed. The high-energy molecules can crossover energy barrier yielding the expected aromatic products. At higher temperatures (450°C), percentage of aromatic products was lower than reaction temperature at 400°C. From these results, it can be explained that the aromatic products could be degraded yielding back the small hydrocarbon molecule as the cracking products because of the high-energy [19].

Additionally, the curves in Figure 4.8 and 4.9 suggested that at lower temperature (400°C), the energy of system were not enough to achieve the activation energy to crossover the energy barrier for aromatization of *n*-hexane [11].

Finally, the percentages of aromatic products at various reaction temperatures were compared. (See Figure 4.11)

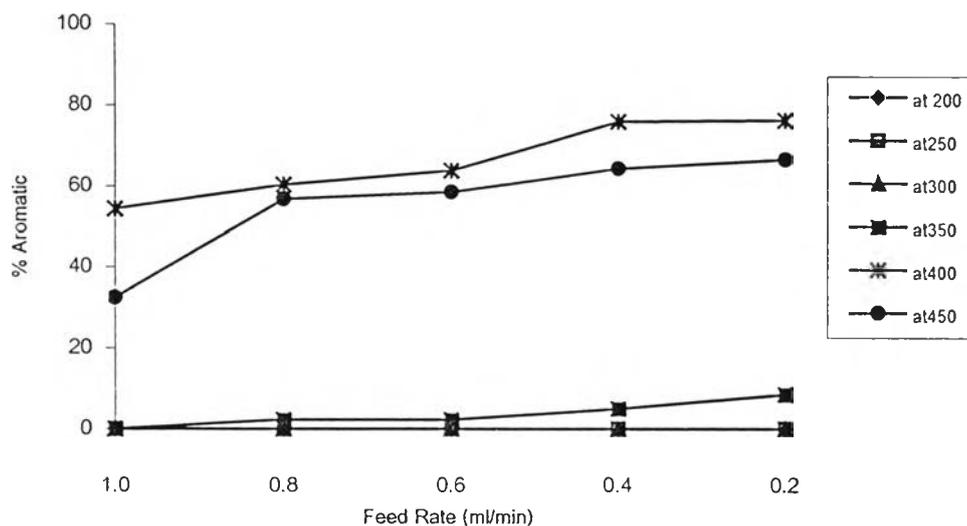


Figure 4.11 The comparison of percent aromatics from *n*-hexane aromatization using 2% Pd/ZSM-5 as catalyst under various feeding rates at the different temperatures.

From Figure 4.11, the results indicated that the optimum temperature for *n*-hexane aromatization using 2%Pd/ZSM-5 as catalyst was 400°C. The suitable feeding rate for the continuous reactor was 0.4 ml/min. For 200, 250 and 300°C, they produce only trace amount of aromatic and the graphs are superimposed together at the bottom.

4.4.2 Effect of Catalyst Concentration

The effect of catalyst concentration for aromatization of *n*-hexane was investigated at various reaction temperatures (300, 350, 400, and 450°C) on Pd (0.5, 1.0, and 2.0%) in ZSM-5 supports under 0.4 ml/min of feeding rate.

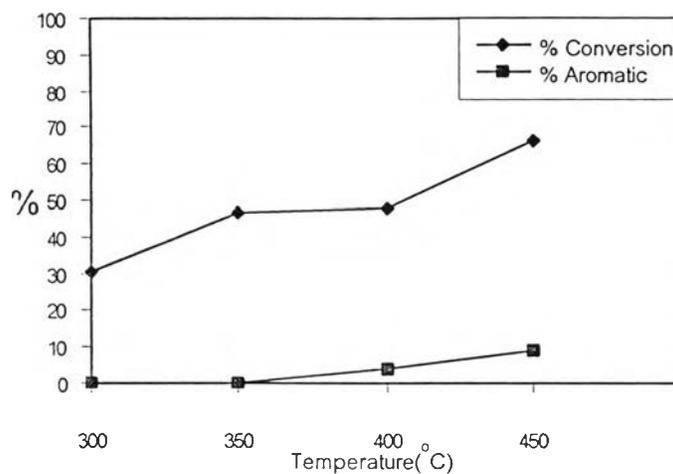


Figure 4.12 The percentage of conversion and aromatics from *n*-hexane aromatization using 0.5%Pd/ZSM-5 as catalyst under 0.4 ml/min feeding rate at the different temperatures

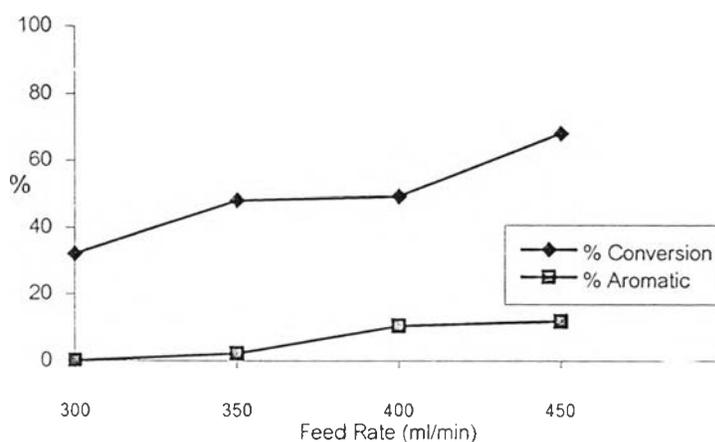


Figure 4.13 The percentage of conversion and aromatics from *n*-hexane aromatization using 1.0%Pd/ZSM-5 as catalyst under 0.4 ml/min feeding rate at the different temperatures

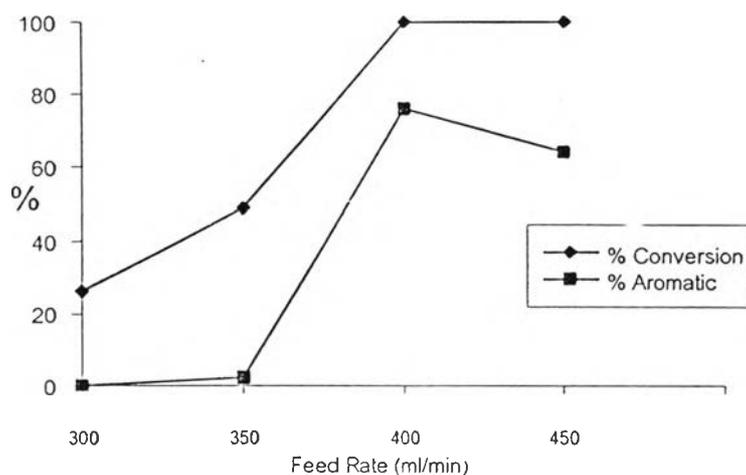


Figure 4.14 The percentage of conversion and aromatics from *n*-hexane aromatization using 2.0%Pd/ZSM-5 as catalyst under 0.4 ml/min feeding rate at the different temperatures

From the data in Tables B11, B12, and B13, which as plotted as presented in Figures 4.12, 4.13, and 4.14, respectively. It indicated that temperature below than 400°C is not enough to produce aromatic products. At 350°C the small amount of aromatic products are observed. However at 400°C and above, the reactions gave higher aromatic products.

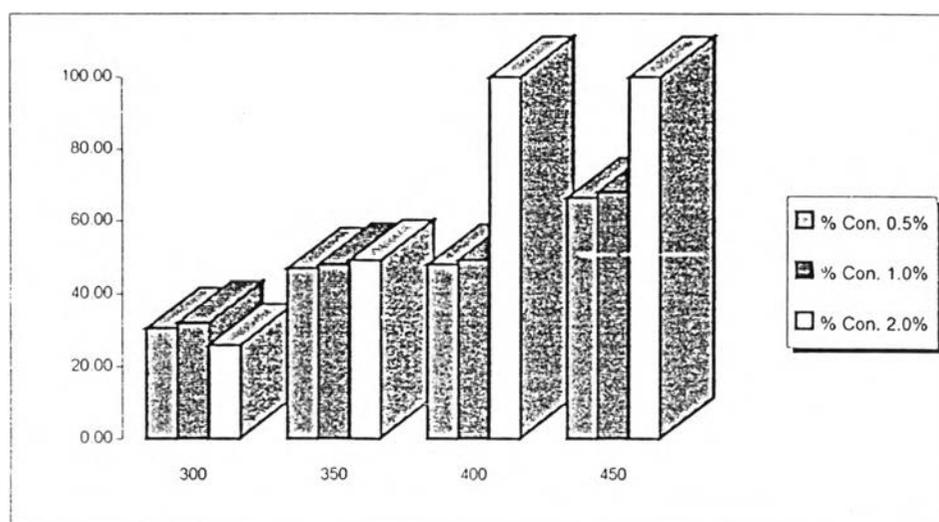


Figure 4.15 The comparison of percentage conversion from *n*-hexane aromatization under 0.4 ml/min feeding rate at various temperatures between (0.5,1.0 and 2.0%)Pd/ZSM-5 catalysts

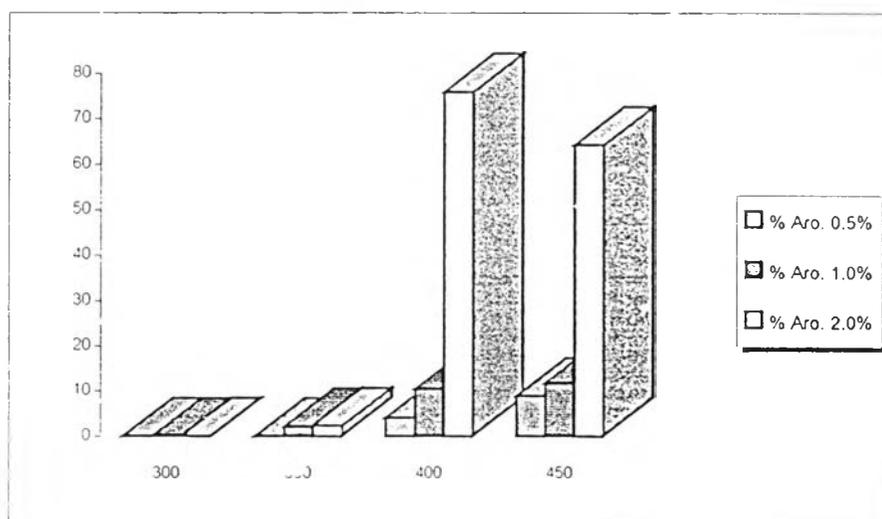


Figure 4.16 The comparison of percentage aromatics from *n*-hexane aromatization under 0.4 ml/min feeding rate at various temperatures between (0.5,1.0 and 2.0%)Pd/ZSM-5 as catalysts

These curves in Figure 4.15 and Figure 4.16 indicated that the percentages of aromatics from *n*-hexane aromatization at 0.4 ml/min feeding rate was obtained at reaction temperature in all catalyst concentration. The highest aromatics percentage was yielded from the highest catalyst concentration, 2.0%Pd/ZSM-5. In contrast, the lowest aromatics percentage was obtained from the lowest catalyst concentration, 0.5%Pd/ZSM-5.

Reproducibility of used catalyst

The reproducibility of the reaction was observed using 2.0%Pd/ZSM-5 catalyst, under 0.4 ml/min feeding rate and at 300-450°C

The results from Tables B16 and B17 in appendix are plotted and shown in Figure 4.17 and Figure 4.18

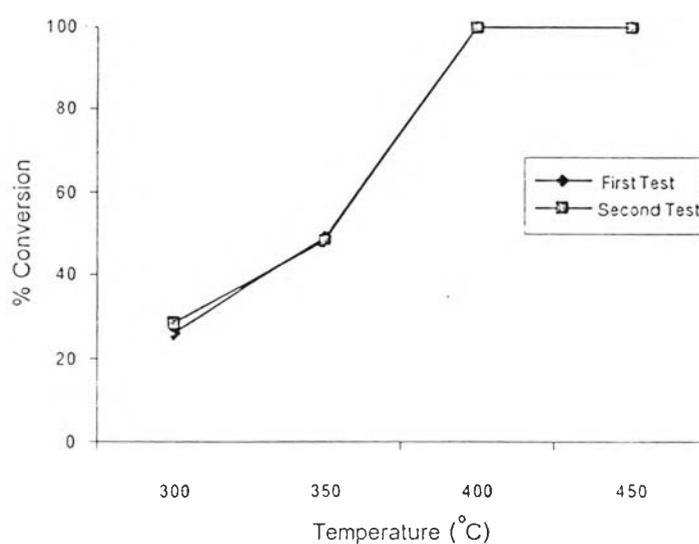


Figure 4.17 The comparison of percentage conversion of reproducibility test under 0.4 ml/min feeding rate by 2.0%Pd/ZSM-5 as catalyst

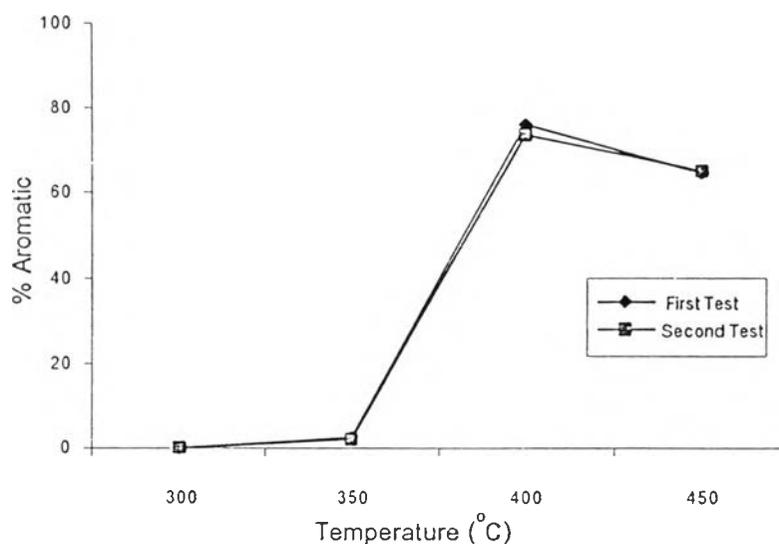


Figure 4.18 The comparison of percentage aromatics of reproducibility test under 0.4 ml/min feeding rate by 2.0%Pd/ZSM-5 as catalyst

The curves in Figures 4.17 and 4.18 confirmed that the reaction is reproducible. As we can see that only insignificant variation of the percentage of aromatic products was observed.

Activity of used catalyst

The activities of used catalysts were observed using 2.0%Pd/ZSM-5 catalyst, under 0.4 ml/min feeding rate at 300-450°C

The results from Tables B13, B15, and B16 in appendix were plotted and shown in Figure 4.19 and Figure 4.20. Table B13 was represented for the fresh catalyst data, Table B15 and Table B16 were used for the first regenerated catalyst and the second regenerated catalyst, respectively.

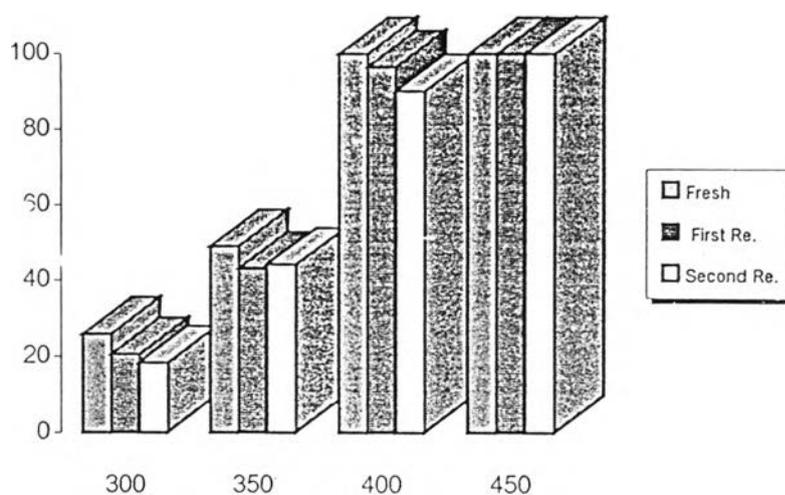


Figure 4.19 The comparison of percentage conversion of activity with used catalyst test under 0.4 ml/min feeding rate by 2.0%Pd/ZSM-5 as catalyst

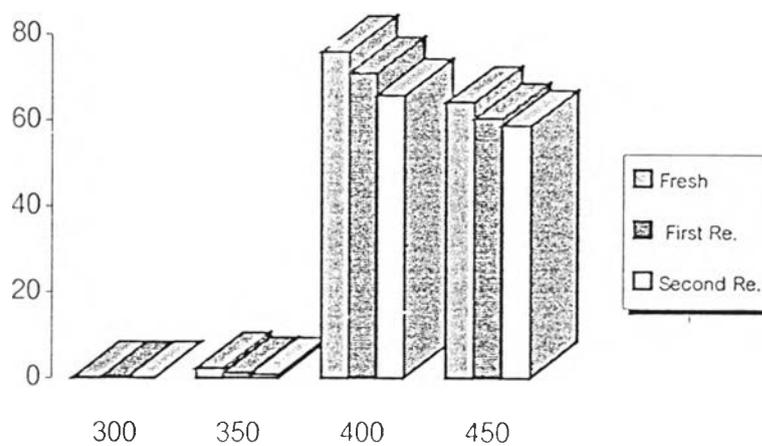


Figure 4.20 The comparison of percentage aromatics of activity with used catalyst test under 0.4 ml/min feeding rate by 2.0%Pd/ZSM-5 as catalyst

Figures 4.19 and 4.20 showed that the fresh catalyst gave the highest percentage conversion and percentage of aromatics. Moreover, the first regenerated catalyst and the second regenerated catalyst were less active than the freshly prepared catalysts. The second regenerated catalyst was found to lose its activity at about 10% compared to the fresh one.

Additionally, a fresh catalyst will give more aromatics than the first regenerated catalyst. It seemed that the used catalyst had coke formation, which appeared to cover the catalyst surface so that its activity was reduced.

The Selectivity of Catalyst

The shape and size selectivity of ZSM-5 catalyst was studied at selected optimal condition (400°C, 0.4 ml/min) with the concentration of 2%Pd on zeolite ZSM-5. The concentration of aromatics generated from the reactor, which are benzene, toluene, *m*-xylene, *o*-xylene, *p*-xylene were shown in Figure 4.21.

The product selectivity of the aromatization over the Pd/ZSM-5 was shown in Figure 4.1. The *p*-xylene was obtained at the higher percentage than *o*-xylene and *m*-xylene. This can be explained theoretically in comparison with pore diameter of ZSM-5 and kinetic diameter of xylene as follows.

Table 4.3 The kinetic diameter of xylene molecules[17]

Molecule	Kinetic Diameter (nm)
<i>m</i> -Xylene	0.63
<i>p</i> -Xylene	0.58
<i>o</i> -Xylene	0.64

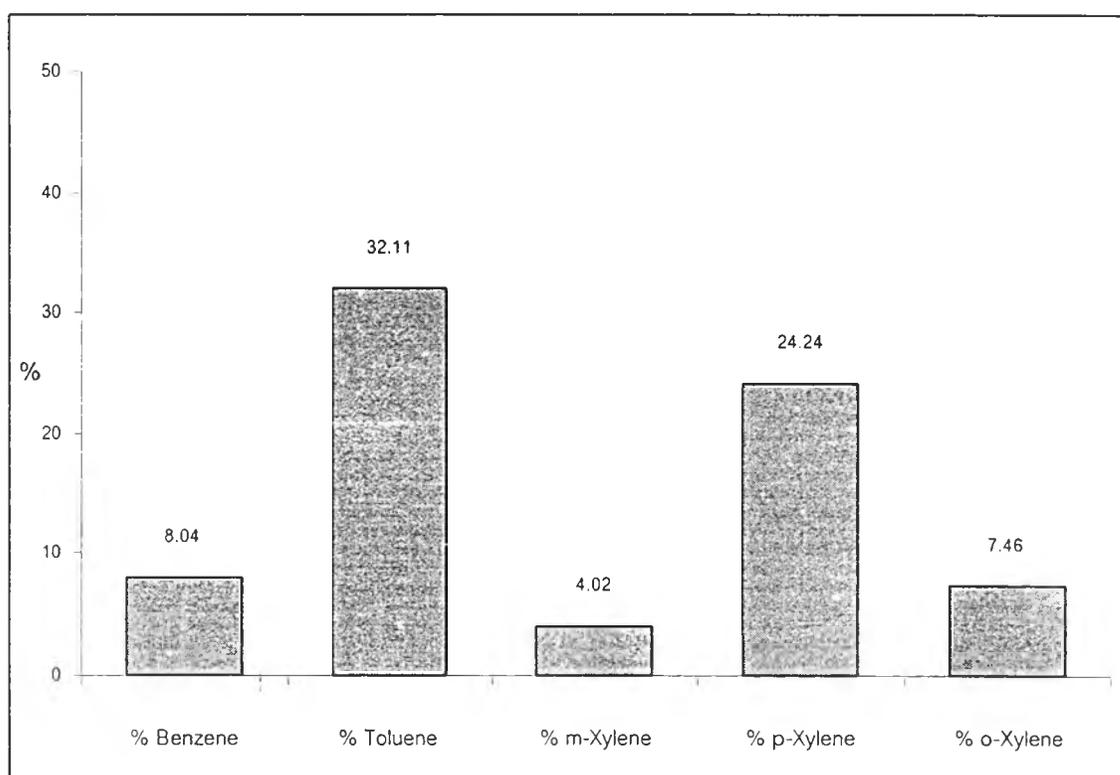


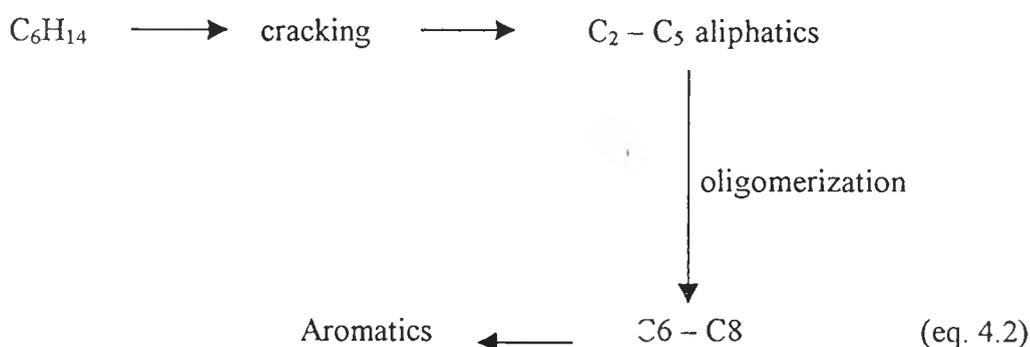
Figure 4.21 The result of products selectivity from the best condition at 400°C and 0.4 ml/min feeding rate by 2%Pd/ZSM-5

The dynamic diameters of *p*-xylene, *m*-xylene and *o*-xylene are 0.58, 0.63 and 0.64 nm. respectively, and the pore diameter of Pd/ZSM-5 is only

cyclocompound for *m*-xylene and *o*-xylene and for the diffusion of *m*-xylene and *o*-xylene in the pore of the Pd/ZSM-5 catalyst. The results of the product analysis indicated that, in the aromatization of C_6 hydrocarbons, *p*-xylene was obtained at higher percentage than *o*-xylene and *m*-xylene.

According to the products of the *n*-hexane aromatization, the main reaction pathways converting hexane to aromatics are explained as follows.

For the Pd/ZSM-5 catalyst, due to the bi-functional property of the catalyst, acidity and metal catalytic property, hexane is cracked to small hydrocarbon molecules and then oligomerized in the zeolite channels. The oligomerization products can undergo either cracking to smaller molecules or dehydro-cyclization (dehydration and cyclization) to aromatic products. The aromatization pathways are simplified as shown below [27].



This research has many advantages especially for its continuously aromatization system. So far in the lab scale research, batch processes have been studied worldwide. But industrial need is continuous system because of the

studied worldwide. But industrial need is continuous system because of the reduction of cost and reaction time [27, 32]. Furthermore, this research starting material is *n*-hexane, which is a saturated hydrocarbon. Saturated hydrocarbons are very stable and very difficult to be reacted because of its strong C-C bonds. Therefore, in the petroleum industry, mixed hydrocarbons such as NGL or naphtha, which composed of many different basic structures (linear, branch chain and aromatics), have been widely used. These compounds can be cyclized or aromatized very easily compared to *n*-hexane.

From the literature review, the comparison was made and shown in the following Table [27, 32, 34, 35, 36, 37].

	This Research	Promart	Bour-nonville	Brand	Kuchar	Bannett	Wei-Qiao
Feed stream	C6	Mixed	90% C5	26.8% C7 36.7% C8	C5/C6	Ethylene Propane	C3/C4
Catalyst	2% Pd/ ZSM-5	0.6% Pd & 0.5% F / Al ₂ O ₃	0.3% Pt & 0.2%Sn / zeolite	0.4% Pt & 0.5% Zr / Al ₂ O ₃	ZSM-5 AlPO ₄	0.8% Ga zeolite	Zn /ZSM-5
System	Continuous	batch	pulse-flow	Split-feed	continuous	pulse-flow	Pulse-flow
Step	1	1	1	1	2	2	1
Temp. (°C)	400	430	480	500	450	550	500
Pressure (psi)	-	40	36.3	0.69	50	3	-
% conversion	100	88	95	-	25	56	92.52
%yield of aromatic	76	83	70	40	30	36	48.72

In this research, simple one-step process was developed which was an easy-to-operate system. The temperature used in this process was reduced to lowest compared to other processes and the conversion was raised to 100% with 76% yield (by weight).