Modeling Aromatics Production from Mixtures of Butanes and Butenes with Chemical Equilibria

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การผลิตอะโรเมติกส์จากสารประกอบไฮโดรคาร์บอน 4 ตัว (C4) เป็นวิธีการที่น่าสนใจเพื่อที่จะเพิ่มคุณค่าทางเศรษฐกิจและเพิ่มทางเลือกการใช้ประโยชน์จากของผสมไฮโดรคาร์บอน 4 ตัว งานวิจัยนี้สร้างแบบจำลองทางคณิตศาสตร์การผลิตอะโรเมติกส์จากจากของผสมบิวเทนและบิวทีนเพื่อเป็นการพัฒนาและทำให้เป็นจริงในเชิงอุตสาหกรรมโดยการลดค่าใช้จ่ายและเวลาในการทำทดลอง แบบจำลองทางคณิตศาสตร์ที่ภาวะสมดุลปฏิกิริยาใช้ตัวเร่งปฏิกิริยา 2 ชนิด ได้แก่ Zn/ZSM-5/ZSM-11 และ Moc/ZSM-5 ที่อุณหภูมิ 480 องศาเซลเซียสความดัน 0.4 เมกะพาสคัลและที่อุณหภูมิ 500 องศาเซลเซียส 1 ความดันบรรยากาศตามลำดับ แบบจำลองทางคณิตศาสตร์จำลองการเกิดปฏิกิริยาเคมีจากโปรแกรม Aspen Plus และคำนวณด้วยโปรแกรมแก้สมการไม่เชิงเส้น ปฏิกิริยาเคมีประกอบด้วยปฏิกิริยาหลักและปฏิกิริยาข้างเคียงโดยตัวเร่งปฏิกิริยาทำหน้าที่เลือกบางปฏิกิริยาให้เกิดขึ้นและไม่เกิดขึ้นได้ นอกจากนี้ประเภทของปฏิกิริยาเคมีถูกจำแนกออกเป็นกลุ่มต่างๆด้วยการแยกเครื่องปฏิกรณ์ออกเป็นหลายเครื่องต่อกันแบบอนุกรมเพื่อหาลำดับการเกิดปฏิกิริยาเคมี จากผลการศึกษาพบว่าบิวเทนและบิวทีนเปลี่ยนเป็นเอทิลไซโคลเฮกเซนก่อนที่จะเปลี่ยนเป็นเอทิลเบนซีน จากนั้นเอทิลเบนซีนถูกเปลี่ยนเป็นอะโรเมติกส์โดยการแตกตัวด้วยไฮโดรเจน (Hydrocracking) ปฏิกิริยาการทำให้เกิดไอโซเมอร์ (Isomerization) และการแตกตัวด้วยตัวเร่งปฏิกิริยา (catalytic cracking) สำหรับตัวเร่งปฏิกิริยา Zn/ZSM-5/ZSM-11 ในขณะที่ตัวเร่งปฏิกิริยา Moc/ZSM-5 เอทิลไซโคลเฮกเซนแตกตัวด้วยไฮโดรเจนเป็นเมทิลไซโคลเฮกเซนและไซโคลเฮกเซนก่อนที่เปลี่ยนเป็นอะโรเมติกส์และแตกตัวด้วยไฮโดรเจนตามลำดับ

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Aromatics production from C4 hydrocarbons is an interesting way to increase economic values and mixed C4 usage alternatives. This study was to model aromatics production from mixtures of butanes and butenes, enabling industrial work to be more developed and actualized by reducing laboratory cost and experimental time. The model was regarded as an equilibrium state in which the forward reaction rate and the reverse reaction rate are equivalent. The catalysts would be Zn loaded on ZSM-5/ZSM-11 under 480 ^{0}C and 0.4 MPa and MoC loaded on HZSM-5 under 500 ^{0}C and 1 atm. The reactions in the models were from the Aspen Plus V9 simulation and non-linear program solver. The reactions included main reactions and side reactions, which the catalysts performed to select and unselect certain reactions. Moreover, the reactions were grouped by splitting reactors, and connected in series to classify a procedure. It has been found that butanes and butenes would be converted to ethylcyclohexane before ethylbenzene. Then, it produced BTX which was formed by hydrocracking, isomerization, and catalytic cracking for Zn loaded on ZSM-5/ZSM-11 catalyst while ethylcyclohexane was cracked by hydrogen to be methylcyclohexane and cyclohexane before aromatization and hydrocracking respectively over MoC loaded on HZSM-5 catalyst.

Field of Study:	Chemical Engineering	Student's Signature ....
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Hataipat Sangwattanakul

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CHAPTER I
INTRODUCTION

1.1 Background

There are many advantages of mixed C4s which would be used to produce various useful components. Initially, they are extracted to receive butadiene after that the rest of mixed C4s that includes butenes, butane and residual butadiene, also known as raffinate 1, is manufactured methyl tertiary butyl ether (MTBE) and diisobutylene (DIB). Then, the residual mixed C4s would be a mixture of n-butenes, butane and some a small amount of butadiene, and they were called raffinate 2, which is used to form secondary butyl alcohol (SBA), methyl ethyl ketone (MEK) and liquefied petroleum gas (LPG).[1, 2] The chemicals has a plenty of benefits. To illustrate, MTBE was added in petroleum for reducing emission and DIB is an intermediate in process of alcohol and solvent manufacturing. Likewise, SBN and MEK are an intermediate for industrial cleaning agents.[2] Besides, the majority of saturated C4 produces LPG which is consumed as fuel for household cooking, cars and heating in agriculture and industry.[3]

According to several journals and studies with different periods of time, they are not distinct utilizations of mixed C4s. Thus, it is worth considering the researches which were emphasized catalyst development in the productions of benzene, toluene and xylene (BTX) instead. Mixtures of benzene, toluene and xylene are aromatic hydrocarbons and are also upstream petrochemicals which are used for further production processes. Around 80% of benzene produce three main chemicals, including ethylbenzene, cumene, and cyclohexane. Furthermore, ethylbenzene is essential for manufacturing polystyrene while cumene is produced for use in packaging, construction and household goods. Next, toluene advantages in commercial have assorted fields, e.g. gasoline, paints, cleaning agents and rubber. Besides, benzene, trinitrotoluene (TNT), nylon, plastics and polyurethanes are also manufactured from toluene. [4] Overall, aromatics are feedstock of plastic pellets and synthetic fibers in various petrochemical industries, for example automotive parts, electronic appliances and textiles.[3]

At the present time, there are many researches demonstrating the experiments converting mixed C4 to aromatics including benzene, toluene and xylene with different conditions, e.g., catalyst, temperature, pressure and reactant components. It is obvious that aromatics production from mixtures of butanes and butenes is value enhancement because not only economic values of the aromatics but also mixed C4 which can be more usage alternatives. Therefore, the objective is to develop the model of benzene, toluene and xylene productions from butanes and butenes mixtures with chemical equilibria over the catalyst. This research is sincerely expected finding optimized models would explain and more clarify the several reactions. Furthermore, it would be beneficial to develop and actualize in commercial part and predict reaction results with other conditions to save laboratory cost. The models would originate from Aspen Plus simulation to fit with research results.

1.2 Objective

1.2.1 To develop the model of benzene, toluene and xylene productions from butanes and butenes mixtures with chemical equilibria over different catalysts

1.3 Scopes of the research

1.3.1 To propose chemical reactions of mixed butanes and butenes to be aromatics (BTX) by using non-linear program solver and Aspen Plus V9 programs for calculation, simulation and comparison with other researches.

1.3.2 Interested variables which effected to the model were temperatures, pressures, and catalysts.

1.3.3 The operating conditions were 480 ^{0}C and 0.4 Mpa for 2 wt% of Zn loaded on ZSM-5/ZSM-11 catalyst, and 500 ^{0}C and 1 atm for 10 wt% of MoC loaded on HZSM-5 catalyst.

1.3.4 Prediction of aromatics production shows varied ratios of butane and butene from the appropriate model.

1.3.5 All existing compounds in the main reactions (aromatization) and the sides reactions would be well-defined hydrocarbons, for example C8 aromatics, C1, C2 and C3, excepting free radicals.

1.3.6 The model would be an equilibrium model and kinetic energy is not considered.

1.3.7 Determine the error using Residua Sum Square (RSS)

1.4 Expected output

The appropriated models over different catalysts from simulation and non-linear program solver will be able to predict mixed butane and butene for aromatics production.

CHAPTER II

THEORY

2.1 Chemical Equilibria

2.1.1 Principle

In a chemical reaction, a reversible reaction enables a closed system to be an equilibrium state at one point when a forward reaction rate is equal to a backward reaction rate. Moreover, at the equilibrium state, the system is not static but it is thoroughly changing, called dynamic equilibrium. If the system is disturbed by external influences, such as temperature or pressure change, the equilibrium state would be destroyed. However, when disturbance is stopped, the system could re-balance itself after the chance.[5] According to Le Chatelier’s principle, result of chemical equilibria of reactions that achieves a new equilibrium state will be predicable when concentration, pressure, or temperature changes.

Adding reactant concentrations will shift the equilibrium to the right, leading to more production while adding product concentrations will shift the equilibrium to the left, enabling the reactants to increase. Besides, pressure or volume alteration will affect to a reaction which reactants and products are gaseous while a system in liquid and solid phases will not be disturbed much. A difference of total product moles and total reactant moles in a reaction is a determination where the reaction will be driven. To illustrate, increasing pressure or decreasing volume will drive a reaction to the side that includes fewer gaseous moles. Likewise, decreasing pressure or increasing volume will drive a reaction to the side of additional gaseous moles. Lastly, a change in temperature will also impact to the equilibrium, which depends on types of the reaction, including endothermic and exothermic reactions. The equilibrium will be restored similarly to the change in concentration. For instant, heat is absorbed in the endothermic reaction and thus the heat would be represented as a reactant while for the exothermic reaction, heat would be represented as a product since heat will be released. Therefore, raising the temperature on the endothermic reaction will drive the reaction to the right because heat is referred to the reactant. Conversely, raising the temperature on the exothermic reaction will drive the reaction to left.

2.1.2 Equilibrium constant

Equilibrium constant is a value of the forward specific reaction rate constant divided by the reverse specific reaction rate constant at equilibrium state.[6] Equilibrium constant (K) is defined as follows:

$$K = \prod_i (a_i)_{eq}^{v_i} \tag{2.1}$$

Where v_i is the stoichiometric number and a_i is the activity of each reactant and product

In detail, stoichiometric number of products will be positive while stoichiometric number of reactants will be negative. Moreover, when the activity is reactant and product molar concentrations, it would be concentration equilibrium constant (Kc). Likewise, when the process of gaseous mixtures inside a closed system carries out and the activity is reactant and product partial pressures, it would be equilibrium constant in terms of partial pressures (Kp). The relation of Kp and Kc is defined as follow:[5]

$$Kp = Kc(RT)^{\sum_i v_i} \tag{2.2}$$

2.2 Catalyst

2.2.1 Performances

Heterogeneous catalysis play an important role in the modern energy and chemical technology since it is capable of improving the selectivity, activity and efficiency of the catalysts. Phases of a reaction will be gas or liquid phase, which is operated over a solid catalyst.[7] The catalyst compositions consist of active phase, support and promoter. A catalyst is a substance that not only increase chemical reaction rate but also control product selectivity without consumption of the catalysis. Generally, the catalyst alter elementary steps and intermediates of the chemical reactions and thus a reaction mechanism also changes, leading to reduction of the activation energy. In addition, selectivity can be controlled by shape selective reactions, which performs over zeolites, molecular sieves and other porous material. There are three main sorting of shape selectivity, including reactant shape selectivity, product shape selectivity and transition state shape selectivity. Firstly, reactant sizes are smaller than the pore size, allowing the reactants to reach the active sites. Next, product sizes are less than the pore sizes, letting the products leave the catalyst. Lastly, types of forming transition states are manipulated by the pore sizes.[8]

2.2.2 Active phase and support

The active phase or the active site is typically dispersed in pores of a support or a carrier in the form of nanocrystallites of 1 nanometer to a few nanometers, leading catalytic efficiency to be the best[9] while adding promoter is to improve physical or chemical properties of the catalyst. The active phase is the site where surface reaction occurs and is ordinarily metal forms, for instance, metals, metal oxides, metal sulfides, metal carbides. However, the support is also an integral part to emphasize capability of the supported metal, especially high surface area for higher quantity of dispersing metal particles.[10] Moreover, the pore diameters are necessary to be suitable for metal sizes, and the pore diameters depend on support materials. There are various the support materials for different purposes, physical and chemical properties. To illustrate, alumina is the most widely used support, following by silica. Others are still important for commercial carriers, consisting of magnesia, titania, aluminosilicates and calcium aluminate.

2.2.3 Pores

Physical properties of pore (e.g. pore volume, pore diameter and pore size distribution) obviously affect to enhance the surface area that locates the active site and restrict reactant and product sizes that influents to the selectivity. However, catalyst agglomeration or growth of metal particles which would be pore blockage is an issue of activity decay because the pore volume decreases. Therefore, the selectivity will also decline.[11, 12]

2.2.4 Zeolite

Generally, a catalyst of aromatics production is ZSM-5, which is a type of a zeolite and perhaps loads metal particles to enhance the catalytic efficiency. The zeolites contain acid sites, involving hydrogenolysis (cracking), isomerization and oligomerization (polymerization). The zeolites basically have wide range of silicon to aluminum ratios and are vastly applied in many applications such as oil refining industry, fine chemical industry, environment protection industry, electrochemical industry and chemical anticorrosion industry. Apart from acid catalyst property, the pore size of the zeolite also can be molecular sieve property for accessible components.[13]

CHAPTER III

LITERATURE REVIEWS

3.1 Conversion of C4 hydrocarbons to aromatics over different catalysts

3.1.1 HZSM-5 catalyst

Butane reacted with HZSM-5 as a catalyst at 550 ^{o}C, and W/F ratio is 20 g.h/mole. Then, products of the reactions would be hydrogen, methane, ethane, ethene, propane, propene, butene and aromatics. The research shows mechanisms of butane transformation, and the reactions are as follows:[14]

$$C_4H_{10} \rightarrow C_2H_4 + C_2H_6 \quad (3.1)$$

$$C_4H_{10} \rightarrow C_3H_6 + CH_4 \quad (3.2)$$

$$C_4H_{10} \rightarrow C_4H_8 + H_2 \quad (3.3)$$

$$nC_4H_8 \rightarrow \text{aromatics} \quad (3.4)$$

Moreover, there are another reaction steps presented with the same conditions. Contrarily, products from the reactions occurred only ethylene, ethane and aromatics as shown below:[14]

$$C_4H_{10} \rightarrow C_2H_4 + C_2H_6 \quad (3.5)$$

$$nC_2H_4 \rightarrow \text{aromatics} \quad (3.6)$$

Lastly, the last reaction mechanism starts with butane converting to butene and by-product is hydrogen before aromatization from butene. However, butene oligomers can crack to be small hydrocarbon components.[14]

$$C_4H_{10} \rightarrow C_4H_8 + H_2 \quad (3.7)$$

$$nC_4H_8 \rightarrow \text{aromatics} \quad (3.8)$$

Above all, it is important for dehydrogenation of butane at the first step by converting to butenes because of aromatic selectivity increase, which is illustrated in figure 1 and 2. They were operated at 550^{o}C, 1 atm and W/F ratios equal to 1.4-11.4 g.h/mole.[15]

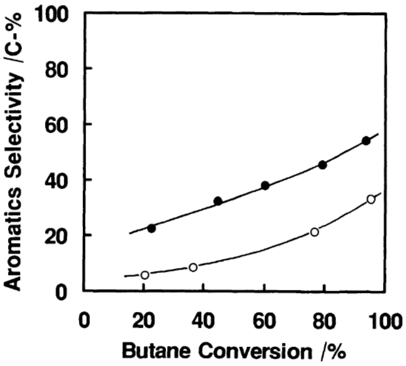

Figure 1 Relation between conversion of butane and selectivity to aromatics on Ga loaded HZSM-5 (●) and HZSM-5 (○) Reaction conditions: 550 ^{0}C, 1.4-11.4 g.h/mole, 1 atm.

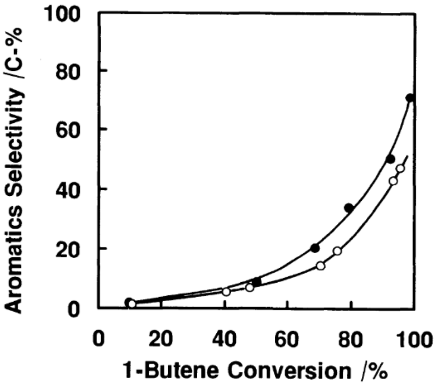

Figure 2 Relation between conversion of 1-butene and selectivity to aromatics on Ga loaded HZSM-5 (●) and HZSM-5 (○) Reaction conditions: 550 ^{0}C, 0.024-11.4 g.h/mole, 1 atm.

From the both figures 1 and 2, it can be seen that the selectivity of 1-butene from the main primary product of butane aromatization over HZSM-5 rose significantly over 1-butene conversion to finish at just under 60% while the butane selectivity is only almost 40%. The aromatics in the products chiefly included benzene, toluene, xylene and trimethylbenzene. In fact, methyl cyclohexadiene was found at the beginning on stream but it was an exception of the conversion. Therefore, butene would be more preferable as a feedstock to reduce unnecessary by-products, especially C1-C3 hydrocarbons which would seldom be aromatic formation.[15]

3.1.2 Ga loaded HZSM-5 catalyst

Butane reacted with Ga-HZSM-5 as a catalyst at 400-550 ^{0}C of reaction temperatures and various W/F ratios. Then, products of the reactions would be methane,

ethane, ethene, propene, butane, hydrogen, and aromatics. Selectivity of the products, was affected by increased conversion, is demonstrated in figure 3.[14] From the research, aromatization steps that were divided into two conditions are demonstrated. Firstly, Ga on HSZM-5 was activated by protonic acidic sites.[14]

$$C_4H_{10} \rightarrow C_3H_6 + CH_4 \tag{3.9}$$

$$nC_3H_6 \rightarrow \text{aromatics} \tag{3.10}$$

$$C_4H_{10} \rightarrow C_4H_8 + H_2 \tag{3.11}$$

$$C_4H_8 \rightarrow \text{aromatics} \tag{3.12}$$

Secondly, Ga affected to the dehydrogenation of butane directly without the protonic sites. It appears that the protonic sites would be desired for aromatization. From the involvement of the protonic sites, oligomers of formed butene could be cracked into smaller molecules.[14] However, Ga loaded on HZSM-5 would significantly enhance aromatization. In detail, a very large majority of butane molecules was influenced by Ga for dehydrogenation accelerating.[14, 15] They are presented in figure 1 for butane and figure 2 for 1-butene which was the primary product of butane.[15]

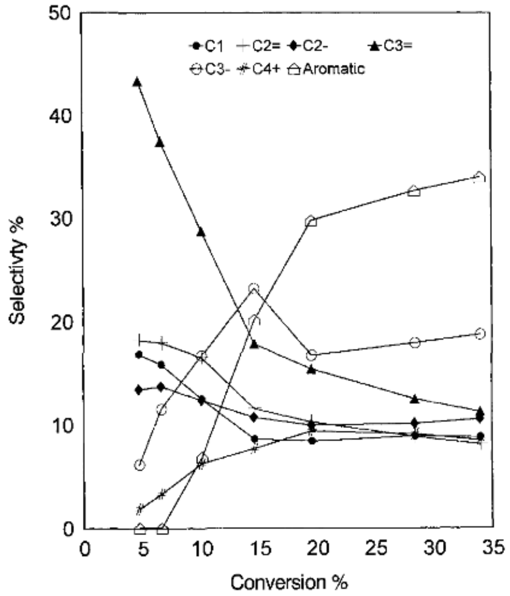

Figure 3 Effect of increased conversion on product selectivity on Ga-HZSM-5 at different W/F ratios. Reaction temperature 550 ^{0}C process time 1 hour.

Temperature could be quite affect to the results, for instance, conversion and product selectivity from table 1.[14]

Table 1 The effect of temperature on the product selectivity at low conversion level over Ga-HZSM-5 (Si/Al = 50) with 0.1 g.h/mole of W/F ration and data at a process time of 1 hour.

Products	Temperature ^{0}C			
	400 ^{0}C	450 ^{0}C	500 ^{0}C	550 ^{0}C
Conversion (%)	0.16	0.45	1.58	4.75
Methane (C1)	17.61	16.09	15.53	16.89
Ethane (C2)	8.22	11.10	12.71	13.43
Ethene (C2)	11.51	13.14	15.59	18.22
Propene (C3)	30.20	36.65	37.88	43.34
Butene (C4)	12.75	7.08	4.14	1.89

3.1.3 Zn loaded ZSM-5/ZSM-11 catalysts

Zn was loaded on the ZSM-5/ZSM-11 zeolite for 2 wt%, which is represented as 2Zn/CDM5 catalyst. Butane was used to be a reactant and was operated at 480 ^{0}C and 0.4 MPa with WHSV (CH2 mass) equal to 0.6 h-1. Conversion and percentage of products are illustrated in table 2. Besides, since aromatics are interested outcome, they are shown distribution in table 3.[16]

Table 2 The reaction performance over the 2ZnCDM5 catalyst.

Conversion (%)	H2 (%)	CH4 (%)	C2H4 (%)	C2H6 (%)	C3H6 (%)	C3H8 (%)	C4 (%)	Aromatics (%)	Others* (%)
86.9	1.6	11.2	0.7	16.7	0.5	42.3	4.5	20.9	1.8

*Other organic compounds in the liquid product

Table 3 The distribution of the aromatic products over the 2ZnCDM5 catalyst.

Benzene (%)	Toluene (%)	Ethylbenzene (%)	Xylene (%)	Ethyltoluene (%)	Trimethylbenzene (%)	C10+ (%)
12.5	42.4	3.1	27.7	4.7	5.1	4.3

In addition, pressure and space velocity differences would be slight influence on the conversion and the product percentages from table 4 and 6. In contrast, temperature distinctness considerably involved the reaction results as shown in table 5.[16]

Table 4 Effect of reaction pressure on the reaction performance over the 2ZnCDM5 catalyst at 510 ^{0}C and 0.6 g(CH2)/h.g(cat).

Pressure (MPa)	Conversion (%)	C1 – C2 (%)	C3 – C4 (%)	Aromatics (%)
0.1	72.4	37.1	30.8	25.1
0.4	92.4	34.9	32.2	28.38
1.1	97.8	39.9	31.4	27.37

Table 5 Effect of reaction temperature on the reaction performance over the 2ZnCDM5 catalyst at 0.4 MPa and 0.6 g(CH2)/h.g(cat).

Temperature (^{0}C)	Conversion (%)	C1 – C2 (%)	C3 – C4 (%)	Aromatics (%)
480	86.9	28.5	47.2	22.1
510	92.4	34.9	32.2	28.4
540	97.5	41.5	15.9	37.2

Table 6 Effect of space velocity on the reaction performance over the 2ZnCDM5 catalyst at 510 ^{0}C and 0.4 MPa.

Space velocity (h-1)	Conversion (%)	C1 – C2 (%)	C3 – C4 (%)	Aromatics (%)
0.3	94.5	32.4	37.5	25.7
0.6	92.4	34.9	32.2	28.4
1.0	88.0	32.9	32.4	30.1

The aromatization was accelerated by Zn similar to Ga and, it also affected the dehydrogenation of butane to increase significantly. As the result, the catalyst obtained higher selectivity of aromatics than not only HZSM-5 but also Ga at the same conversion as shown in figure 4. [14]

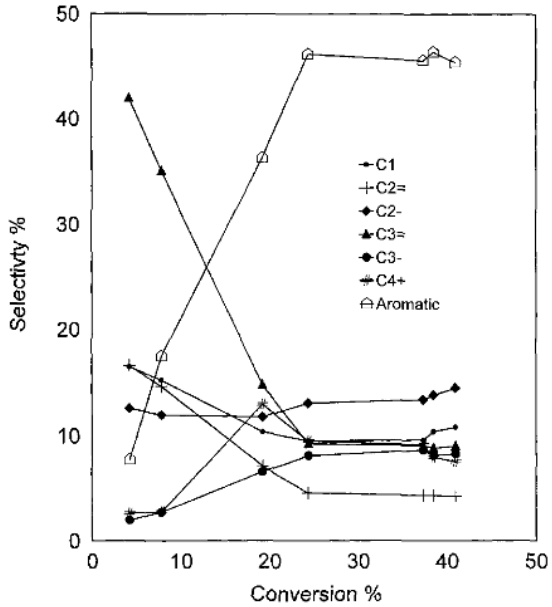

Figure 4 Effect of increased conversion on product selectivity on Zn-HZSM-5 at different W/F ratios. Reaction temperature 550 ^{0}C process time 1 hour.

3.1.4 Gallosilicate catalyst (Si/Ga=26)

Aromatization from butane over gallosilicate was performed at 400-550 ^{0}C and W/F ratio is 0.1 g.h/mole. Products would be hydrogen, methane, ethane, ethene, propane, propene, butene, C4+ and aromatics from the reaction steps and figure 5 which shows product selectivity versus conversion. Indeed, involvement of temperature to the reaction would be conversion and product results, which present in table 7.[14]

$$C_4H_{10} \rightarrow C_4H_8 + H_2 \tag{3.13}$$

$$C_4H_{10} \rightarrow C_3H_6 + CH_4 \tag{3.14}$$

$$2C_3H_6 \rightarrow C_6H_{12} \tag{3.15}$$

$$C_6H_{12} \rightarrow C_6H_6 \tag{3.16}$$

$$nC_4H_8 \rightarrow \text{aromatics} \tag{3.17}$$

Table 7 The effect of temperature on the product selectivity at low conversion level over Gallosilicate (Si/Ga = 26)

Products	Temperature ^{0}C			
	400 ^{0}C	450 ^{0}C	500 ^{0}C	550 ^{0}C
Conversion (%)	0.11	0.47	1.87	4.66
Methane (C1)	23.81	15.36	16.45	14.41
Ethane (C2)	-	9.09	11.91	10.72
Ethene (C2)	-	12.21	14.96	15.67
Propene (C3)	50.87	40.57	42.02	39.18
Butene (C4)	22.62	15.14	9.79	9.14

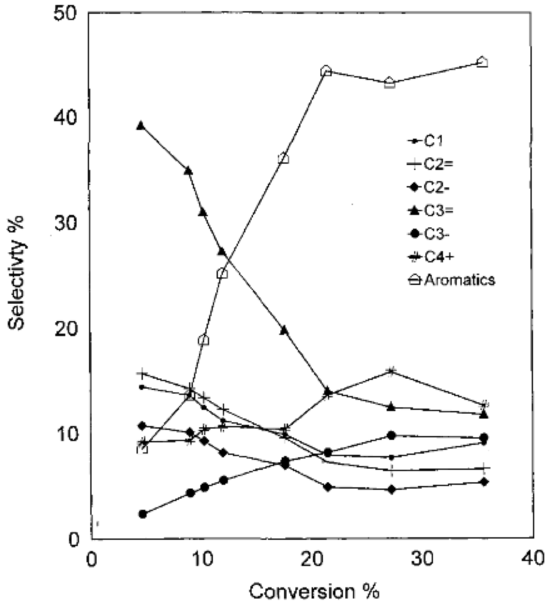

Figure 5 Data at a process time of 1 hour reaction condition, W/F ration is 0.1 g.h/mole.

Effect of increased conversion on product selectivity on gallosilicate Si/Ga = 26 at different W/F ratios. Reaction temperature 550 ^{0}C process time 1 hour.

3.1.5 α-Mo2C/ HZSM-5 catalyst

The aromatization was operated from n-butane over α-Mo2C/HZSM-5 with different concentration at 540 ^{0}C and 1 atm for 1 hour. The products and conversion demonstrate in table 8. Moreover, temperature influence of the reaction illustrates in table 9.[17]

Table 8 Effect of Mo loading on the aromatization on n-C4H10 at 540 ^{0}C over α-MoC/ HZSM-5 catalyst (SiO2/Al2O3 = 80), the data were taken at 60 min on stream)

Mo (wt%)	0	0.5	3	10	15	20	40
Conversion (%)	77.5	58.6	70.4	71.3	64.1	61.7	50.1
Yield of aromatics (%)	10.4	9.6	26.8	28.5	23.6	23.2	17.1
Product distribution (%)							
CH4	9.5	10.0	12.3	12.3	11.4	10.0	10.1
C2H6	17.3	19.3	17.3	16.6	14.5	15.6	11.9
C2H4	20.1	17.6	9.5	8.6	11.0	11.7	11.9
C3H8	14.4	10.7	4.5	4.6	4.6	4.5	3.4
C3H6	17.5	17.0	10.2	9.7	11.5	11.9	14.1
i-C4H10	1.2	1.6	1.8	1.7	1.5	1.6	2.1
C4H8	5.7	6.1	5.9	6.0	5.5	7.3	11.9
C5	0.9	0.8	0.4	0.3	0.5	0.5	0.4
Aromatics	13.4	16.4	38.1	40.0	36.0	36.8	34.1
Aromatics distribution (%)							
C6H6	32.1	33.1	39.3	42.2	43.6	39.0	45.2
C7H8	47.0	46.2	38.7	36.9	35.4	38.4	36.3
C8H10	18.4	17.6	14.3	14.0	13.6	14.1	13.4
C9+	2.8	3.1	7.7	6.8	7.5	8.6	5.2

Table 9 Effect of reaction temperature on the product distribution during the reaction of n-C4H10 over α-MoC/HZSM-5 (10wt.% Mo, SiO2/Al2O3 = 30, the data were taken at 60 min on stream)

Temperature (^{0}C)	380	420	460	500	540
Conversion (%)	17.5	35.1	56.2	84.5	99.1
Product distribution (%)					
CH4	1.1	2.5	6.0	14.8	27.1
C2H6	8.7	15.1	21.9	22.8	16.1
C2H4	2.4	2.4	2.0	2.5	1.4
C3H8	36.4	26.2	14.8	5.1	1.1
C3H6	6.4	5.8	4.6	2.6	0.4
i-C4H10	6.6	3.8	2.2	0.4	0.0
C4H8	4.7	5.4	3.3	1.4	0.1
C5	4.4	1.6	0.2	0.0	0.0
Aromatics	29.2	37.2	45.0	50.4	53.8
Aromatics distribution (%)					
C6H6	11.4	16.2	25.1	39.6	50.8
C7H8	43.9	46.8	43.6	32.6	23.7
C8H10	34.0	27.1	19.6	11.8	5.2
C9+	10.8	9.8	11.6	16.0	20.3

3.1.6 Pt-SAPO-11-OX catalyst

Reaction temperatures were varied, including 470 ^{0}C, 500 ^{0}C and 530 ^{0}C with WSHV equal to 2.5 h-1. The reaction is butane converting to aromatics over Pt-SAPO-11-OX catalyst. Products from the reaction would be methane, ethane, ethene, propane, propene, trans-2-butene, 1-butene, iso-butene, cis-2-butene, butadiene, pentene, benzene and toluene. Conversion and selectivity change from different reaction temperatures present in figure 6 and 7, respectively.[18]

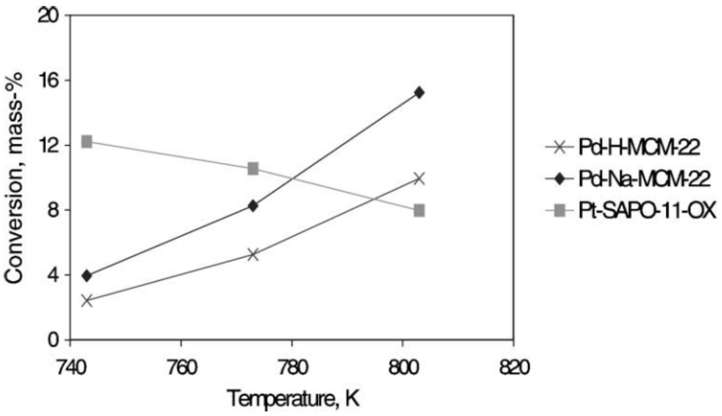

Figure 6 The effect of temperature on the conversion of n-butane over Pd-Na-MCM-22, Pd-H-MCM-22 and Pt-SAPO-11-OXcatalyst.

3.1.7 MCM-22 catalyst

Butane was reacted by using Pd-Na-MCM-22 and Pd-H-MCM-22 catalysts at 470 ^{0}C, 500 ^{0}C and 530 ^{0}C. WSHV is equal to 2.5 h-1. Hydrocarbons were formed from the reaction were methane, ethane, ethene, propane, propene, 1-butene, iso-butene, cis-2-butene, butadiene, pentane, pentene, hexane, benzene, toluene and xylenes. Conversion and selectivity change from different reaction temperatures present in figure 6 and 7, respectively.[18]

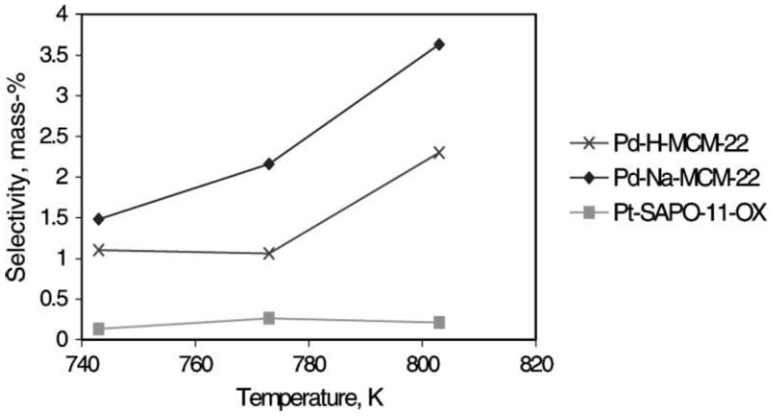

Figure 7 The effect of temperature on the selectivity to aromatics over Pd-Na-MCM-22, Pd-H-MCM-22 and Pt-SAPO-11-OXcatalyst

3.1.8 H-GaAlMFI catalyst

Aromatization from n-butene was performed at 400 ^{0}C over H-GaAlMFI zeolite with different space velocities from 3100 to 58100 CM^3/g.h. Certain products appear in figure 8, 9 and 10 which also show product selectivity and distribution.[19]

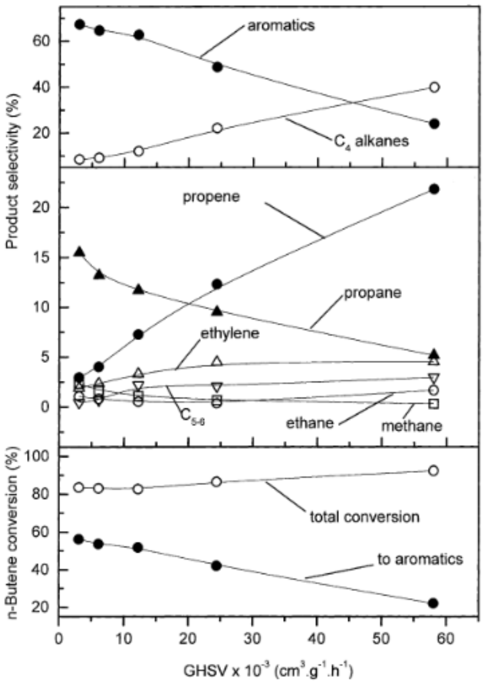

Figure 8 Variation with the space velocity of n-butane conversion (total and to aromatics) and product selectivity in the n-butene aromatization.

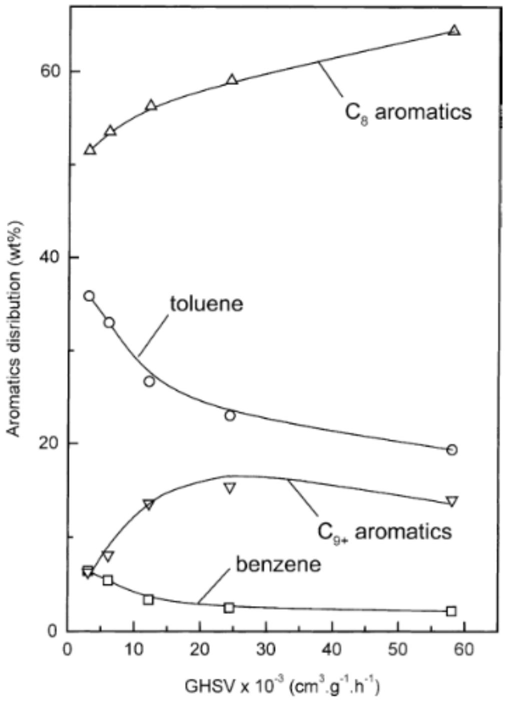

Figure 9 Dependence on the space velocity of the aromatics formed in the n-butene aromatization.

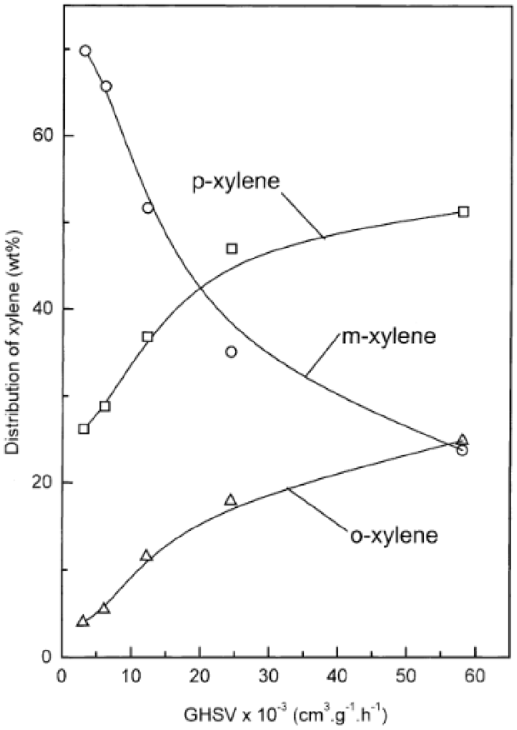

Figure 10 Dependence on the space velocity of the distribution of xylene isomers formed in the n-butene aromatization

3.2 Equilibrium modeling

3.2.1 Modeling of methane to ethylene with chemical equilibria

The model demonstrates the oxidative coupling of methane reaction (OCM) over three different catalysts which were Mn/Na_2WO_4/SiO_2, La_2O_3/CaO and PbO/Al_2O_3. There were three proposed models including uni-equilibrium reaction model, Duo-equilibrium reaction model and trio-equilibrium reaction model, operating isothermally between 650 ^{0}C and 900 ^{0}C and feeding methane to oxygen ratio was around 3-10.[20] From the research, all possible chemical reactions were proposed and based, containing catalytic reaction, non-catalytic reaction and both catalytic and non-catalytic reaction. Then, all variables were calculated with Aspen Plus program, which was run with RK-Soave and Peng-Rob methods based on Aspen Plus component guideline and industrial guideline. As a result, the models were verified by using statistics of components in effluence and reactor performance. For the verification using components in effluence, Residue Sum Square (RSS) was utilized as a model validation:

$$RSS = \sum_{i=1}^{N}\left[\frac{(M_{exp}-M_{model})}{M_{exp}}\right]^2 \tag{3.18}$$

Where M_{exp} and M_{model} are effluent mole flow of the experiment and the chemical equilibrium model, respectively. For the verification using reactor performance, conversion, yield and selectivity as a variable for performance evaluation were represented in terms of average absolute relative deviation (AARD) which is statistical information:

$$AARD = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{(P_{exp}-P_{model})}{P_{exp}}\right| \tag{3.19}$$

Where P_{exp} and P_{model} are the variable from the experiment and the equilibrium model, respectively.[20]

Chapter IV

SIMULATION

4.1 Overview

Since mixed butanes and butenes include plenty of components, there are several reactions occurring for aromatization, for example thermal cracking, hydrogenation, and isomerization. Nowadays, most manufacturing industries involve catalytic processes, and consequently the models with different catalysts are interesting to further develop. Moreover, the catalysts affected selectivity, enabling not only few unselective reactions to occur but also some selective reactions to disappear. Therefore, all possible reactions that would appear will be calculated in the model, and remarkable reactions will be selected for each catalyst by comparing with the researches.

While a single equilibrium reactor represented a process without catalyst, catalytic consequence cannot input in the software directly, enabling equilibrium reactor to connect in series to define reaction procedures. According to the literature review, aromatics production increased when longer time of stream, indicating approach equilibrium point. Consequently, the models with equilibria also regards as maximum aromatics production.

The reactions were from non-linear solver and Aspen Plus V9 simulation for more accuracy and approaching actual values. Proposing all possible reaction schemes of aromatization and all possible reactions, including solutions and necessary principles are demonstrated next.

4.2 Proposed model

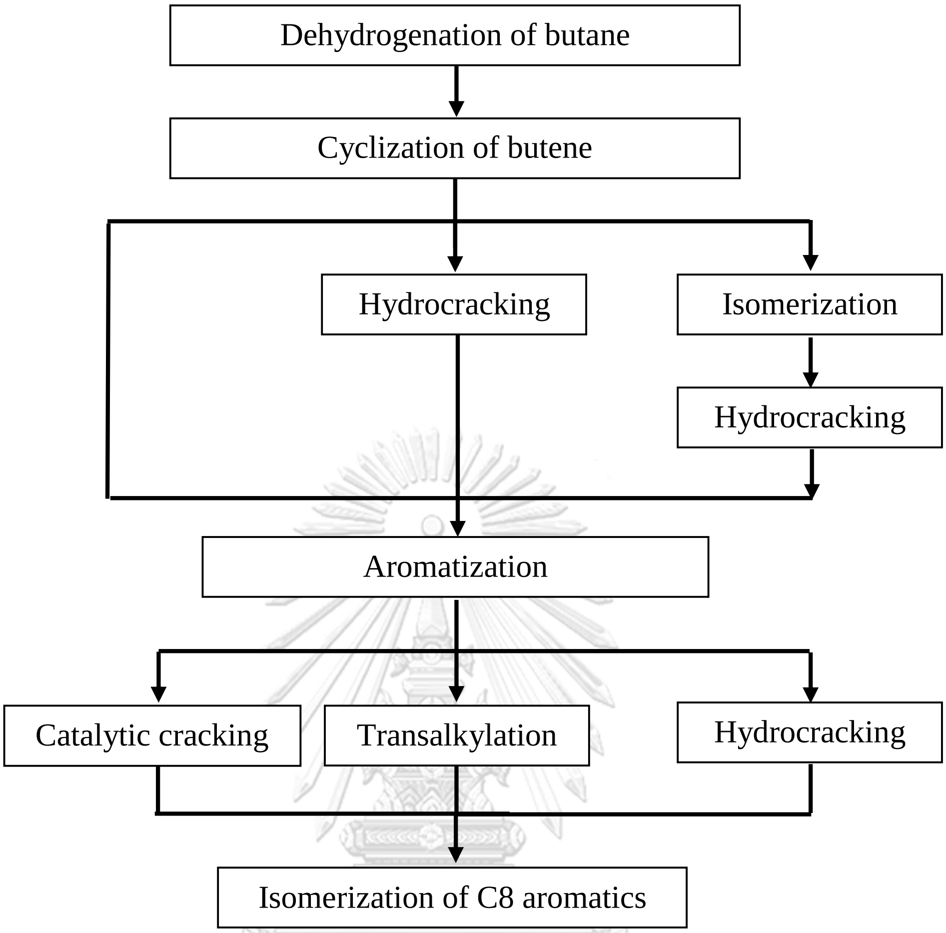

Figure 11 Propose all possible reaction schemes of aromatization

There are many pathways of aromatization and thus figure 11 shows all possible reaction schemes which would be the possible models. After aromatization occurred, catalytic cracking, transalkylation, and hydrocracking adjusted benzene, toluene, and xylenes ratios while isomerization of C8 aromatics especially affect to ethylbenzene and xylenes ratios.

4.3 Propose all possible chemical reactions

The reactions were from Aspen Plus V9 simulation for more accuracy and approaching actual value as possible as. The reactions would be divided into main reactions and side reactions. The main reactions were reaction producing benzene toluene and xylene directly while the side reactions were unexpected reactions, particularly thermal cracking, hydrogenation, dehydrogenation and hydrocracking. Then, all possible chemical reactions were proposed.

- Dehydrogenation

$C_4H_{10} \rightarrow C_4H_8 + H_2$ (4.1)

- Hydrogenation

$C_2H_4 + H_2 \rightarrow C_2H_6$ (4.2)

$C_3H_6 + H_2 \rightarrow C_3H_8$ (4.3)

$C_4H_8 + H_2 \rightarrow C_4H_{10}$ (4.4)

- Cyclization

$2C_4H_8 \rightarrow C_8H_{16}$(ethylcyclohexane (ECH)) (4.5)

$2C_4H_8 \rightarrow C_8H_{16}$(cis-1,2-dimethylcyclohexane (cis-1,2)) (4.6)

$2C_4H_8 \rightarrow C_8H_{16}$(trans-1,2-dimethylcyclohexane (trans-1,2)) (4.7)

$2C_4H_8 \rightarrow C_8H_{16}$(cis-1,3-dimethylcyclohexane (cis-1,3)) (4.8)

$2C_4H_8 \rightarrow C_8H_{16}$(trans-1,3-dimethylcyclohexane (trans-1,3)) (4.9)

$2C_4H_8 \rightarrow C_8H_{16}$(cis-1,4-dimethylcyclohexane (cis-1,4)) (4.10)

$2C_4H_8 \rightarrow C_8H_{16}$(trans-1,4-dimethylcyclohexane (trans-1,4)) (4.11)

- Hydrocracking

$C_4H_8 + 2H_2 \rightarrow 2C_2H_6$ (4.12)

$C_4H_{10} + H_2 \rightarrow C_3H_8 + CH_4$ (4.13)

$C_4H_{10} + H_2 \rightarrow 2C_2H_6$ (4.14)

C_6H_6(benzene (b)) + $6H_2 \rightarrow 3C_2H_6$ (4.15)

C_7H_8(toluene (t)) + $H_2 \rightarrow C_6H_6$(b) + CH_4 (4.16)

C_7H_{14}(methylcyclohexane (MCH)) + $H_2 \rightarrow C_6H_{12}$(cyclohexane (CH)) + CH_4 (4.17)

C_8H_{10}(ethylbenzene (e)) + $H_2 \rightarrow C_7H_8$(t) + CH_4 (4.18)

C_8H_{10}(p-xylene(p)) + $H_2 \rightarrow C_7H_8$(t) + CH_4 (4.19)

C_8H_{10}(o-xylene(o)) + $H_2 \rightarrow C_7H_8$(t) + CH_4 (4.20)

C_8H_{10}(m-xylene(m)) + $H_2 \rightarrow C_7H_8$(t) + CH_4 (4.22)

C_8H_{16}(ECH) + $H_2 \rightarrow C_7H_{14}$(MCH) + CH_4 (4.23)

- Aromatization

$2C_4H_{10} \rightarrow C_6H_6$(b) + $C_2H_4 + 5H_2$ (4.24)

$2C_4H_{10} \rightarrow C_8H_{10}$(p) + $5H_2$ (4.25)

$2C_4H_{10} \rightarrow C_8H_{10}$(e) + $5H_2$ (4.26)

C_6H_{12}(CH) $\rightarrow C_6H_6$ (b) + $3H_2$ (4.27)

$$C_7H_{14}(\text{MCH}) \rightarrow C_7H_8(\text{t}) + 3H_2 \tag{4.28}$$

$$C_8H_{16}(\text{ECH}) \rightarrow C_8H_{10}(\text{e}) + 3H_2 \tag{4.29}$$

$$C_8H_{16}(\text{cis-1,2}) \rightarrow C_8H_{10}(\text{o}) + 3H_2 \tag{4.30}$$

$$C_8H_{16}(\text{trans-1,2}) \rightarrow C_8H_{10}(\text{o}) + 3H_2 \tag{4.31}$$

$$C_8H_{16}(\text{cis-1,3}) \rightarrow C_8H_{10}(\text{m}) + 3H_2 \tag{4.32}$$

$$C_8H_{16}(\text{trans-1,3}) \rightarrow C_8H_{10}(\text{m}) + 3H_2 \tag{4.33}$$

$$C_8H_{16}(\text{cis-1,4}) \rightarrow C_8H_{10}(\text{p}) + 3H_2 \tag{4.34}$$

$$C_8H_{16}(\text{trans-1,4}) \rightarrow C_8H_{10}(\text{p}) + 3H_2 \tag{4.35}$$

- Thermal cracking

$$C_4H_{10} \rightarrow CH_4 + C_3H_6 \tag{4.36}$$

$$C_4H_{10} \rightarrow C_2H_4 + C_2H_6 \tag{4.37}$$

$$C_8H_{10}(\text{e}) \rightarrow C_6H_6(\text{b}) + C_2H_4 \tag{4.38}$$

- Catalytic cracking

$$2C_7H_8(\text{t}) \rightarrow 2C_6H_6(\text{b}) + C_2H_4 \tag{4.39}$$

$$C_8H_{10}(\text{p}) \rightarrow C_6H_6(\text{b}) + C_2H_4 \tag{4.40}$$

$$C_8H_{10}(\text{o}) \rightarrow C_6H_6(\text{b}) + C_2H_4 \tag{4.41}$$

$$C_8H_{10}(\text{m}) \rightarrow C_6H_6(\text{b}) + C_2H_4 \tag{4.42}$$

$$2C_8H_{10}(\text{p}) \rightarrow 2C_7H_8(\text{t}) + C_2H_4 \tag{4.43}$$

$$2C_8H_{10}(\text{o}) \rightarrow 2C_7H_8(\text{t}) + C_2H_4 \tag{4.44}$$

$$2C_8H_{10}(\text{m}) \rightarrow 2C_7H_8\ (\text{t}) + C_2H_4 \tag{4.45}$$

$$C_8H_{10}(\text{p}) + C_8H_{10}(\text{o}) \rightarrow 2C_7H_8 + C_2H_4 \tag{4.46}$$

$$C_8H_{10}(\text{p}) + C_8H_{10}(\text{m}) \rightarrow 2C_7H_8 + C_2H_4 \tag{4.47}$$

$$C_8H_{10}(\text{o}) + C_8H_{10}(\text{m}) \rightarrow 2C_7H_8 + C_2H_4 \tag{4.48}$$

- Isomerization

$$C_8H_{10}(\text{e}) \rightarrow C_8H_{10}(\text{p}) \tag{4.49}$$

$$C_8H_{10}(\text{e}) \rightarrow C_8H_{10}(\text{o}) \tag{4.50}$$

$$C_8H_{10}(\text{e}) \rightarrow C_8H_{10}(\text{m}) \tag{4.51}$$

$$C_8H_{16}(\text{ECH}) \rightarrow C_8H_{16}(\text{cis-1,2}) \tag{4.52}$$

$$C_8H_{16}(\text{ECH}) \rightarrow C_8H_{16}(\text{trans-1,2}) \tag{4.53}$$

$$C_8H_{16}(\text{ECH}) \rightarrow C_8H_{16}(\text{cis-1,3}) \tag{4.54}$$

$$C_8H_{16}(\text{ECH}) \rightarrow C_8H_{16}(\text{trans-1,3}) \tag{4.55}$$

C_8H_{16}(ECH) → C_8H_{16}(cis-1,4) (4.56)

C_8H_{16}(ECH) → C_8H_{16}(trans-1,4) (4.57)

- Transalkylation

$2C_7H_8$(t) → C_6H_6(b) + C_8H_{10}(p) (4.58)

$2C_7H_8$(t) → C_6H_6(b) + C_8H_{10}(o) (4.59)

$2C_7H_8$(t) → C_6H_6(b) + C_8H_{10}(m) (4.60)

4.4 Simulation with Aspen Plus V9

4.4.1 Parameters

The model was regarded as equilibrium state which the forward reaction rate and the reverse reaction rate are equivalent and thus equilibrium reactors were operated completely. In addition, butane was fed in the reactor which was connected to other reactors in series for recording mass fractions of the effluents and thus influent flow rate could be ignorable. Next, the components in the process are hydrocarbons, then Peng-Robinson method was preferred as a base method because it is necessary to consider interaction between each components in the mixtures. Moreover, Sequential Modular (SM) strategy was operated to compute inlet stream, outlet stream, and each block. The SM basically solves a problem, having no degree of freedom, and model inputs and parameters are fixed.

4.4.2 Operating conditions

There are two catalysts which were considered because the experimental result information was presented thoroughly, enabling create a model. The interesting catalysts would be Zn loaded on ZSM-5/ZSM-11 and MoC loaded on HZSM-5.

- Zn loaded on ZSM-5/ZSM-11

For the experiment, Zn was loaded on the ZSM-5/ZSM-11 zeolite for 2 wt%, which is represented as 2Zn/CDM5 catalyst. Butane was used to be a reactant and was operated at 480 ^{0}C and 0.4 MPa with WHSV (CH2 mass) equal to 0.6 h-1. The data were taken at 3-6 hours on stream. Therefore, the simulation operated butane as a reactant at 480 ^{0}C and 0.4 MPa with equilibrium reactors.

- MoC loaded on HZSM-5

For the experiment, the aromatization was operated from n-butane over 10wt.% of MoC loaded HZSM-5, which represented ratio of silicon dioxide to aluminium oxide stands at 30. Operating temperature and pressure were 500 ^{0}C and 1 atm with time on stream is 60 minutes. Therefore, the simulation operated butane as a reactant at 500 ^{0}C and 1 atm with equilibrium reactors.

4.5 Simulation with non-linear solver

4.5.1 Parameters

- Gibbs energy of reaction

Gibbs energy of formation of individual components in a reaction is desired in order to calculation Gibbs energy of reaction as follows:

$$\Delta G_{reaction} = \sum(n\Delta G_f)_{products} - \sum(n\Delta G_f)_{reactants} \qquad (4.61)$$

Gibbs energy of formation at any temperature obtained from the chemical properties handbook.[21] When Gibbs energy of reaction is negative value, the reaction is favorable outcome to reject unnecessary reactions.

- Relation of Gibbs energy of reactions and equilibrium constant[22]

$$\Delta G^0 = -RTlnK \qquad (4.62)$$

Likewise $Kp_{(n)}$ is the expression for equilibrium constant of any reaction when there is more than one reaction, $\Delta G_n{}^0$ is also represented as Gibbs energy of any reactions as shown below:

$$\Delta G_1{}^0 = -RTlnK_1 \qquad (4.63)$$

$$\Delta G_2{}^0 = -RTlnK_2 \qquad (4.64)$$

- Reacted mole(x)

In the reactors, there are several chemical reactions and thus negative of x represented as reactant consumption while positive of x represented as product accumulation for each reaction.

- Pressure

Since the processes were performed at high temperature, total components were gaseous phase. Hence, pressures were essential for calculation, especially partial pressure which represented as mole fractions.

- Equilibrium constant

For a gas-phase reaction, aA(g) + bB(g) ⇋ cC(g) + dD(g), the expression for Kp is:[22]

$$Kp = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b} \tag{4.65}$$

In fact, there are many reactions occurring in the reactor, hence Kp would be represented as $Kp_{(n)}$ where n is a number of any reaction. To illustrate, there are reactions as follows:

$$rR(g) \leftrightharpoons sS(g) + tT(g) \tag{4.66}$$

$$xX(g) \leftrightharpoons yY(g) + zZ(g) \tag{4.67}$$

Then, Kp of both reactions would be

$$Kp_1 = \frac{(P_S)^s(P_T)^t}{(P_R)^r} \tag{4.68}$$

and

$$Kp_2 = \frac{(P_Y)^y(P_Z)^z}{(P_X)^x} \tag{4.69}$$

- Initial guess

Since solving non-linear equations obtains many answers which depend on the power of all variables, initial guess is important to affect to the answer which can be investigated by realistic outcome.

4.5.2 Operating conditions

For 2Zn/CDM5 catalyst, operating temperature and pressure were 753 K and 3.95 atm at equilibrium state of model Zn.11 at reactor 1. The units are more convenient for calculation codes.

4.6 Verification of models using statistics

After all proposed models were simulated, effluent components were compared with the experimental result. Therefore, Residua Sum Square (RSS) was utilized to validate the proposed model. Since RSS is the value of deviations calculated from summation of square difference between effluent mass fraction of each component from the experiment (M_{exp}) and chemical equilibrium model (M_{model}). Then, the lowest RSS would present the appropriate model.

$$RSS = \sum_{i=1}^{N} \left[\frac{(M_{exp} - M_{model})}{M_{exp}} \right]^2 \tag{4.70}$$

4.7 Prediction from the appropriate model

4.7.1 Prediction from the appropriate model by varying mixed butane and butene ratios

From the experiment, there is no butene as a reactant and thus butene would be fed in the models to anticipate aromatics production from mixed butane and butene with various ratios.

4.7.2 Prediction from the appropriate model by varying temperature

Operating temperatures were varied to anticipate aromatics production from butane by the appropriate model, and comparing with the experimental results. There were 480 °C, 510 °C, and 540 °C.

4.7.3 Prediction from the appropriate model by varying pressure

Operating pressures were varied to anticipate aromatics production from butane by the appropriate model, and comparing with the experimental results. There were 0.1 MPa, 0.4 MPa, and 1.1 MPa.

CHAPTER V
RESULT AND DISCUSSION

5.1 Aspen Plus V9 simulator

5.1.1 Zn loaded on ZSM-5/ZSM-11

- Model Zn.1

Reactor 1

$C_4H_{10} \rightarrow CH_4 + C_3H_6$, $C_3H_6 + H_2 \rightarrow C_3H_8$
$2C_4H_{10} \rightarrow C_6H_6(b) + C_2H_4 + 5H_2$, $2C_4H_{10} \rightarrow C_8H_{10}(p) + 5H_2$
$2C_4H_{10} \rightarrow C_8H_{10}(e) + 5H_2$, $2C_7H_8(t) \rightarrow C_6H_6(b) + C_8H_{10}(p)$

Reactor 2

$C_4H_{10} \rightarrow CH_4 + C_3H_6$, $C_3H_6 + H_2 \rightarrow C_3H_8$
$C_4H_{10} \rightarrow C_4H_8 + H_2$, $C_4H_{10} \rightarrow C_2H_4 + C_2H_6$
$C_2H_4 + H_2 \rightarrow C_2H_6$

Model Zn.1 shows two reactors connected in series. Butane converted to aromatics directly while only toluene was formed by reveres of transalkylation. Moreover, thermal cracking and hydrogenation occurred in the reactor 1 and 2 because operating temperature was high and aromatization produced a large amount of hydrogen, respectively.

- Model Zn.2

Reactor 1

$C_4H_{10} \rightarrow CH_4 + C_3H_6$, $C_8H_{16}(ECH) \rightarrow C_8H_{10}(e) + 3H_2$
$C_4H_{10} \rightarrow C_4H_8 + H_2$, $C_8H_{10}(e) \rightarrow C_6H_6(b) + C_2H_4$
$C_3H_6 + H_2 \rightarrow C_3H_8$, $C_8H_{10}(e) \rightarrow C_8H_{10}(p)$
$2C_4H_8 \rightarrow C_8H_{16}(ECH)$, $2C_7H_8(t) \rightarrow C_6H_6(b) + C_8H_{10}(p)$

Reactor 2

$C_4H_{10} \rightarrow CH_4 + C_3H_6$, $C_3H_6 + H_2 \rightarrow C_3H_8$
$C_4H_{10} \rightarrow C_4H_8 + H_2$, $C_4H_{10} \rightarrow C_2H_4 + C_2H_6$
$C_2H_4 + H_2 \rightarrow C_2H_6$

Model Zn.2 shows different way of aromatics production with the same composition results as in the appendix A but the aromatics were produced from ethylbenzene which was converted from ethylcyclohexane, combining of 1-butenes. In contrast, toluene production was also formed by reveres of transalkylation similar to model Zn.1. Moreover, the reactor 2 is also as the same with model Zn.1. As the results, the reactor 1 and the reactor 2 of model Zn.1 and Zn.2 are very close to each other. Moreover, ethylcyclohexane from the model was close to zero, it could be as an intermediate of the mechanism.

Since aromatics production from mixture butanes and butenes is an interesting model, there are dehydrogenation of butane in the reactor 1 in order to find equilibrium between them before converting to ethylcyclohexane and ethylbenzene, sequentially. Then, the second model is chosen because feed mixtures might be n-butane and 1-butene.

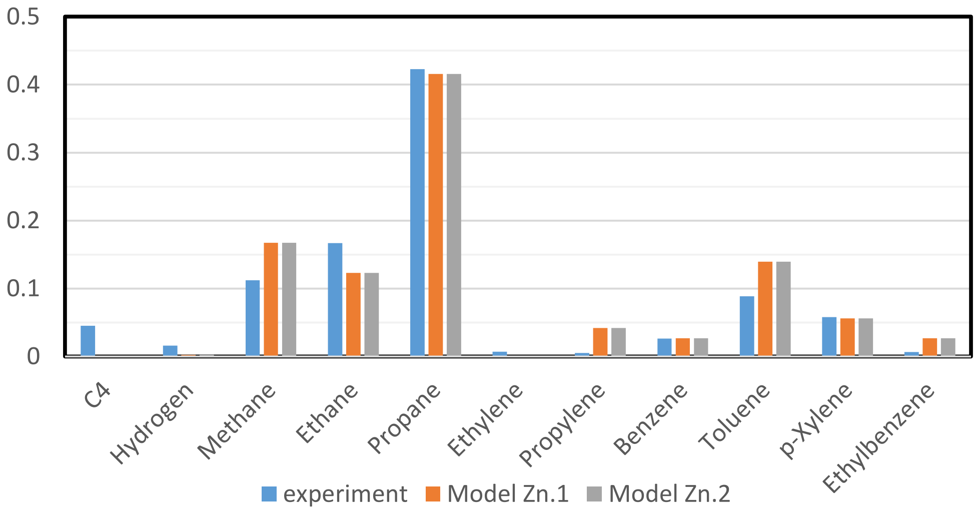

Figure 12 Effluent mass fractions of the experiment, model Zn.1 and Zn.2

- Model Zn.3

Reactor 1

$C_4H_{10} \rightarrow C_4H_8 + H_2$, $2C_4H_8 \rightarrow C_8H_{16}(ECH)$

$C_8H_{16}(ECH) \rightarrow C_8H_{10}(e) + 3H_2$

Reactor 2

$C_8H_{10}(e) + H_2 \rightarrow C_7H_8(t) + CH_4$, $C_4H_{10} + H_2 \rightarrow C_3H_8 + CH_4$

$C_4H_{10} + H_2 \rightarrow 2C_2H_6$

Reactor 3

$2C_7H_8(t) \rightarrow C_6H_6(b) + C_8H_{10}(p)$, $2C_7H_8(t) \rightarrow C_6H_6(b) + C_8H_{10}(o)$

$2C_7H_8(t) \rightarrow C_6H_6(b) + C_8H_{10}(m)$

Model Zn.3 grouped the same types of reactions into three reactors, connected in series. Firstly, butane was dehydrogenated to butene before cyclization to ethylcyclohexane in order to aromatize to be ethylbenzene. Likewise, the first aromatic was formed is ethylbenzene in the reactor 1. Secondly, toluene was produced from hydrocracking of ethylbenzene in the reactor 2. In addition, butane also was cracked by hydrogen to be propane, ethane and methane. Finally, transalkylation of toluene produced benzene and xylene isomers. However, the aromatic mass fractions were higher than the experiment over a half.

- Model Zn.4

Reactor 1

$C_4H_{10} \rightarrow C_4H_8 + H_2$, $2C_4H_8 \rightarrow C_8H_{16}(ECH)$

$C_4H_{10} + H_2 \rightarrow C_3H_8 + CH_4$, $C_8H_{16}(ECH) \rightarrow C_8H_{10}(e) + 3H_2$

$C_4H_{10} + H_2 \rightarrow 2C_2H_6$

Reactor 2

$C_8H_{10}(e) + H_2 \rightarrow C_7H_8(t) + CH_4$

Reactor 3

$2C_7H_8(t) \rightarrow C_6H_6(b) + C_8H_{10}(p)$, $2C_7H_8(t) \rightarrow C_6H_6(b) + C_8H_{10}(o)$

$2C_7H_8(t) \rightarrow C_6H_6(b) + C_8H_{10}(m)$

Hydrocracking of butane in the reactor 2 of model Zn.3 was moved to the reactor 1 in model Zn.4 in order to reduce ethylbenzene production that converted to aromatics in the next steps, then ethylbenzene production in the reactor 1 decreased. Likewise, toluene production was from ethylbenzene. In addition, hydrogen in the reactor 2 which is necessary in the reaction decreased significantly and thus toluene which was used to produce benzene and xylenes reduced dramatically while there was a great amount of excess ethylbenzene as shown in figure 13 and the appendix A.

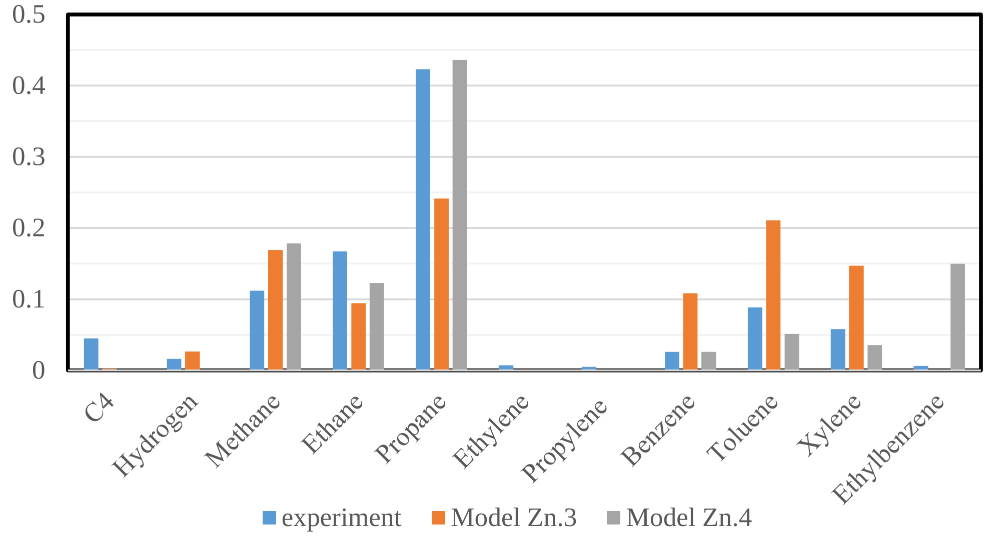

Figure 13 Effluent mass fractions of the experiment, model Zn.3 and Zn.4

- Model Zn.5

Reactor 1

$C_4H_{10} \rightarrow C_4H_8 + H_2$, $2C_4H_8 \rightarrow C_8H_{16}(ECH)$

$C_4H_{10} + H_2 \rightarrow C_3H_8 + CH_4$, $C_8H_{16}(ECH) \rightarrow C_8H_{10}(e) + 3H_2$

$C_4H_{10} + H_2 \rightarrow 2C_2H_6$

Reactor 2

$C_8H_{10}(e) + H_2 \rightarrow C_7H_8(t) + CH_4$

Reactor 3

$2C_7H_8(t) \rightarrow C_6H_6(b) + C_8H_{10}(p)$, $2C_7H_8(t) \rightarrow C_6H_6(b) + C_8H_{10}(o)$

$2C_7H_8(t) \rightarrow C_6H_6(b) + C_8H_{10}(m)$

Reactor 4

$C_8H_{10}(e) \rightarrow C_8H_{10}(p)$, $C_8H_{10}(e) \rightarrow C_8H_{10}(o)$

$C_8H_{10}(e) \rightarrow C_8H_{10}(m)$

From model Zn.5, isomerization of ethylbenzene to xylenes was added in the reactor 4 since there was a great amount of excess ethylbenzene in model Zn.6, then the amount of ethylbenzene decreased extremely, converting into xylene. Therefore, the amount of xylenes is greater than the experimental result in triple figures.

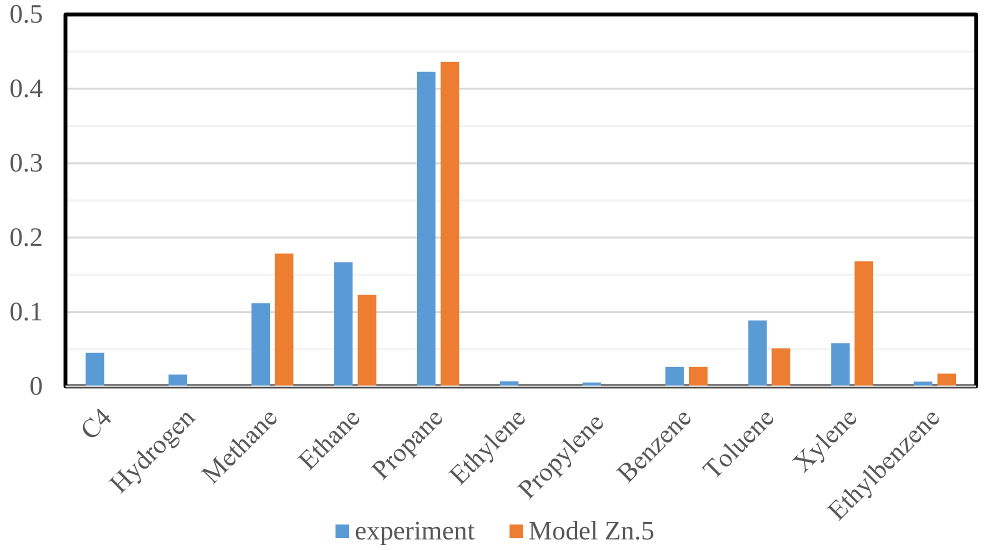

Figure 14 Effluent mass fractions of the experiment and model Zn.5

- Model Zn.6

Reactor 1

$C_4H_{10} \rightarrow C_4H_8 + H_2,$ $2C_4H_8 \rightarrow C_8H_{16}(ECH)$

$C_8H_{16}(ECH) \rightarrow C_8H_{10}(e) + 3H_2$

Reactor 2

$C_8H_{10}(e) + H_2 \rightarrow C_7H_8(t) + CH_4,$ $C_4H_{10} + H_2 \rightarrow C_3H_8 + CH_4$

$C_7H_8(t) + H_2 \rightarrow C_6H_6(b) + CH_4,$ $C_4H_{10} + H_2 \rightarrow 2C_2H_6$

Reactor 3

$C_8H_{10}(e) \rightarrow C_8H_{10}(p),$ $C_8H_{10}(e) \rightarrow C_8H_{10}(o)$

$C_8H_{10}(e) \rightarrow C_8H_{10}(m)$

Model Zn.6 shows three reactors connected in series. Firstly, butane was dehydrogenated to butene before cyclization to ethylcyclohexane in order to aromatize to be ethylbenzene. Likewise, the first aromatic was formed is ethylbenzene in the reactor 1. Secondly, toluene and benzene were produced from hydrocracking of ethylbenzene and toluene in reactor 2, respectively. In addition, butane also was cracked by hydrogen to be propane, ethane and methane. Finally, ethylbenzene remaining converted to the three isomers of xylene, including para-xylene, ortho-xylene and meta-xylene.

In the reactor 2, by-product of both toluene and benzene production reactions was methane because different by-product strongly influenced reaction equilibrium shifting and aromatics production, especially toluene and benzene fractions. As a result, the amount of hydrogen from the reactor 1 was formed extremely, allowing remaining hydrogen to react in the reactor 2, especially benzene production. Therefore, there was hardly no ethylbenzene which isomerized in the reactor 3.

- Model Zn.7

Reactor 1

$C_4H_{10} \rightarrow C_4H_8 + H_2$, $2C_4H_8 \rightarrow C_8H_{16}(\text{ECH})$

$C_4H_{10} + H_2 \rightarrow C_3H_8 + CH_4$, $C_8H_{16}(\text{ECH}) \rightarrow C_8H_{10}(\text{e}) + 3H_2$

$C_4H_{10} + H_2 \rightarrow 2C_2H_6$

Reactor 2

$C_8H_{10}(\text{e}) + H_2 \rightarrow C_7H_8(\text{t}) + CH_4$, $C_7H_8(\text{t}) + H_2 \rightarrow C_6H_6(\text{b}) + CH_4$

Reactor 3

$C_8H_{10}(\text{e}) \rightarrow C_8H_{10}(\text{p})$, $C_8H_{10}(\text{e}) \rightarrow C_8H_{10}(\text{o})$

$C_8H_{10}(\text{e}) \rightarrow C_8H_{10}(\text{m})$

Hydrocracking of butane were moved to the reactor 1, and it has seen that aromatics fractions are more similar to the experimental result as shown in figure 15 since ethylbenzene production which would be converted to other aromatics halved approximately. The butane hydrocracking is competitive reaction, which Zn loaded on ZSM-5/ZSM-11 catalyst could not wholly eliminate, the experimental products were lower. Therefore, the desired product will be higher if another catalyst has functional elimination of the reactions from the reactor 1; however, the reactions are proper in the reactor 1 for the catalyst.

Significantly different xylene amounts of models Zn.6 and Zn.7 depend on remaining hydrogen from the reactor 1 because of xylene production from existing ethylbenzene in the reactor 2, which certain part was converted to toluene by the remaining hydrogen. Therefore, hydrocracking reactions of butane are necessary in the reactor 1 to reduce the hydrogen, reacting with ethylbenzene and toluene in the reactor 2 in order to continue to produce greater xylene amount in the reactor 3

However, although the amounts of toluene and xylene were similar to the experimental values, quantity of benzene was extremely lower. Then, the next model would be created to improve and more accuracy.

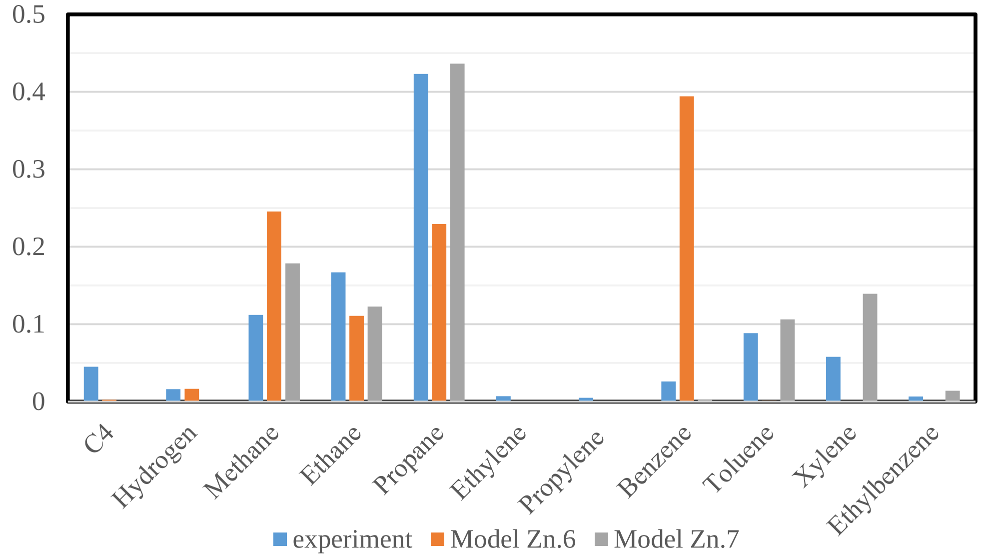

Figure 15 Effluent mass fractions of the experiment, model Zn.6 and Zn.7

- Model Zn.8

Reactor 1

$C_4H_{10} \rightarrow C_4H_8 + H_2$, $2C_4H_8 \rightarrow C_8H_{16}(ECH)$

$C_4H_{10} + H_2 \rightarrow C_3H_8 + CH_4$, $C_8H_{16}(ECH) \rightarrow C_8H_{10}(e) + 3H_2$

$C_4H_{10} + H_2 \rightarrow 2C_2H_6$

Reactor 2

$C_8H_{10}(e) + H_2 \rightarrow C_7H_8(t) + CH_4$, $C_7H_8(t) + H_2 \rightarrow C_6H_6(b) + CH_4$

Reactor 3

$C_8H_{10}(e) \rightarrow C_8H_{10}(p)$, $C_8H_{10}(e) \rightarrow C_8H_{10}(o)$

$C_8H_{10}(e) \rightarrow C_8H_{10}(m)$

Reactor 4

$C_8H_{10}(e) \rightarrow C_6H_6(b) + C_2H_4$, $C_8H_{10}(p) \rightarrow C_6H_6(b) + C_2H_4$

$C_8H_{10}(o) \rightarrow C_6H_6(b) + C_2H_4$, $2C_7H_8(t) \rightarrow 2C_6H_6(b) + C_2H_4$

The reactor 4, represented thermal cracking and catalytic cracking, were added in model Zn.8 in order to adjust aromatic proportions to the experimental result, especially increasing benzene. Besides, there was no hydrogen in the reactor 4 because it had been extremely depleted since reactor 2, then hydrocracking disappeared. Likewise, ethylbenzene, xylene and toluene in model Zn.8 is the same production method as the reactor 2, excepting benzene because of adding the reactor 4. Xylene and toluene were cracked by the catalyst to be benzene. Thus, it was found a larger deal of benzene in the reactor 4.

- Model Zn.9

Reactor 1

$C_4H_{10} \rightarrow C_4H_8 + H_2$, $2C_4H_8 \rightarrow C_8H_{16}(ECH)$

$C_4H_{10} + H_2 \rightarrow C_3H_8 + CH_4$, $C_8H_{16}(ECH) \rightarrow C_8H_{10}(e) + 3H_2$

$C_4H_{10} + H_2 \rightarrow 2C_2H_6$

Reactor 2

$C_8H_{10}(e) + H_2 \rightarrow C_7H_8(t) + CH_4$, $C_7H_8(t) + H_2 \rightarrow C_6H_6(b) + CH_4$

Reactor 3

$C_8H_{10}(e) \rightarrow C_6H_6(b) + C_2H_4$, $2C_7H_8(t) \rightarrow 2C_6H_6(b) + C_2H_4$

Reactor 4

$C_8H_{10}(e) \rightarrow C_8H_{10}(p)$, $C_8H_{10}(e) \rightarrow C_8H_{10}(o)$

$C_8H_{10}(e) \rightarrow C_8H_{10}(m)$

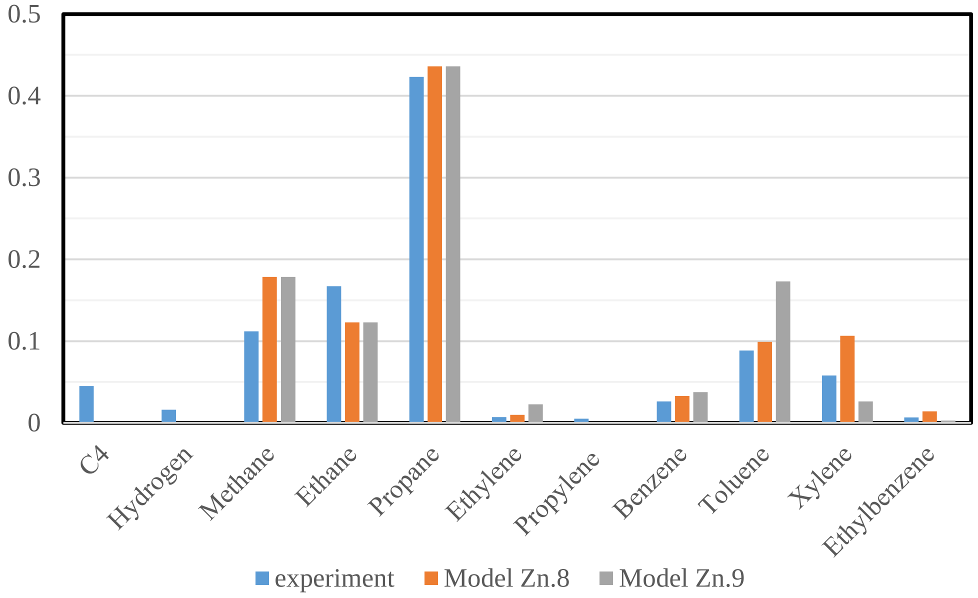

Figure 16 Effluent mass fractions of the experiment, model Zn.8 and Zn.9

Model Zn.9 was designed to visualize how thermal cracking and catalytic cracking had occurred before isomerization happened. Then, the reactors 3 and 4 would be switched from model Zn.8. Ethylbenzene and xylene in model Zn.9 is the same production method as the reactor 2 while the majority of benzene was from thermal cracking of ethylbenzene in the reactor 3. Since benzene was risen dramatically by ethylbenzene, enabling toluene to be increased noticeably for reaching equilibrium state. Likewise, the reaction was reversible, which it is observable from significant rising of toluene.

- Model Zn.10

Reactor 1

$C_4H_{10} \rightarrow C_4H_8 + H_2$, $2C_4H_8 \rightarrow C_8H_{16}(ECH)$

$C_4H_{10} + H_2 \rightarrow C_3H_8 + CH_4$, $C_8H_{16}(ECH) \rightarrow C_8H_{10}(e) + 3H_2$

$C_4H_{10} + H_2 \rightarrow 2C_2H_6$

Reactor 2

$C_8H_{10}(e) + H_2 \rightarrow C_7H_8(t) + CH_4$, $C_7H_8(t) + H_2 \rightarrow C_6H_6(b) + CH_4$

Reactor 3

$C_8H_{10}(e) \rightarrow C_8H_{10}(p)$, $C_8H_{10}(e) \rightarrow C_8H_{10}(o)$

$C_8H_{10}(e) \rightarrow C_8H_{10}(m)$

Reactor 4

$2C_8H_{10}(p) \rightarrow 2C_7H_8(t) + C_2H_4$, $C_8H_{10}(p) + C_8H_{10}(o) \rightarrow 2C_7H_8 + C_2H_4$

$2C_8H_{10}(o) \rightarrow 2C_7H_8(t) + C_2H_4$, $C_8H_{10}(p) + C_8H_{10}(m) \rightarrow 2C_7H_8 + C_2H_4$

$2C_8H_{10}(m) \rightarrow 2C_7H_8\ (t) + C_2H_4$, $C_8H_{10}(o) + C_8H_{10}(m) \rightarrow 2C_7H_8 + C_2H_4$

$2C_7H_8(t) \rightarrow 2C_6H_6(b) + C_2H_4$

Model Zn.10 explains how possible catalytic cracking ways of the aromatics could be performed thoroughly in the reactor 4 since all effluent compositions of model Zn.10 are exactly equal to model Zn.8. Then, it illustrates that xylenes would be cracked by the catalyst to be toluene before it would be also cracked to be benzene.

- Model Zn.11

Reactor 1

$C_4H_{10} \rightarrow C_4H_8 + H_2$, $2C_4H_8 \rightarrow C_8H_{16}(ECH)$

$C_4H_{10} + H_2 \rightarrow C_3H_8 + CH_4$, $C_8H_{16}(ECH) \rightarrow C_8H_{10}(e) + 3H_2$

$C_4H_{10} + H_2 \rightarrow 2C_2H_6$

Reactor 2

$C_8H_{10}(e) + H_2 \rightarrow C_7H_8(t) + CH_4$, $C_7H_8(t) + H_2 \rightarrow C_6H_6(b) + CH_4$

Reactor 3

$C_8H_{10}(e) \rightarrow C_8H_{10}(p)$, $C_8H_{10}(e) \rightarrow C_8H_{10}(o)$

$C_8H_{10}(e) \rightarrow C_8H_{10}(m)$, $2C_7H_8(t) \rightarrow 2C_6H_6(b) + C_2H_4$

$2C_8H_{10}(p) \rightarrow 2C_7H_8(t) + C_2H_4$, $C_8H_{10}(p) + C_8H_{10}(o) \rightarrow 2C_7H_8 + C_2H_4$

$2C_8H_{10}(o) \rightarrow 2C_7H_8(t) + C_2H_4$, $C_8H_{10}(p) + C_8H_{10}(m) \rightarrow 2C_7H_8 + C_2H_4$

$2C_8H_{10}(m) \rightarrow 2C_7H_8\ (t) + C_2H_4$, $C_8H_{10}(o) + C_8H_{10}(m) \rightarrow 2C_7H_8 + C_2H_4$

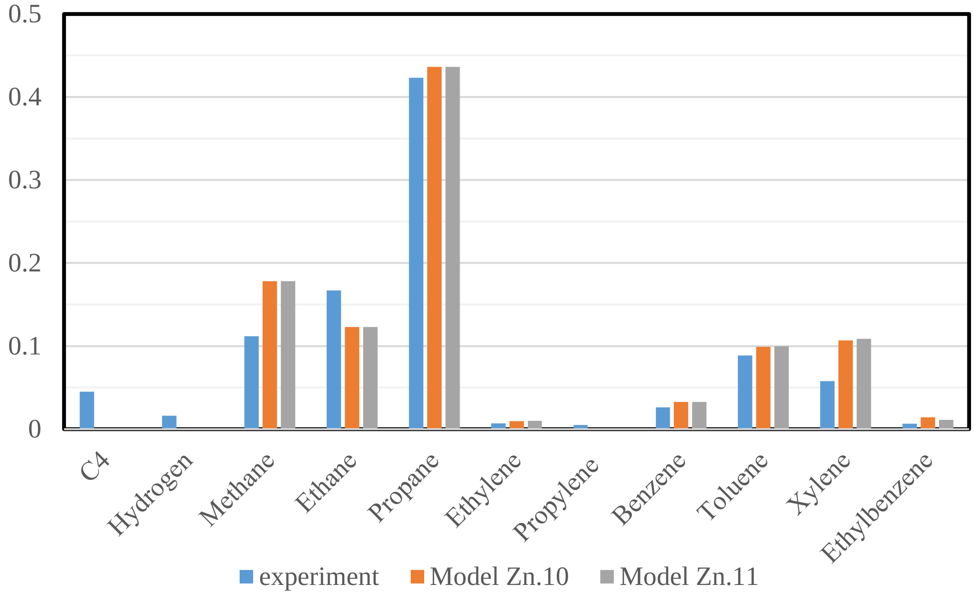

Figure 17 Effluent mass fractions of the experiment, model Zn.10 and Zn.11

On the other hand, the reactors 3 and 4 or isomerization and catalytic cracking grouped together in model Zn.11. Although the effluents are not quite different, and the almost models are closer to the experimental result than model Zn.6 as shown in the figures and thus an exact model should be defined. Hence, Residua Sum Square (RSS) was applied to indicate the most suitable model as shown in tables 10 and 11.

5.1.2 MoC loaded on HZSM-5

- Model MoC.1

Reactor 1

$C_4H_{10} \rightarrow C_4H_8 + H_2$, $2C_4H_8 \rightarrow C_8H_{16}(ECH)$

$C_4H_{10} + H_2 \rightarrow C_3H_8 + CH_4$, $C_8H_{16}(ECH) \rightarrow C_8H_{10}(e) + 3H_2$

$C_4H_{10} + H_2 \rightarrow 2C_2H_6$

Reactor 2

$C_8H_{10}(e) + H_2 \rightarrow C_7H_8(t) + CH_4$, $C_7H_8(t) + H_2 \rightarrow C_6H_6(b) + CH_4$

Reactor 3

$C_8H_{10}(e) \rightarrow C_8H_{10}(p)$, $C_8H_{10}(e) \rightarrow C_8H_{10}(o)$

$C_8H_{10}(e) \rightarrow C_8H_{10}(m)$, $2C_7H_8(t) \rightarrow 2C_6H_6(b) + C_2H_4$

$2C_8H_{10}(p) \rightarrow 2C_7H_8(t) + C_2H_4$, $C_8H_{10}(p) + C_8H_{10}(o) \rightarrow 2C_7H_8 + C_2H_4$

$2C_8H_{10}(o) \rightarrow 2C_7H_8(t) + C_2H_4$, $C_8H_{10}(p) + C_8H_{10}(m) \rightarrow 2C_7H_8 + C_2H_4$

$2C_8H_{10}(m) \rightarrow 2C_7H_8\ (t) + C_2H_4$, $C_8H_{10}(o) + C_8H_{10}(m) \rightarrow 2C_7H_8 + C_2H_4$

Due to model Zn.11 being the best model achievable, it is appropriate to use model Zn.11 as a prototype for model MoC.1. As a result, the amount of toluene was greater than benzene while in the experiment, the amount of benzene was greater than toluene. Furthermore, the huge amount of propane was produced in the reactor 1, comparing with the experiment. Therefore, a pattern would be changed entirely in the next model.

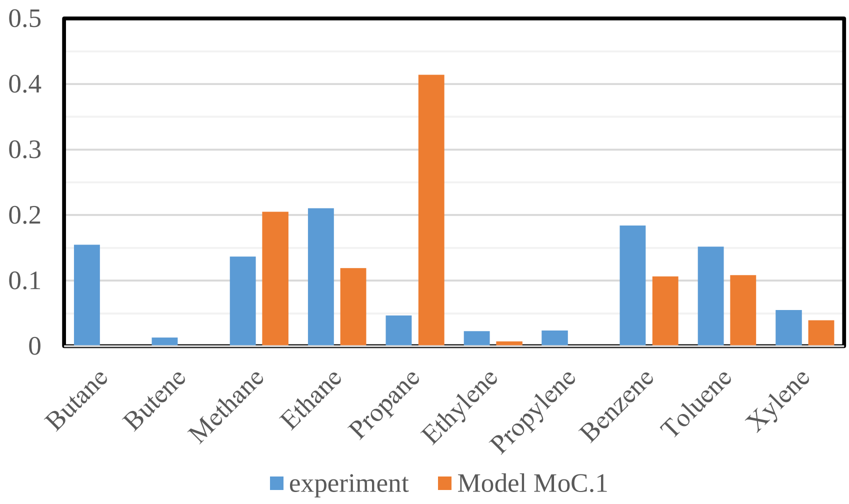

Figure 18 Effluent mass fractions of the experiment and model MoC.1

- Model MoC.2

Reactor 1

$C_4H_{10} \rightarrow C_4H_8 + H_2$, $C_4H_{10} + H_2 \rightarrow C_3H_8 + CH_4$

$2C_4H_8 \rightarrow C_8H_{16}(ECH)$, $C_4H_{10} + H_2 \rightarrow 2C_2H_6$

$C_8H_{16}(ECH) + H_2 \rightarrow C_7H_{14}(MCH) + CH_4$

$C_7H_{14}(MCH) + H_2 \rightarrow C_6H_{12}(CH) + CH_4$

Reactor 2

$C_6H_{12}(CH) \rightarrow C_6H_6\,(b) + 3H_2$, $C_7H_{14}(MCH) \rightarrow C_7H_8(t) + 3H_2$

$C_8H_{16}(ECH) \rightarrow C_8H_{10}(e) + 3H_2$

Reactor 3

$C_8H_{10}(e) \rightarrow C_8H_{10}(p)$, $C_8H_{10}(e) \rightarrow C_8H_{10}(o)$

$C_8H_{10}(e) \rightarrow C_8H_{10}(m)$

Model Moc.2 explains aromatics production by hydrocracking of ethylcyclohexane instead of ethylbenzene, likewise, the pathway would be altered from hydrocracking after aromatization to before aromatization instead. In the reactor 1, dehydrogenation of butane to butene started to undergo cyclization of butene to ethylcyclohexane before hydrocracking to methylcyclohexane and cyclohexane. Moreover, butane was cracked by hydrogen to be propane, ethane and methane. Then, aromatization occurred in the reactor 2 to produce benzene, toluene and ethylbenzene. Finally, there was isomerization of ethylbenzene to three xylene isomers in the reactor 3. As a result, the amount of benzene was greater than toluene similar to the experiment; however, xylenes were seldom manufactured in the reactor 3 because ethylbenzene being a reactant for isomerization remained meagerly from the reactor 2.

- Model MoC.3

Reactor 1

$C_4H_{10} \rightarrow C_4H_8 + H_2$, $2C_4H_8 \rightarrow C_8H_{16}(ECH)$

$C_8H_{16}(ECH) + H_2 \rightarrow C_7H_{14}(MCH) + CH_4$

$C_7H_{14}(MCH) + H_2 \rightarrow C_6H_{12}(CH) + CH_4$

Reactor 2

$C_6H_{12}(CH) \rightarrow C_6H_6\,(b) + 3H_2$, $C_7H_{14}(MCH) \rightarrow C_7H_8(t) + 3H_2$

$C_8H_{16}(ECH) \rightarrow C_8H_{10}(e) + 3H_2$

Reactor 3

$C_8H_{10}(e) \rightarrow C_8H_{10}(p)$, $C_4H_{10} + H_2 \rightarrow C_3H_8 + CH_4$

$C_8H_{10}(e) \rightarrow C_8H_{10}(o)$, $C_4H_{10} + H_2 \rightarrow 2C_2H_6$

$C_8H_{10}(e) \rightarrow C_8H_{10}(m)$

Hydrocracking of butane to propane, ethane and methane was moved to the reactor 3 in model MoC.3 in order to increase aromatics production, especially xylenes from ethylbenzene expectantly. In fact, the reaction in the reactor 1 shifted to cyclohexane production because of hydrogen forming without hydrogen consumption in hydrocracking reactions. Then, the huge amount of benzene was formed and thus the hydrocracking reactions should be in the reactor 1, and the mechanism was improved in the next model in order to rise xylene forming.

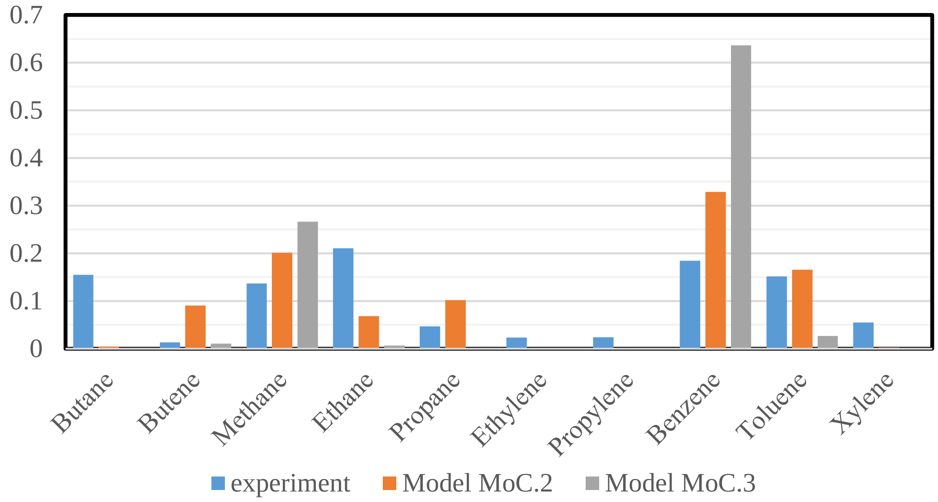

Figure 19 Effluent mass fractions of the experiment, model MoC.2 and model MoC.3

- Model MoC.4

Reactor 1

$C_4H_{10} \rightarrow C_4H_8 + H_2$, $2C_4H_8 \rightarrow C_8H_{16}(ECH)$

$C_8H_{16}(ECH) \rightarrow C_8H_{16}(cis\text{-}1,2)$, $C_8H_{16}(ECH) \rightarrow C_8H_{16}(trans\text{-}1,2)$

$C_8H_{16}(ECH) \rightarrow C_8H_{16}(cis\text{-}1,3)$, $C_8H_{16}(ECH) \rightarrow C_8H_{16}(trans\text{-}1,3)$

$C_8H_{16}(ECH) \rightarrow C_8H_{16}(cis\text{-}1,4)$, $C_8H_{16}(ECH) \rightarrow C_8H_{16}(trans\text{-}1,4)$

$C_4H_{10} + H_2 \rightarrow C_3H_8 + CH_4$, $C_4H_{10} + H_2 \rightarrow 2C_2H_6$

$C_8H_{16}(ECH) + H_2 \rightarrow C_7H_{14}(MCH) + CH_4$

$C_7H_{14}(MCH) + H_2 \rightarrow C_6H_{12}(CH) + CH_4$

Reactor 2

$C_6H_{12}(CH) \rightarrow C_6H_6$ (b) + $3H_2$, $C_7H_{14}(MCH) \rightarrow C_7H_8(t) + 3H_2$

$C_8H_{16}(cis\text{-}1,2) \rightarrow C_8H_{10}(o) + 3H_2$, $C_8H_{16}(trans\text{-}1,2) \rightarrow C_8H_{10}(o) + 3H_2$

C_8H_{16} $(cis\text{-}1,3) \rightarrow C_8H_{10}(m) + 3H_2$, $C_8H_{16}(trans\text{-}1,3) \rightarrow C_8H_{10}(m) + 3H_2$

$C_8H_{16}(cis\text{-}1,4) \rightarrow C_8H_{10}(p) + 3H_2$, $C_8H_{16}(trans\text{-}1,4) \rightarrow C_8H_{10}(p) + 3H_2$

$C_8H_{16}(ECH) \rightarrow C_8H_{10}(e) + 3H_2$

Reactor 3

$C_4H_{10} + H_2 \rightarrow C_3H_8 + CH_4$, $C_4H_{10} + H_2 \rightarrow 2C_2H_6$

$C_4H_8 + H_2 \rightarrow C_4H_{10}$

After ethylcyclohexane was manufactured in the reactor 1, it isomerized to be dimethylcyclohexane isomers, letting it convert to xylenes while the majority of ethylcyclohexane was cracked by hydrogen to be methylcyclohexane and cyclohexane. Then, the aromatics were produced in the reactor 2. Hence, the amount of xylenes was still low production. It is necessary to adjust a pathway as shown in the next model. Since the great amount of hydrogen was formed in the reactor 2, it probably cracked and hydrogenated butane and butene, respectively..

- Model MoC.5

Reactor 1

$C_4H_{10} \rightarrow C_4H_8 + H_2$, $2C_4H_8 \rightarrow C_8H_{16}(ECH)$

$C_8H_{16}(ECH) \rightarrow C_8H_{16}(cis\text{-}1,2)$, $C_8H_{16}(ECH) \rightarrow C_8H_{16}(trans\text{-}1,2)$

$C_8H_{16}(ECH) \rightarrow C_8H_{16}(cis\text{-}1,3)$, $C_8H_{16}(ECH) \rightarrow C_8H_{16}(trans\text{-}1,3)$

$C_8H_{16}(ECH) \rightarrow C_8H_{16}(cis\text{-}1,4)$, $C_8H_{16}(ECH) \rightarrow C_8H_{16}(trans\text{-}1,4)$

$C_8H_{16}(cis\text{-}1,2) \rightarrow C_8H_{10}(o) + 3H_2$, $C_8H_{16}(trans\text{-}1,2) \rightarrow C_8H_{10}(o) + 3H_2$

C_8H_{16} $(cis\text{-}1,3) \rightarrow C_8H_{10}(m) + 3H_2$, $C_8H_{16}(trans\text{-}1,3) \rightarrow C_8H_{10}(m) + 3H_2$

$C_8H_{16}(cis\text{-}1,4) \rightarrow C_8H_{10}(p) + 3H_2$, $C_8H_{16}(trans\text{-}1,4) \rightarrow C_8H_{10}(p) + 3H_2$

$C_4H_{10} + H_2 \rightarrow C_3H_8 + CH_4$, $C_4H_{10} + H_2 \rightarrow 2C_2H_6$

$C_8H_{16}(ECH) \rightarrow C_8H_{10}(e) + 3H_2$

Reactor 2

$C_8H_{16}(ECH) + H_2 \rightarrow C_7H_{14}(MCH) + CH_4$

$C_7H_{14}(MCH) + H_2 \rightarrow C_6H_{12}(CH) + CH_4$

$C_6H_{12}(CH) \rightarrow C_6H_6$ (b) + $3H_2$, $C_7H_{14}(MCH) \rightarrow C_7H_8(t) + 3H_2$

Reactor 3

$C_8H_{10}(p) + H_2 \rightarrow C_7H_8(t) + CH_4$, $C_8H_{10}(o) + H_2 \rightarrow C_7H_8(t) + CH_4$

$C_8H_{10}(m) + H_2 \rightarrow C_7H_8(t) + CH_4$, $C_7H_8(t) + H_2 \rightarrow C_6H_6(b) + CH_4$

A pathway of model MoC.5 started xylenes aromatization of dimethylcyclohexane isomers being from ethylcyclohexane in the reactor 1 while the majority of benzene and toluene was manufactured in the reactor 3 by hydrocracking because remaining ethylcyclohexane in the reactor 2 was inadequate. However, the amount of xylenes was still small in the reactor 3 and thus the next model was development to eliminate the issue.

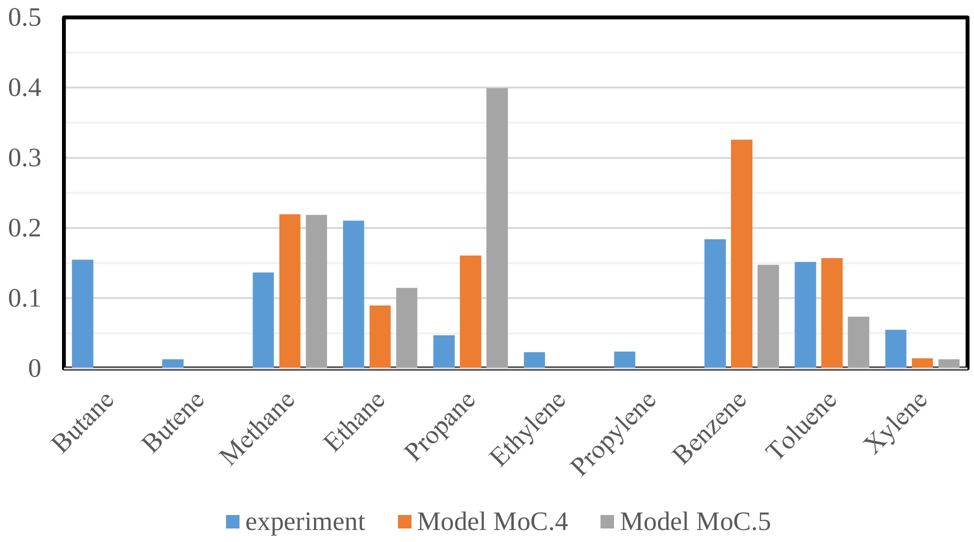

Figure 20 Effluent mass fractions of the experiment, model MoC.4 and model MoC.5

- Model MoC.6

Reactor 1

$C_4H_{10} \rightarrow C_4H_8 + H_2$,

$2C_4H_8 \rightarrow C_8H_{16}$(cis-1,2), $2C_4H_8 \rightarrow C_8H_{16}$(trans-1,2)

$2C_4H_8 \rightarrow C_8H_{16}$(cis-1,3), $2C_4H_8 \rightarrow C_8H_{16}$(trans-1,3)

$2C_4H_8 \rightarrow C_8H_{16}$(cis-1,4), $2C_4H_8 \rightarrow C_8H_{16}$(trans-1,4)

Reactor 2

$C_4H_{10} \rightarrow C_4H_8 + H_2$, $2C_4H_8 \rightarrow C_8H_{16}(ECH)$

$C_4H_{10} + H_2 \rightarrow C_3H_8 + CH_4$, $C_4H_{10} + H_2 \rightarrow 2C_2H_6$

$C_8H_{16}(ECH) + H_2 \rightarrow C_7H_{14}(MCH) + CH_4$

$$C_7H_{14}(\text{MCH}) + H_2 \rightarrow C_6H_{12}(\text{CH}) + CH_4$$

Reactor 3

$$C_6H_{12}(\text{CH}) \rightarrow C_6H_6\ (\text{b}) + 3H_2, \qquad C_7H_{14}(\text{MCH}) \rightarrow C_7H_8(\text{t}) + 3H_2$$

$$C_8H_{16}(\text{cis-1,2}) \rightarrow C_8H_{10}(\text{o}) + 3H_2, \quad C_8H_{16}(\text{trans-1,2}) \rightarrow C_8H_{10}(\text{o}) + 3H_2$$

$$C_8H_{16}\ (\text{cis-1,3}) \rightarrow C_8H_{10}(\text{m}) + 3H_2, \quad C_8H_{16}(\text{trans-1,3}) \rightarrow C_8H_{10}(\text{m}) + 3H_2$$

$$C_8H_{16}(\text{cis-1,4}) \rightarrow C_8H_{10}(\text{p}) + 3H_2, \quad C_8H_{16}(\text{trans-1,4}) \rightarrow C_8H_{10}(\text{p}) + 3H_2$$

$$C_8H_{16}(\text{ECH}) \rightarrow C_8H_{10}(\text{e}) + 3H_2$$

Reactor 4

$$C_4H_8 + 2H_2 \rightarrow 2C_2H_6, \qquad C_6H_6(\text{b}) + 6H_2 \rightarrow 3C_2H_6$$

Dimethylcyclohexane was produced by cyclization of butene in the reactor 1, then butene cyclized to be ethylcyclohexane before hydrocracking in the reactor 2. Besides, there was hydrocracking of butane to be propane, ethane and methane. Next, the ring structures aromatized in the reactor 3, allowing benzene, toluene, xylenes and hydrogen appearance. Then, the large amount of hydrogen would cracked butene and benzene.

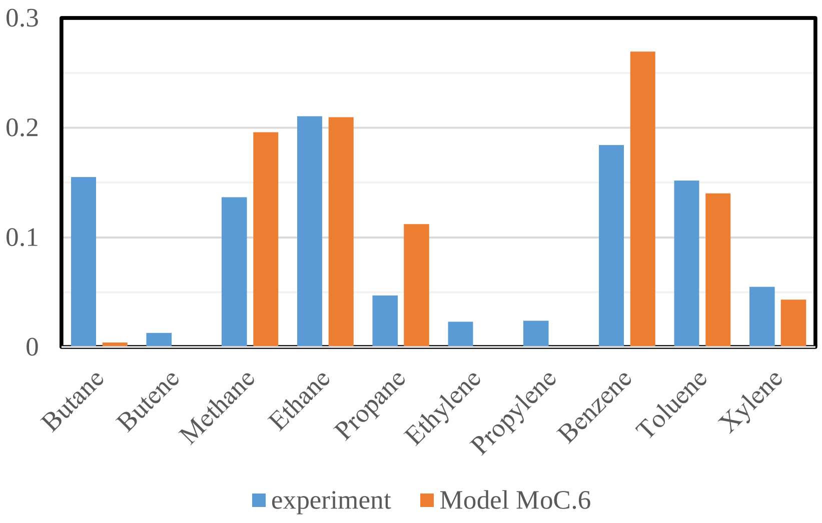

Figure 21 Effluent mass fractions of the experiment and model MoC.6

It is obvious that model MoC.6 is the appropriate model for MoC loaded on HZSM-5 catalyst from figures 18-21. Besides, RSS is necessary to evaluate and thus effluence differences and RSS show in table 12.

5.2 Verification of models using statistics

Tables 10 and 11 present effluent differences of mass fraction between the experiment and the model results, where the negative sign represents greater model outlet than the experiment while the positive sign represents smaller model outlet. Furthermore, the smallest RSS value signified the appropriate model, which would be model Zn.11, accounting for 4.52. In addition, the majority products of a catalyst which has functional as in models Zn.3 and Zn.6 would be aromatics since hydrocracking will be prevented from appearing in the reactor. Thus, ethylcyclohexane in reactor 1 remarkably increases, enabling high aromatization.

Table 10 Effluent differences and RSS of models Zn.1 - Zn.5

component	Model Zn.1	Model Zn.2	Model Zn.3	Model Zn.4	Model Zn.5
C4	0.99	0.99	0.95	0.99	0.99
hydrogen	0.86	0.86	-0.59	1.00	1.00
methane	-0.42	-0.42	-0.44	-0.52	-0.52
ethane	0.30	0.30	0.46	0.30	0.30
propane	0.06	0.06	0.46	0.02	0.02
ethylene	0.87	0.87	1.00	1.00	1.00
propylene	-6.99	-6.99	1.00	1.00	1.00
benzene	0.03	0.03	-2.95	0.04	0.04
toluene	-0.50	-0.50	-1.27	0.45	0.45
xylene	0.08	0.08	-1.42	0.41	-1.77
ethylbenzene	-2.91	-2.91	1.00	-20.96	-1.51
RSS	60.30	60.32	17.21	443.99	9.96

Table 12 shows effluent differences between the experiment and the model results. According to figures 18-12 model MoC.6 is the appropriate model, accounting for 6.31. Moreover, RSS in table 12 validly confirms that RSS of model 6 is the lowest difference between the experiment and the model.

According to the RSS values, summations of aromatics production, including benzene, toluene, and xylene are obvious that the effluents from the appropriate models are higher than the experimental results since reaching equilibrium state represented the maximum aromatics production. Consequently, excess low RSS cannot indicate the verifiable models for the equilibrium state, comparing with Wongwailikhit, 2013, having RSS values of equilibrium models between 0.95 and 1.50.

Table 11 Effluent differences and RSS of models Zn.6 - Zn.11

component	Model Zn.6	Model Zn.7	Model Zn.8	Model Zn.9	Model Zn.10	Model Zn.11
C4	0.95	0.99	0.99	0.99	0.99	0.99
hydrogen	0.02	1.00	1.00	1.00	1.00	1.00
methane	-1.09	-0.52	-0.52	-0.52	-0.52	-0.52
ethane	0.37	0.30	0.30	0.30	0.30	0.30
propane	0.48	0.02	0.02	0.02	0.02	0.02
ethylene	1.00	1.00	-0.32	-2.10	-0.32	-0.34
propylene	1.00	1.00	1.00	1.00	1.00	1.00
benzene	-13.41	0.90	-0.20	-0.38	-0.20	-0.20
toluene	0.99	-0.15	-0.07	-0.86	-0.07	-0.08
xylene	1.00	-1.29	-0.76	0.57	-0.76	-0.79
ethylbenzene	1.00	-1.08	-1.08	0.61	-1.08	-0.62
RSS	187.18	8.01	5.23	9.32	5.23	4.52

Table 12 Effluent differences and RSS of models MoC.1 – MoC.6

component	Model MoC.1	Model MoC.2	Model MoC.3	Model MoC.4	Model MoC.5	Model MoC.6
butane	0.999255	0.972989	1	0.999905	0.999493	0.97399
butene	0.997944	-6.01364	0.166565	0.999916	0.998959	0.999276
methane	-0.49295	-0.47129	-0.95007	-0.60766	-0.60126	-0.4334
ethane	0.436459	0.676142	0.967749	0.574327	0.454419	0.003961
propane	-7.76017	-1.15926	0.983843	-2.41403	-7.48038	-1.3825
ethylene	0.682546	1	1	1	1	1
propylene	1	1	1	1	1	1
benzene	0.425034	-0.78568	-2.45494	-0.76787	0.198512	-0.46303
toluene	0.288332	-0.09403	0.82263	-0.03677	0.512942	0.076917
xylene	0.28244	0.95373	0.999371	0.740133	0.758894	0.211543
RSS	64.45755	42.6695	13.53707	11.66507	61.39947	6.311422

5.3 Simulation with non-linear solver

Model Zn.11 is the appropriate model for Zn loaded on ZSM-5/ZSM-11 catalyst from RSS calculation and thus simulation with non-linear solver by python codes in the appendix B performed the reactor 1 of model Zn.11. There are five reactions as shown in below, and the results illustrate in table 12 and the appendix C with difference initial guesses.

Model Zn.11: Reactor 1

$C_4H_{10} \rightarrow C_4H_8 + H_2$ ----- (5.1)

$2C_4H_8 \rightarrow C_8H_{16}(ECH)$ ----- (5.2)

$C_8H_{16}(ECH) \rightarrow C_8H_{10}(e) + 3H_2$ ----- (5.3)

$C_4H_{10} + H_2 \rightarrow C_3H_8 + CH_4$ ----- (5.4)

$C_4H_{10} + H_2 \rightarrow 2C_2H_6$ ----- (5.5)

Table 13 Non-linear program solver result of model Zn.11 at reactor 1

Reacted and produced mole*	Initial guess of x	Result of x	Component	Mass fraction from non-linear solver	Mass fraction from simulation
x1	0.31	0.31548096	n-butane	0.02009	0.000276
x2	0.16	0.15831117	1-butene	-0.00110	0.000025
x3	0.15	0.15831117	hydrogen	0.00437	0.002466
x4	0.55	0.55511456	methane	0.15320	0.158708
x5	0.1	0.10931171	ethane	0.11311	0.122879
			propane	0.42120	0.436239
			ethylbenzene	0.28919	0.279407
			ethylcyclohexane	0.00000	0.000000

* Reacted and produced mole for reactions 1-5

In conclusion, the effluent mass fractions were calculated by results of reacted and produced mole which there were flexible results depending on the initial guesses. The proper initial guess for the reactor 1 is presented in table 12 since the mass fractions most approached to the model by trial and error method. From the appendix C, the initial guess values were close for each set but the results were definitely different. Hence, simulations with more complex and many equations are rather impractical, especially the reactors 2 and 3 because feeding had more components, and many equations will be also from the various reactions.

5.4 Prediction from the appropriate model

5.4.1 Prediction from the appropriate model by varying mixed butane and butene ratios

Aromatics production from mixed butane and butene was interesting but the experimental reactant is only butane, then model Zn.11 is the best way to anticipate since there is dehydrogenation of butane to butene in the reactor 1, leading to equilibrium outcome between butane and butenes for the production in next steps. The prediction performed various mole fraction ratios of butane and butene as is presented in figure 22 and the appendix D.

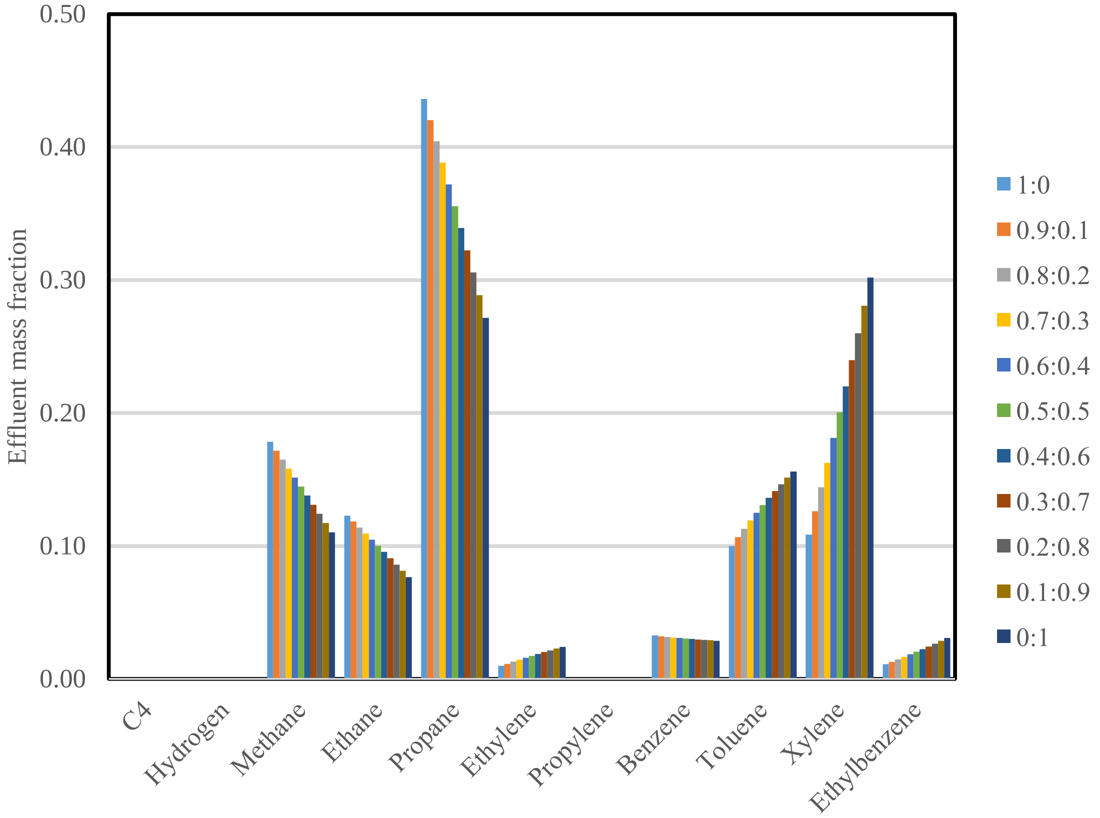

Figure 22 Aromatics production from mixed butane and butene with various ratios in model Zn.11 by mole fraction of butane: butene

As a result, when butene ratio increases, benzene gradually decreases while toluene and xylene significantly increase. Explanation would be divided into three parts for each reactor. Firstly, butane ratio of influent decreased, causing hydrogen from dehydrogenation of butane to decline. Thus, propane, ethane and ethane from hydrocracking of butane also waned gradually. However, there was an enlargement of ethylcyclohexane and ethylbenzene because of butene addition. Secondly, hydrogen from the reactor 1 went down, enabling benzene and toluene in the reactor 2 to drop slightly but substantial ethylbenzene augmentation. Lastly, a huge amount of the remaining ethylbenzene in the reactor 3 converted to three isomers of xylenes. Then, the xylenes were cracked by heat to be toluene and ethylene; however, it was not a high production because of less ethylene stability, comparing with xylenes. Then, benzene production from toluene was also low. In conclusion, butane and butene ratios affected to equilibrium of the reactions, allowing toluene and xylene to rise considerably but benzene to reduce fractionally when butene ratio was added.

5.4.2 Prediction from the appropriate model by varying temperatures

Model Zn.11 was simulated by varying temperature, including 480 ^{o}C, 510 ^{o}C, and 540 ^{o}C. According to figure 23, the experimental effluents significantly increased and decreased while the model effluents were slight changing and steady. Consequently, the model would be simply appropriate at 480 ^{o}C.

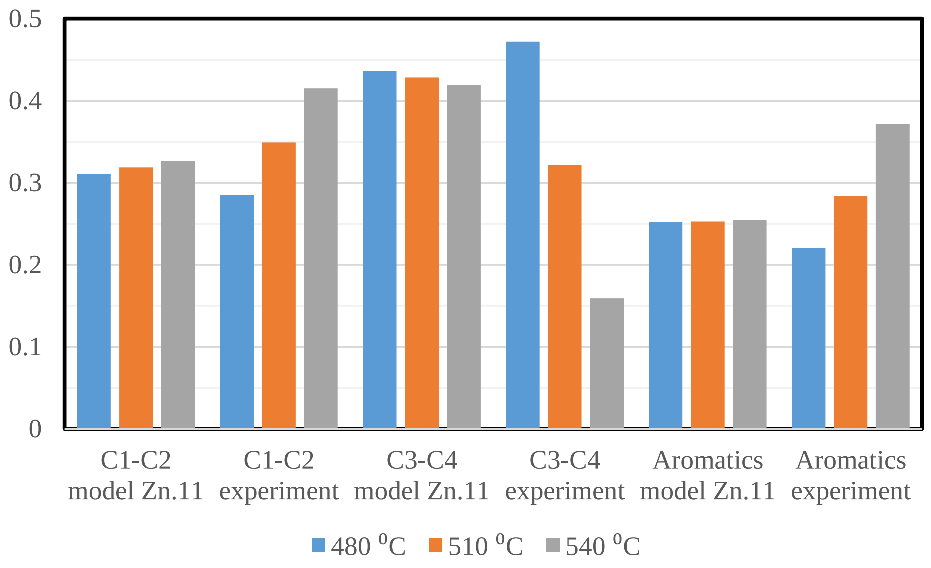

Figure 23 Prediction from model Zn.11 by varying temperatures

5.4.3 Prediction from the appropriate model by varying pressures

Model Zn.11 was simulated by varying pressure, including 0.1 MPa, 0.4 MPa, and 1.1 MPa. According to figure 24, the experiment effluent at 0.4 MPa obtained the highest aromatics production while the model effluent was stable. However, the pressures gradually affected to the experiment and the model results. Hence, the model is efficient to anticipate aromatics production from butane when the pressures were adjusted between 0.1 MPa and 1.1 MPa.

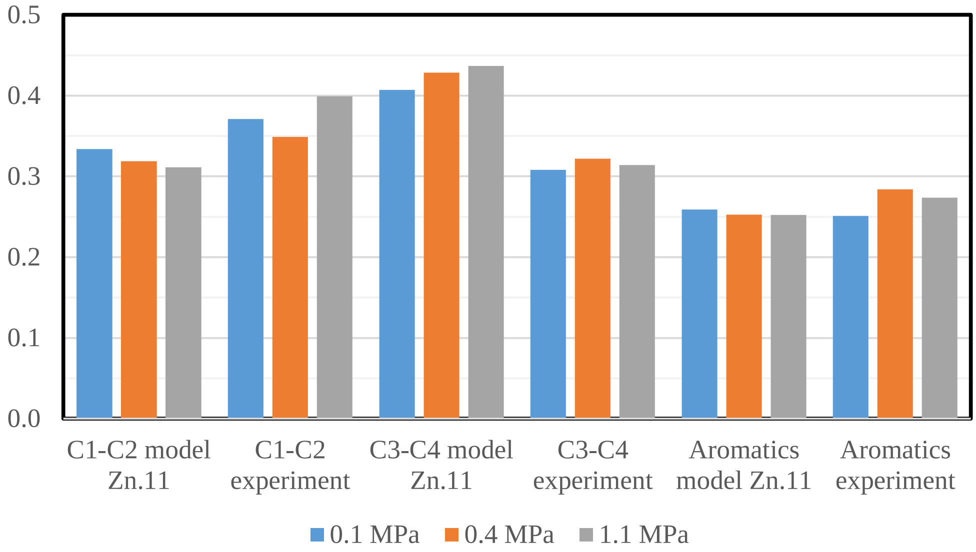

Figure 24 Prediction from model Zn.11 by varying pressures

CHAPTER VI
CONCLUSION

6.1 Conclusion

To summarize, the appropriate model from simulation is model 6 from RSS calculation since the lowest RSS represents the smallest differences between the model and the experimental results for Zn loaded on ZSM-5/ZSM-11 catalyst being 4.52. It has three connected reactors in series to explain sequentially equilibrium steps. To begin, butane was dehydrogenated to butene before cyclization to ethylcyclohexane. Then, ethylbenzene was formed by ethylcyclohexane as aromatization in the reactor 1. Next, there was hydrocracking of ethylbenzene to toluene which was also cracked by hydrogen to benzene afterward in the reactor 2. For the last one, the left ethylbenzene from the reactor 2 was isomerized to three xylene isomers, and then they were cracked by heat to toluene and benzene in the process. On the other hand, the appropriate model with 6.31 of RSS for MoC loaded on HZSM-5 catalyst is model MoC.6, which butane was dehydrogenated to butene before cyclization to dimethylcyclohexane and ethylcyclohexane. Then, ethylcyclohexane was cracked by hydrogen to be methylcyclohexane which was cracked again to cyclohexane. Moreover, there were hydrocracking reactions of butane to propane, ethane and methane in the reactor 2. Next, all cycloalkanes aromatized to benzene, toluene, xylene and ethylbenzene in the reactor 3. Finally, hydrocracking also occurred in the reactor 4.

From non-linear program solver, python codes can calculate effluent components which were close to the simulation model. However, initial guess is significant for the result since non-linear equations will probably provide many answers. Therefore, simulations with more complex and many equations are rather impractical.

Lastly, dehydrogenation of butane to butene in the model is necessary to find equilibrium point for prediction of mixed butane and butene to aromatics. For model Zn.11, prediction varied ratios butane and butene, which found that it outstandingly affected on xylene and slightly influenced to toluene proportions while benzene proportions were almost steady. Consequently, higher butene ratio led to more aromatics production, especially xylene and toluene.

6.2 Recommendation

The model from non-linear program solver could be further developed for the reactors 2 and 3. Unfortunately, initial guessing needed time for trials and errors since there were more variables and non-linear equations

APPENDIX

Appendix A: Effluent mass fractions of equilibrium model

Table A.1 Effluent mass fractions of equilibrium model Zn.1

component	**Reactor1**	**Reactor2**
n-butane	0.000238	0.000295
1-butene	0	0.000029
hydrogen	0.003912	0.002322
methane	0.191517	0.167185
ethane	0	0.123109
propane	0.494592	0.415677
ethylene	0.03079	0.000948
propylene	0.030373	0.041857
benzene	0.026578	0.026578
toluene	0.139556	0.139556
p-xylene	0.055818	0.055818
ethylbenzene	0.026625	0.026625

Table A.2 Effluent mass fractions of equilibrium model Zn.2

component	**Reactor1**	**Reactor2**
n-butane	0.000238	0.000295
1-butene	0.000015	0.000029
hydrogen	0.003912	0.002322
methane	0.191515	0.167187
ethane	0	0.12311
propane	0.494587	0.415674
ethylene	0.03079	0.000948
propylene	0.030373	0.041866
benzene	0.026578	0.026578
toluene	0.139553	0.139553
p-xylene	0.055816	0.055816
ethylbenzene	0.026624	0.026624
ethylcyclohexane	0.000000	0.000000

Table A.3 Effluent mass fractions of equilibrium model Zn.3

component	**Reactor1**	**Reactor2**	**Reactor3**
n-butane	0.409495	0.000015	0.000015
1-butene	0.002413	0.002413	0.002413
hydrogen	0.05107	0.026672	0.026672
methane	0	0.168998	0.168998
ethane	0	0.094341	0.094341
propane	0	0.241486	0.241486
benzene	0	0	0.108098
toluene	0	0.466042	0.211023
o-xylene	0	0	0.038145
m-xylene	0	0	0.077397
p-xylene	0	0	0.031379
ethylbenzene	0.537011	0.000021	0.000021
ethylcyclohexane	0.000011	0.000011	0.000011

Table A.4 Effluent mass fractions of equilibrium model Zn.4

component	**Reactor1**	**Reactor2**	**Reactor3**
n-butane	0.000276	0.000276	0.000276
1-butene	0.000025	0.000025	0.000025
hydrogen	0.002465	0.000000	0.000000
methane	0.158708	0.178323	0.178323
ethane	0.122878	0.122879	0.122879
propane	0.436239	0.436239	0.436239
benzene	0	0	0.026131
toluene	0	0.112659	0.051012
o-xylene	0	0	0.009221
m-xylene	0	0	0.01871
p-xylene	0	0	0.007585
ethylbenzene	0.2794	0.1496	0.1496
ethylcyclohexane	0.000000	0.000000	0.000000

Table A.5 Effluent mass fractions of equilibrium model Zn.5

component	**Reactor1**	**Reactor2**	**Reactor3**	**Reactor4**
n-butane	0.000276	0.000276	0.000276	0.000276
1-butene	0.000025	0.000025	0.000025	0.000025
hydrogen	0.002466	0.000000	0.000000	0.000000
methane	0.158708	0.178323	0.178323	0.178323
ethane	0.122879	0.122879	0.122879	0.122879
propane	0.436239	0.436239	0.436239	0.436239
benzene	0	0	0.026131	0.026131
toluene	0	0.112659	0.051012	0.051012
o-xylene	0	0	0.009221	0.043617
m-xylene	0	0	0.01871	0.088501
p-xylene	0	0	0.007585	0.035881
ethylbenzene	0.279407	0.149598	0.149598	0.017115
ethylcyclohexane	0.000000	0.000000	0.000000	0.000000

Table A.6 Effluent mass fractions of equilibrium model Zn.6

component	**Reactor1**	**Reactor2**	**Reactor3**
n-butane	0.409495	0.000034	0.000034
1-butene	0.002413	0.002413	0.002413
hydrogen	0.051070	0.016502	0.016502
methane	0	0.245539	0.245539
ethane	0	0.110829	0.110829
propane	0	0.229382	0.229382
benzene	0	0.394109	0.394109
toluene	0	0.001181	0.001181
o-xylene	0	0	0.000000
m-xylene	0	0	0.000000
p-xylene	0	0	0.000000
ethylbenzene	0.537011	0.000000	0.000000
ethylcyclohexane	0.000011	0.000011	0.000011

Table A.7 Effluent mass fractions of equilibrium model Zn.7

component	**Reactor1**	**Reactor2**	**Reactor3**
n-butane	0.000276	0.000276	0.000276
1-butene	0.000025	0.000025	0.000025
hydrogen	0.002466	0.000000	0.000000
methane	0.158708	0.178324	0.178324
ethane	0.122879	0.122879	0.122879
propane	0.436239	0.436239	0.436239
benzene	0	0.002681	0.002681
toluene	0	0.106337	0.106337
o-xylene	0	0	0.036106
m-xylene	0	0	0.073261
p-xylene	0	0	0.029702
ethylbenzene	0.279407	0.153237	0.014168
ethylcyclohexane	0.000000	0.000000	0.000000

Table A.8 Effluent mass fractions of equilibrium model Zn.8

component	**Reactor1**	**Reactor2**	**Reactor3**	**Reactor4**
n-butane	0.000276	0.000276	0.000276	0.000276
1-butene	0.000025	0.000025	0.000025	0.000025
hydrogen	0.002466	0.000000	0.000000	0.000000
methane	0.158708	0.178324	0.178324	0.178324
ethane	0.122879	0.122879	0.122879	0.122879
propane	0.436239	0.436239	0.436239	0.436239
ethylene	0	0	0	0.009685
benzene	0	0.002681	0.002681	0.032765
toluene	0	0.106337	0.106337	0.098985
o-xylene	0	0	0.036106	0.02769
m-xylene	0	0	0.073261	0.056185
p-xylene	0	0	0.029702	0.022779
ethylbenzene	0.279407	0.153237	0.014168	0.014168
ethylcyclohexane	0.000000	0.000000	0.000000	0.000000

Table A.9 Effluent mass fractions of equilibrium model Zn.9

component	**Reactor1**	**Reactor2**	**Reactor3**	**Reactor4**
n-butane	0.000276	0.000276	0.000276	0.000276
1-butene	0.000025	0.000025	0.000025	0.000025
hydrogen	0.002466	0.000000	0.000000	0.000000
methane	0.158708	0.178324	0.178324	0.178324
ethane	0.122879	0.122879	0.122879	0.122879
propane	0.436239	0.436239	0.436239	0.436239
ethylene	0	0	0.022722	0.022722
benzene	0	0.002681	0.037693	0.037693
toluene	0	0.106337	0.172994	0.172994
o-xylene	0	0	0	0.006797
m-xylene	0	0	0	0.013792
p-xylene	0	0	0	0.005592
ethylbenzene	0.279407	0.153237	0.028848	0.002667
ethylcyclohexane	0.000000	0.000000	0.000000	0.000000

Table A.10 Effluent mass fractions of equilibrium model Zn.10

component	**Reactor1**	**Reactor2**	**Reactor3**	**Reactor4**
n-butane	0.000276	0.000276	0.000276	0.000276
1-butene	0.000025	0.000025	0.000025	0.000025
hydrogen	0.002466	0.000000	0.000000	0.000000
methane	0.158708	0.178324	0.178324	0.178324
ethane	0.122879	0.122879	0.122879	0.122879
propane	0.436239	0.436239	0.436239	0.436239
ethylene	0	0	0	0.009685
benzene	0	0.002681	0.002681	0.032765
toluene	0	0.106337	0.106337	0.098985
o-xylene	0	0	0.036106	0.02769
m-xylene	0	0	0.073261	0.056185
p-xylene	0	0	0.029702	0.022779
ethylbenzene	0.279407	0.153237	0.014168	0.014168
ethylcyclohexane	0.000000	0.000000	0.000000	0.000000

Table A.11 Effluent mass fractions of equilibrium model Zn.11

component	**Reactor1**	**Reactor2**	**Reactor3**
n-butane	0.000276	0.000276	0.000276
1-butene	0.000025	0.000025	0.000025
hydrogen	0.002466	0.000000	0.000000
methane	0.158708	0.178324	0.178324
ethane	0.122879	0.122879	0.122879
propane	0.436239	0.436239	0.436239
ethylene	0	0	0.009848
benzene	0	0.002681	0.032811
toluene	0	0.106337	0.099948
o-xylene	0	0	0.028192
m-xylene	0	0	0.057202
p-xylene	0	0	0.023192
ethylbenzene	0.279407	0.153237	0.011062
ethylcyclohexane	0.000000	0.000000	00.000000

Table A.12 Effluent mass fractions of equilibrium model MoC.1

component	**Reactor1**	**Reactor2**	**Reactor3**
n-butane	0.000116	0.000116	0.000116
1-butene	0.000027	0.000027	0.000027
hydrogen	0.00679	0.000014	0.000014
methane	0.150045	0.203973	0.203973
ethane	0.118611	0.118611	0.118611
propane	0.412427	0.412427	0.412427
ethylene	0	0	0.007326
benzene	0	0.052055	0.105933
toluene	0	0.186922	0.107942
o-xylene	0	0	0.008401
m-xylene	0	0	0.010324
p-xylene	0	0	0.020669
ethylbenzene	0.311984	0.025855	0.004237
ethylcyclohexane	0.000000	0.000000	0.000000

Table A.13 Effluent mass fractions of equilibrium model MoC.2

component	**Reactor1**	**Reactor2**	**Reactor3**
n-butane	0.004187	0.004187	0.004187
1-butene	0.090643	0.090643	0.090643
hydrogen	0.000062	0.036585	0.036585
methane	0.201014	0.201014	0.201014
ethane	0.068164	0.068164	0.068164
propane	0.101658	0.101658	0.101658
benzene	0	0.328999	0.328999
toluene	0	0.165937	0.165937
o-xylene	0	0	0.000542
m-xylene	0	0	0.000666
p-xylene	0	0	0.001333
ethylbenzene	0	0.002813	0.000273
ethylcyclohexane	0.002974	0.000000	0.000000
methylcyclohexane	0.176829	0.000000	0.000000
cyclohexane	0.354471	0.000000	0.000000

Table A.14 Effluent mass fractions of equilibrium model MoC.3

component	**Reactor1**	**Reactor2**	**Reactor3**
n-butane	0.007563	0.007563	0.000000
1-butene	0.010771	0.010771	0.010771
hydrogen	0.000977	0.052027	0.051765
methane	0.266149	0.266149	0.266426
ethane	0	0	0.006788
propane	0	0	0.000761
benzene	0	0.636548	0.636548
toluene	0	0.026903	0.026903
o-xylene	0	0	0.000007
m-xylene	0	0	0.000009
p-xylene	0	0	0.000018
ethylbenzene	0	0.000038	0.000004
ethylcyclohexane	0.000040	0.000000	0.000000
methylcyclohexane	0.028668	0.000000	0.000000
cyclohexane	0.685831	0.000000	0.000000

Table A.15 Effluent mass fractions of equilibrium model MoC.4

component	**Reactor1**	**Reactor2**	**Reactor3**
n-butane	0.004139	0.004139	0.000015
1-butene	0.086185	0.086185	0.000001
hydrogen	0.000064	0.036561	0.030225
methane	0.199362	0.199362	0.219645
ethane	0.068984	0.068984	0.089593
propane	0.104981	0.104981	0.160732
benzene	0	0.325718	0.325718
toluene	0	0.157252	0.157252
o-xylene	0	0.003628	0.003628
m-xylene	0	0.003558	0.003558
p-xylene	0	0.007080	0.007080
ethylbenzene	0	0.002552	0.002552
ethylcyclohexane	0.002697	0.000000	0.000000
methylcyclohexane	0.167573	0.000000	0.000000
cyclohexane	0.350935	0.000000	0.000000
C8H16(cis-1,2)	0.001088	0.000000	0.000000
C8H16(trans-1,2)	0.002673	0.000000	0.000000
C8H16(cis-1,3)	0.004849	0.000000	0.000000
C8H16(trans-1,3)	0.002635	0.000000	0.000000
C8H16(cis-1,4)	0.001337	0.000000	0.000000
C8H16(trans-1,4)	0.002498	0.000000	0.000000

Table A.16 Effluent mass fractions of equilibrium model MoC.5

component	**Reactor1**	**Reactor2**	**Reactor3**
n-butane	0.000079	0.000079	0.000079
1-butene	0.000014	0.000014	0.000014
hydrogen	0.009345	0.009345	0.000107
methane	0.145253	0.145253	0.218771
ethane	0.114831	0.114831	0.114831
propane	0.399255	0.399255	0.399255
benzene	0	0.000000	0.147668
toluene	0	0.000000	0.073874
o-xylene	0.063778	0.063778	0.002823
m-xylene	0.078382	0.078382	0.003469
p-xylene	0.156899	0.156899	0.006945
ethylbenzene	0.032164	0.032164	0.032164
ethylcyclohexane	0.000000	0.000000	0.000000
methylcyclohexane	0	0.000000	0.000000
cyclohexane	0	0.000000	0.000000
C8H16(cis-1,2)	0.000000	0.000000	0.000000
C8H16(trans-1,2)	0.000000	0.000000	0.000000
C8H16(cis-1,3)	0.000000	0.000000	0.000000
C8H16(trans-1,3)	0.000000	0.000000	0.000000
C8H16(cis-1,4)	0.000000	0.000000	0.000000
C8H16(trans-1,4)	0.000000	0.000000	0.000000

Table A.17 Effluent mass fractions of equilibrium model MoC.6

component	**Reactor1**	**Reactor2**	**Reactor3**	**Reactor4**
n-butane	0.812848	0.004032	0.004032	0.004032
1-butene	0.134909	0.077378	0.077378	0.000009
hydrogen	0.006491	0.000069	0.036468	0.023395
methane	0	0.195837	0.195837	0.195837
ethane	0	0.070673	0.070673	0.209641
propane	0	0.112168	0.112168	0.112168
benzene	0	0	0.318078	0.269552
toluene	0	0	0.140008	0.140008
o-xylene	0	0	0.011008	0.011008
m-xylene	0	0	0.010797	0.010797
p-xylene	0	0	0.021482	0.021482
ethylbenzene	0	0	0.002072	0.002072
ethylcyclohexane	0	0.00219	0.000000	0.000000
methylcyclohexane	0	0.149198	0.000000	0.000000
cyclohexane	0	0.342704	0.000000	0.000000
C8H16(cis-1,2)	0.003302	0.003302	0.000000	0.000000
C8H16(trans-1,2)	0.00811	0.00811	0.000000	0.000000
C8H16(cis-1,3)	0.014711	0.014711	0.000000	0.000000
C8H16(trans-1,3)	0.007995	0.007995	0.000000	0.000000
C8H16(cis-1,4)	0.004055	0.004055	0.000000	0.000000
C8H16(trans-1,4)	0.00758	0.00758	0.000000	0.000000

Appendix B: Python Codes of equilibrium model

Model Zn.11: Reactor 1

```
######## IMPORT ##############
from math import exp
from scipy.optimize import least_squares
##############################

####### CONSTANT #############
T = 753
P = 3.95 #atm
R = 8.314 #J/mol.K
##############################
#rxn1 n-C4H10->C4H8+H2
#rxn2 2C4H8->C8H16(ECH)
#rxn3 C8H16(ECH)->C8H10(e)+3H2
#rxn4 C4H10+H2->C3H8+CH4
#rxn5 C4H10+H2->2C2H6

####### Gibbs (kJ/mol) #######
GC4H10 = -128.375+(3.6047E-01*T)+(3.8256E-05* (T**2) )
GCH4 = -75.262+(7.5925E-02*T)+(1.8700E-05* (T**2) )
GC2H6 = -85.787+(1.6858E-01*T)+(2.6853E-05* (T**2) )
GC3H8 = -105.603+(2.6475E-01*T)+(3.2500E-05*T**2)
GC4H8 = -1.692+(2.3442E-01*T)+(3.1582E-05* (T**2) )
GH2 = 0
GECH =  -177.580+(7.0980E-01*T)+(5.1198E-05*T**2)
GE = 27.421+(3.3327E-01*T)+(3.8542E-05* (T**2) )

deltaG1 = ((GC4H8+GH2)-(GC4H10))*1000 #J/mol
deltaG2 = ((GECH)-(2*GC4H8))*1000 #J/mol
deltaG3 = ((GE+3*GH2)-(GECH))*1000 #J/mol
deltaG4 = ((GC3H8+GCH4)-(GC4H10+GH2))*1000 #J/mol
deltaG5 = ((2*GC2H6)-(GC4H10+GH2))*1000 #J/mol

Kp1 = exp(-deltaG1/(R*T))
Kp2 = exp(-deltaG2/(R*T))
Kp3 = exp(-deltaG3/(R*T))
Kp4 = exp(-deltaG4/(R*T))
Kp5 = exp(-deltaG5/(R*T))

##############################

###### Defining function for Least Squares #######
def equations(p):
    ### Defining Variables
    x1, x2, x3, x4, x5 = p
```

```
    ### Constructing Equation
    Total = 1+x1-x2+3*x3
    C4H10 = (P*(1-x1-x4-x5))/Total
    CH4 = (P*x4)/Total
    C3H8 = (P*x4)/Total
    C2H6 = (P*2*x5)/Total
    C4H8 = (P*(x1-2*x2))/Total
    H2 = (P*(x1+3*x3-x4-x5))/Total
    ECH = (P*(x2-x3))/Total
    E = (P*x3)/Total

    F1 = (C4H8*H2/C4H10)-Kp1
    F2 = (ECH/C4H8**2)-Kp2
    F3 = (E*(H2**3)/ECH)-Kp3
    F4 = (C3H8*CH4/(C4H10*H2))-Kp4
    F5 = (C2H6**2/(C4H10*H2))-Kp5

    ### Returning Values
    return (F1,F2,F3,F4,F5)
#######################################

####### Applying Least Squares ######
initial_guess = (0.31,0.16,0.15,0.55,0.1)
lower_bounds = [0,0,0,0,0]
upper_bounds = [1,1,1,1,1]

res = least_squares(equations, initial_guess, bounds = (lower_bounds, upper_bounds))
#######################################

############# Displaying ############
# print each initial guess
print("initial guess =", initial_guess)

# print x = ....
print("===== RESULT ======")
i = 1
for each_x in res.x :
    print("x" + str(i) + " = " + str(each_x))
    i = i + 1

print("===== RESULT ======")
i = 1
for each_x in res.x :
    print(str(each_x))
    i = i + 1
```

```
# Set x = result gained from least squares
x1, x2, x3, x4, x5 = res.x

# sub x into each equation
Total = 1+x1-x2+3*x3
C4H10 = (P*(1-x1-x4-x5))/Total
CH4 = (P*x4)/Total
C3H8 = (P*x4)/Total
C2H6 = (P*2*x5)/Total
C4H8 = (P*(x1-2*x2))/Total
H2 = (P*(x1+3*x3-x4-x5))/Total
ECH = (P*(x2-x3))/Total
E = (P*x3)/Total

# print each result
print("===================")
print("Total =", Total)
print("C4H10 =", C4H10)
print("CH4 =", CH4)
print("C3H8 =", C3H8)
print("C2H6 =", C2H6)
print("C4H8 =", C4H8)
print("H2 =", H2)
print("ECH =", ECH)
print("E =", E)

#####################################
```

Appendix C: Non-Linear Program Solver Results

Table C.1 Non-linear program solver result of model Zn.11 at reactor 1 with different initial guess of x

Reacted and produced mole*	Initial guess of x	Result of x	Component	Mass fraction from non-linear solver	Mass fraction from simulation
x1	0.001	0.000918445	n-butane	0.83694	0.000276
x2	0.005	0.008404525	1-butene	-0.01534	0.000025
x3	0.01	0.008404539	hydrogen	-0.00472	0.002466
x4	0.005	0.074883523	methane	0.02067	0.158708
x5	0.01	0.087250781	ethane	0.09028	0.122879
			propane	0.05682	0.436239
			ethylbenzene	0.01535	0.279407
			ethylcyclohexane	0.00000	0.000000
x1	0.1	0.100001796	n-butane	0.64999	0.000276
x2	0.08	0.095441883	1-butene	-0.08774	0.000025
x3	0.05	0.050001973	hydrogen	0.00000	0.002466
x4	0.2	0.199705024	methane	0.05511	0.158708
x5	0.05	0.050298508	ethane	0.05205	0.122879
			propane	0.15153	0.436239
			ethylbenzene	0.09134	0.279407
			ethylcyclohexane	0.08773	0.000000
x1	0.3	0.30613734	n-butane	0.00028	0.000276
x2	0.25	0.2386443	1-butene	-0.16523	0.000025
x3	0.15	0.15338397	hydrogen	0.00252	0.002466
x4	0.55	0.55026741	methane	0.15186	0.158708
x5	0.1	0.14331205	ethane	0.14829	0.122879
			propane	0.41752	0.436239
			ethylbenzene	0.28019	0.279407
			ethylcyclohexane	0.16461	0.000000
x1	0.35	0.35147699	n-butane	0.04950	0.000276
x2	0.2	0.19717828	1-butene	-0.04140	0.000025
x3	0.18	0.19717818	hydrogen	0.01193	0.002466
x4	0.5	0.49918278	methane	0.13776	0.158708
x5	0.1	0.09983716	ethane	0.10331	0.122879
			propane	0.37876	0.436239
			ethylbenzene	0.36019	0.279407
			ethylcyclohexane	0.00000	0.000000

Appendix D: Prediction from the appropriate model

Table D.1 Effluent mass fractions of model Zn.11: Varying mixed butane and butene ratios at 480 ^{0}C and 0.4 MPa

n-butan : 1-butene (mole fraction)			1 : 0
component	**Reactor1**	**Reactor2**	**Reactor3**
n-butan	0.000276	0.000276	0.000276
1-butene	0.000025	0.000025	0.000025
hydrogen	0.002466	0.000000	0.000000
methane	0.158708	0.178324	0.178324
ethane	0.122879	0.122879	0.122879
propane	0.436239	0.436239	0.436239
ethylene	0	0	0.009848
benzene	0	0.002681	0.032811
toluene	0	0.106337	0.099948
o-xylene	0	0	0.028192
m-xylene	0	0	0.057202
p-xylene	0	0	0.023192
ethylbenzene	0.279407	0.153237	0.011062
ethylcyclohexane	0.000000	0.000000	0.000000
n-butan : 1-butene (mole fraction)			0.9 : 0.1
n-butan	0.000269	0.000269	0.000269
1-butene	0.000025	0.000025	0.000025
hydrogen	0.00235	0.000000	0.000000
methane	0.152938	0.171633	0.171633
ethane	0.118411	0.118411	0.118411
propane	0.420378	0.420378	0.420378
ethylene	0	0	0.011429
benzene	0	0.002067	0.032135
toluene	0	0.1025	0.106642
o-xylene	0	0	0.03277
m-xylene	0	0	0.066491
p-xylene	0	0	0.026957
ethylbenzene	0.30563	0.184717	0.012858
ethylcyclohexane	0.000000	0.000000	0.000000
n-butan : 1-butene (mole fraction)			0.8 : 0.2
n-butan	0.000262	0.000262	0.000262
1-butene	0.000025	0.000025	0.000025
component	**Reactor1**	**Reactor2**	**Reactor3**
hydrogen	0.002238	0.000000	0.000000

methane	0.147117	0.164926	0.164926
ethane	0.113904	0.113904	0.113904
propane	0.404379	0.404379	0.404379
ethylene	0	0	0.012981
benzene	0	0.001627	0.031592
toluene	0	0.098447	0.113024
o-xylene	0	0	0.037442
m-xylene	0	0	0.075972
p-xylene	0	0	0.030801
ethylbenzene	0.332075	0.21643	0.014692
ethylcyclohexane	0.000000	0.000000	0.000000
n-butan : 1-butene (mole fraction)			0.7 : 0.3
n-butan	0.000253	0.000253	0.000253
1-butene	0.000025	0.000025	0.000025
hydrogen	0.002131	0.000000	0.000000
methane	0.141247	0.158199	0.158199
ethane	0.10936	0.10936	0.10936
propane	0.388244	0.388244	0.388244
ethylene	0	0	0.014498
benzene	0	0.001301	0.031138
toluene	0	0.094295	0.11914
o-xylene	0	0	0.04221
m-xylene	0	0	0.085646
p-xylene	0	0	0.034724
ethylbenzene	0.35874	0.248322	0.016563
ethylcyclohexane	0.000000	0.000000	0.000000
n-butan : 1-butene (mole fraction)			0.6 : 0.4
n-butan	0.000245	0.000245	0.000245
1-butene	0.000024	0.000024	0.000024
hydrogen	0.002026	0.000000	0.000000
methane	0.135329	0.15145	0.15145
ethane	0.104777	0.104777	0.104777
propane	0.371976	0.371976	0.371976
ethylene	0	0	0.015978
benzene	0	0.001052	0.030744
toluene	0	0.090107	0.125018
o-xylene	0	0	0.047074
m-xylene	0	0	0.095516
component	**Reactor1**	**Reactor2**	**Reactor3**
p-xylene	0	0	0.038725

ethylbenzene	0.385623	0.280369	0.018472
ethylcyclohexane	0.000000	0.000000	0.000000
n-butan : 1-butene (mole fraction)			0.5 : 0.5
component	**Reactor1**	**Reactor2**	**Reactor3**
n-butan	0.000235	0.000235	0.000235
1-butene	0.000024	0.000024	0.000024
hydrogen	0.001924	0.000000	0.000000
methane	0.129362	0.144673	0.144673
ethane	0.100157	0.100157	0.100157
propane	0.355575	0.355575	0.355575
ethylene	0	0	0.01742
benzene	0	0.000858	0.030389
toluene	0	0.085916	0.130681
o-xylene	0	0	0.052036
m-xylene	0	0	0.105584
p-xylene	0	0	0.042807
ethylbenzene	0.412722	0.31256	0.020418
ethylcyclohexane	0.000000	0.000000	0.000000
n-butan : 1-butene (mole fraction)			0.4 : 0.6
n-butan	0.000226	0.000226	0.000226
1-butene	0.000023	0.000023	0.000023
hydrogen	0.001825	0.000000	0.000000
methane	0.123347	0.137868	0.137868
ethane	0.0955	0.0955	0.0955
propane	0.339042	0.339042	0.339042
ethylene	0	0	0.018823
benzene	0	0.000704	0.030058
toluene	0	0.081743	0.13614
o-xylene	0	0	0.057096
m-xylene	0	0	0.115851
p-xylene	0	0	0.046969
ethylbenzene	0.440037	0.344893	0.022404
ethylcyclohexane	0.000000	0.000000	0.000000
n-butan : 1-butene (mole fraction)			0.3 : 0.7
n-butan	0.000215	0.000215	0.000215
1-butene	0.000023	0.000023	0.000023
hydrogen	0.001728	0.000000	0.000000
methane	0.117284	0.131033	0.131033
component	**Reactor1**	**Reactor2**	**Reactor3**
ethane	0.090806	0.090806	0.090806

propane	0.322376	0.322376	0.322376
ethylene	0	0	0.020186
benzene	0	0.00058	0.02974
toluene	0	0.077598	0.141404
o-xylene	0	0	0.062256
m-xylene	0	0	0.126319
p-xylene	0	0	0.051214
ethylbenzene	0.467568	0.377369	0.024428
ethylcyclohexane	0.000000	0.000000	0.000000
n-butan : 1-butene (mole fraction)			0.2 : 0.8
n-butan	0.000205	0.000205	0.000205
1-butene	0.000022	0.000022	0.000022
hydrogen	0.001633	0.000000	0.000000
methane	0.111172	0.124164	0.124164
ethane	0.086074	0.086074	0.086074
propane	0.305578	0.305578	0.305578
ethylene	0	0	0.021508
benzene	0	0.000479	0.029427
toluene	0	0.073486	0.146479
o-xylene	0	0	0.067516
m-xylene	0	0	0.136993
p-xylene	0	0	0.055541
ethylbenzene	0.495315	0.409992	0.026493
ethylcyclohexane	0.000000	0.000000	0.000000
n-butan : 1-butene (mole fraction)			0.1 : 0.9
n-butan	0.000194	0.000194	0.000194
1-butene	0.000022	0.000022	0.000022
hydrogen	0.001539	0.000000	0.000000
methane	0.105013	0.11726	0.11726
ethane	0.081305	0.081305	0.081305
propane	0.288648	0.288648	0.288648
ethylene	0	0	0.02279
benzene	0	0.000395	0.029111
toluene	0	0.06941	0.151368
o-xylene	0	0	0.072879
m-xylene	0	0	0.147874
p-xylene	0	0	0.059953
ethylbenzene	0.523279	0.442766	0.028597
component	**Reactor1**	**Reactor2**	**Reactor3**
ethylcyclohexane	0.000000	0.000000	0.000000

n-butan : 1-butene (mole fraction)			0 : 1
n-butan	0.000183	0.000183	0.000183
1-butene	0.000021	0.000021	0.000021
hydrogen	0.001447	0.000000	0.000000
methane	0.098805	0.110321	0.110321
ethane	0.076499	0.076499	0.076499
propane	0.271584	0.271584	0.271584
ethylene	0	0	0.02403
benzene	0	0.000326	0.028789
toluene	0	0.065369	0.15607
o-xylene	0	0	0.078345
m-xylene	0	0	0.158967
p-xylene	0	0	0.06445
ethylbenzene	0.551461	0.475697	0.030742
ethylcyclohexane	0.000000	0.000000	0.000000

Table D.2 Effluent mass fractions of model Zn.11: Varying temperatures at 0.4 MPa

Temperature	480 ^{0}C	510 ^{0}C	540 ^{0}C
C1-C2	0.311051	0.318640	0.326689
C3-C4	0.436541	0.428578	0.419064
Aromatics	0.252408	0.252781	0.254246

Table D.2 Effluent mass fractions of model Zn.11: Varying pressures at 510 ^{0}C

Pressure	0.1 MPa	0.4 MPa	1.1 MPa
C1-C2	0.333732	0.318640	0.311201
C3-C4	0.407156	0.428578	0.436681
Aromatics	0.259112	0.252781	0.252117

REFERENCES

1. Stacia M Edwards, Stephen J Stanley, and M.M. Shreehan, *Relative economics of mixed C4 processing routes*, in *Digital Refining*. 1998, PTQ Magazine: UK.
2. *Mixed C4s Product Stewardship Summary*. 2017, Shell Chemicals.
3. Covavisaruch, S., et al., *What are petroleum chemicals?*, in *Petrochemical Encyclopedia*, K. Bunyakiat, Editor. 2011, WPS(Thailand)Co..Ltd.: Bangkok. p. 14-67.
4. *Documentation of the TLVs and BEIs with Other World Wide Occupational Exposure Values*. 7 ed. American Conference of Governmental Industrial Hygienists. 2013, Cincinnati.
5. Apisit Songsasen, Arthit Sakultantimetha, and S. Bangkedphol, *General chemistry for engineers 02*. 2012, Bangkok: Triple education.
6. Fogler, H.S., *Elements of Chemical Reaction Engineering*. Pearson New International Edition, ed. 4th. 2013, Harlow, United Kingdom: Pearson Education Limited. 880.
7. Munnik, P., P.E. de Jongh, and K.P. de Jong, *Recent Developments in the Synthesis of Supported Catalysts.* Chemical Reviews, 2015. **115**(14): p. 6687-6718.
8. Suib, S.L., *Selectivity in Catalysis*, in *Selectivity in Catalysis*. 1993, American Chemical Society. p. 1-19.
9. Suresh, A., *Metallic Nanocrystallites and their Interaction with Microbial Systems*. 2012.
10. Sakata, Y., et al., *Preparation of a New Type of CaSiO3 with High Surface Area and Property as a Catalyst Support*, in *Studies in Surface Science and Catalysis*, E.M. Gaigneaux, et al., Editors. 2006, Elsevier. p. 331-338.
11. Kumar, M., et al., *Role of pore size analysis in development of zeolite reforming catalyst.* Catalysis Today, 2008. **130**(2): p. 501-508.
12. Akay, G., *Co-Assembled Supported Catalysts: Synthesis of Nano-Structured Supported Catalysts with Hierarchic Pores through Combined Flow and Radiation Induced Co-Assembled Nano-Reactors.* Catalysts, 2016. **6**: p. 80.
13. *ZSM-5*, in *Molecular sieve used for the removal of VOCs*. 2018, Dalian Haixin Chemical Industrial
14. Ishaq, M., M. Arsala Khan, and T. Yashima, *Mechanism of Butane Transformation*. Vol. 47. 2000.
15. Yashima, T., S. Fujita, and T. Komatsu, *Reaction Scheme of Aromatization of Butane over Ga Loaded HZSM-5 Catalyst.* Journal of The Japan Petroleum Institute, 1998. **41**(1): p. 37-44.
16. Song, C., et al., *Influence of reaction conditions on the aromatization of cofeeding n-butane with methanol over the Zn loaded ZSM-5/ZSM-11 zeolite catalyst.* Fuel Processing Technology, 2014. **126**: p. 60-65.
17. Yuan, S., et al., *Preparation of Mo2C/HZSM-5 and its catalytic performance for the conversion of n-butane into aromatics.* Journal of Molecular Catalysis A: Chemical, 2002. **184**(1): p. 257-266.
18. Kumar, N., et al., *Synthesis and characterization of Pd-MCM-22 and Pt-SAPO-11 catalysts for transformation of n-butane to aromatic hydrocarbons.* Applied Catalysis A: General, 2002. **227**(1): p. 97-103.
19. Choudhary, V.R., D. Panjala, and S. Banerjee, *Aromatization of propene and n-butene over H-galloaluminosilicate (ZSM-5 type) zeolite.* Applied Catalysis A: General, 2002. **231**(1): p. 243-251.

20. Wongwailikhit, K., *Modeling of Oxidative Coupling of Methane to Ethylene with Chemical Equilibria*, in *Chemical Engineering*. 2013, Chulalongkorn University.
21. Carl L. Yaws, P.D., *Chemical Properties Handbook*. 1999, New York: McGraw-Hill Education.
22. Smith, J.M., H.C. Van Ness, and M.M. Abbott, *Introduction to chemical engineering thermodynamics*. 2005, Boston: McGraw-Hill.

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