การปรับปรุงกระบวนการโอเลฟินไฮโดรจิเนชันและลดการสูญเสียสารอะโรเมติกส์ในอุตสาหกรรมการผลิตเบนซีน โทลูอีน และไซลีน

นาย ธวัช อินทร

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OLEFIN HYDROGENATION PROCESS IMPROVEMENT AND AROMATICS LOSS MINIMIZATION IN BTX PRODUCTION INDUSTRY

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering
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ธวัช อินทร : การปรับปรุงกระบวนการโอเลฟินไฮโดรจิเนชันและลดการสูญเสียสารอะโรเมติกส์ในอุตสาหกรรมการผลิตเบนซีน โทลูอีน และไซลีน (OLEFIN HYDROGENATION PROCESS IMPROVEMENT AND AROMATICS LOSS MINIMIZATION IN BTX PRODUCTION INDUSTRY) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: รศ.ดร.บรรเจิด จงสมจิตร, 73 หน้า

หน่วยโอเลฟินไฮโดรจิเนชันมีวัตถุประสงค์เพื่อกำจัดสารโอเลฟินในรีฟอร์เมท เพื่อป้องกันตัวเร่งปฏิกิริยาและตัวดูดซับในหน่วยการผลิตอื่นๆให้เสื่อมสภาพน้อยที่สุด งานวิจัยนี้มีวัตถุประสงค์เพื่อศึกษาการเปลี่ยนแปลงรูปแบบกระบวนการผลิตของถังปฏิกรณ์จากอนุกรมเป็นถังปฏิกรณ์เดี่ยว เพื่อป้องกันการเสื่อมสภาพของตัวเร่งปฏิกิริยาในถังปฏิกรณ์ทั้งสองถังในเวลาใกล้เคียงกัน การเสื่อมสภาพของตัวเร่งปฏิกิริยามีสาเหตุจากสารปนเปื้อนในรีฟอร์เมท โดยเฉพาะสารประกอบซัลเฟอร์ซึ่งจะถูกดูดซับไว้บนตัวเร่งปฏิกิริยาแบบถาวรที่อุณหภูมิสูง จะเกิดขึ้นมากเมื่อตัวเร่งปฏิกิริยาใกล้เสื่อมสภาพเพราะต้องใช้อุณหภูมิในการทำงานที่สูงขึ้น การทำงานแบบถังปฏิกรณ์เดี่ยวทำให้ความรุนแรงของปฏิกิริยาลดลงและส่งผลโดยตรงต่อปฏิกิริยาไฮโดรจิเนชันของโอเลฟินและสารอะโรเมติกส์โดย ร้อยละการเปลี่ยนแปลงโดยรวมของโอเลฟินลดลงจาก 95-99 เหลือ 85-92 ร้อยละโดยมวล โดยยังคงไม่ส่งผลกระทบต่อกระบวนการผลิตอื่นๆ อีกทั้งยังลดการสูญเสียเบนซีนจาก 0.25-0.5 เหลือ 0.2-0.3 ร้อยละโดยโมล และลดการสูญเสียของโทลูอีนจาก 0.05-0.1 เหลือ 0.03-0.07 ร้อยละโดยโมล การลดการสูญเสียดังกล่าวเสมือนหนึ่งเป็นการเพิ่มการผลิตเบนซีนและไซลีน โดยสามารถเพิ่มรายได้ให้กับบริษัทประมาณสี่แสนเหรียญสหรัฐต่อปี และงานวิจัยนี้ได้ศึกษาถึงผลกระทบของตัวแปรต่างๆ ได้แก่อุณหภูมิ ความดัน H_2:HC และ LHSV จากการทดลองพบว่าอุณหภูมิผลโดยตรงต่อความรุนแรงของปฏิกิริยา อุณหภูมิที่สูงขึ้นทำให้โอเลฟินถูกไฮโดรจิเนทได้มากขึ้นแต่ในขณะเดียวกันก็จะทำให้สูญเสียสารอะโรเมติกส์มากขึ้นด้วย ในขณะที่ตัวแปรอื่นๆ ส่งผลไม่มากนัก ดังนั้นควรใช้อุณหภูมิที่ต่ำที่สุดในการควบคุมปฏิกิริยาไฮโดรจิเนชันโดยไม่ส่งผลกระทบต่อหน่วยการผลิตอื่น นอกจากนี้ยังได้ปรับปรุงระบบการควบคุมสัดส่วนไฮโดรเจนต่อไฮโดรคาร์บอน และศึกษาผลของการฟื้นฟูสภาพตัวเร่งปฏิกิริยาอีกด้วย

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TAWATH INTORN: OLEFIN HYDROGENATION PROCESS IMPROVEMENT AND AROMATICS LOSS MINIMIZATION IN BTX PRODUCTION INDUSTRY. THESIS ADVISOR: ASSOC. PROF. BUNJERD JONGSOMJIT, Ph.D., 73 pp.

The olefin hydrogenation process is used to remove the olefin in reformate to prevent the catalyst and adsorbent damage in downstream processes. This research aims to change the reactor operation mode from a series to a single bed operation. The plant reliability is expected to be improved in the single bed operation by preventing catalyst deactivation in both reactors at the same time. The catalyst deactivations normally cause by the feed contaminants. Particularly, the sulfur compounds have a very high potential to permanently absorb on catalyst at high temperature, especially at the end of run conditions. In single bed operation, the reaction severity is decreased. The total olefin conversion is reduced from 95-99 wt% in the series to 85-92 wt% in single bed, while the effluent qualities still meet the downstream processes requirement. The other effect is the decreasing of aromatics loss. The amount of benzene loss is reduced from 0.25-0.5 mol% to 0.2-0.3 mol%. Toluene loss is reduced from 0.05-0.1 mol% to 0.03-0.07 mol%, which are increased the aromatics productivity and improve the benefit around 0.43 million US$ per year. The research is to study the variable control parameters, such as reactor inlet temperature, pressure, H_2:HC ratio and LHSV. Higher temperatures cause more hydrogenation of olefin and aromatics while other parameters are not significantly effect. As result, running at the lowest temperature which still makes the product quality acceptable is the operating goal. Furthermore, the H_2:HC ratio controller is improved by apply the advance process control. The in situ catalyst regeneration is studied also.

Department: ……Chemical Engineering… Student's Signature…………………..

Field of Study: …Chemical Engineering…. Advisor's Signature……Bunjerd Jongsomjit

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CHAPTER I

INTRODUCTION

1.1 Company Profile

PTT Aromatics and Refining Public Company Limited (PTTAR) was established following the resolutions of shareholders' meetings of Aromatics (Thailand) Public Company Limited (ATC) and Rayong Refinery Public Company Limited (RRC) on September 13, 2007 to amalgamate both businesses.

PTTAR is thus Thailand's largest integrated aromatics refinery with enhanced competitiveness, thereby able to elevate the industry and create sustainable growth for the country's energy and petrochemical industry.

PTTAR was officially registered on December 27, 2007 and has commenced its business since then. The integration enables PTTAR to become Thailand's no. 1 integrated refinery and manufacturer of aromatics products with a refining capacity of 280,000 barrels per day and aromatics production capacity of 2,228,000 tons per year in 1Q/2009.

PTTAR is an integrated aromatics refinery company, covering four business categories: petroleum refining and supply of refined petroleum, products, manufacturing and sale of Aromatics products, intermediate products and joint venture business

1.2 The Aromatics Business

The Company is a manufacturer and distributor of Aromatics i.e. Benzene, Paraxylene, Orthoxylene, Toluene, Mixed Xylenes, and Cyclohexane. Other petroleum products from the production process include Light Naphtha, Raffinate, Liquefied Petroleum Gas, Condensate Residue, and Heavy Aromatics. These products are used as raw materials in various industries. The Company has 2 Aromatics units, as follows:

Table 1.1 Aromatics product capacity of PTTAR.

Unit : tons/year

Product	Aromatics I	Aromatics II	Total
Paraxylene	540,000	655,000	1,195,000
Benzene	307,000	355,000	662,000
Cyclohexane	200,000	-	200,000
Orthoxylene	66,000	-	66,000
Mixed Xylenes	76,000	-	76,000
Toluene	-	60,000	60,000
Total	**1,189,000**	**1,070,000**	**2,259,000**

1.3 Aromatics II Process Overview

The Olefin Hydrogenation Process can be placed in most locations that utilize clay. The figure 1.1 below shows the Olefin Hydrogenation Process incorporated into a fully integrated aromatic complex:

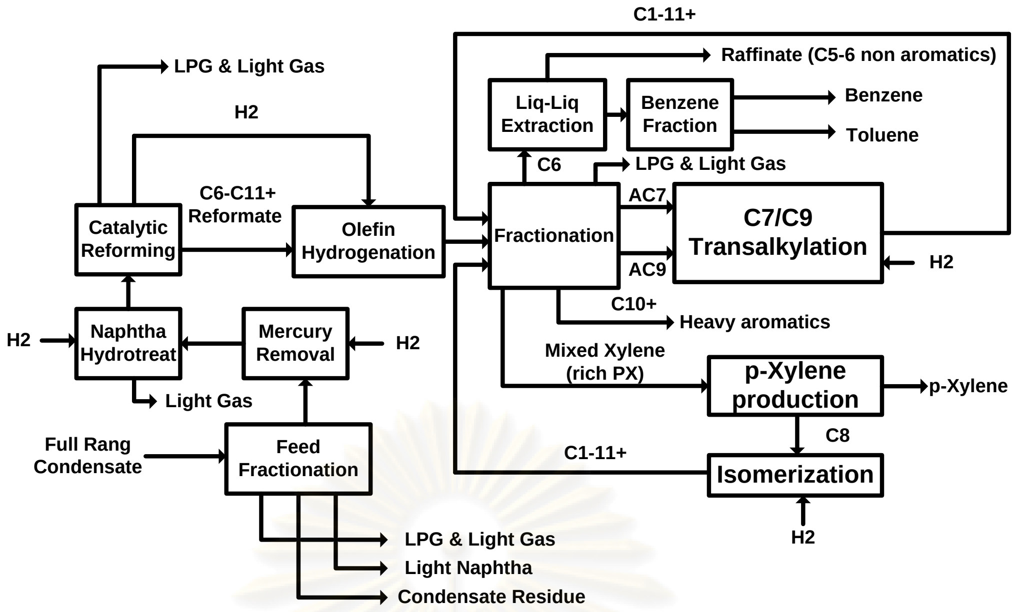


Figure 1.1 Simplify block flow diagram of BTX production.

Full Range Condensate is fed to Feed Fractionation unit to fractionate feed stream into four product streams. The unit produces LPG and light gas, light naphtha, heavy naphtha suitable for mercury removal unit and condensate residue by-product stream. Heavy naphtha is fed to a hydro-treating unit to remove sulfur and nitrogen species which are detrimental to the Catalytic Reforming unit catalyst. Some feed contaminants are also removed in the naphtha hydro-treating unit which can contribute to fouling of the unit. Normally the sulfur and nitrogen leave the unit in the gas phase as H2S and ammonia.

In the Catalytic Reforming unit some of the charge is converted from naphthene and paraffin material to aromatics. Typically very little non-aromatic material is left in the fraction that boils with the C8 aromatics and heavier. Some quantities of non-aromatic material are left in the fraction that boils with the toluene and benzene. In the lighter fraction of the product, boiling with benzene and toluene, the bromine reactive species are typically normal olefins or iso-olefins. The olefins in the C8 aromatic and heavier fractions are typically olefins that are attached to the aromatic rings, the alkenylbenzene materials.

The Aromatics Fractionation unit fractionates feed streams into four product streams. The feed streams are the C7/C9 Transalkylation Stripper Column bottoms and the recycle xylene stream from the Isomerization unit. The unit produces *para*-Xylene Production quality feed, a toluene cut, a C9+ cut suitable for processing in C7/C9 Transalkylation and a heavy aromatics by-product stream.

The unconverted toluene is removed from the C7/C9 Transalkylation Stripper bottoms stream in the toluene column and is collected in the toluene column receiver. From the receiver, it is sent to C7/C9 Transalkylation. The toluene column bottoms material is sent to the xylene column. The recycle xylenes from the Isomerization unit are also sent to the xylene column. The AC8 product is taken overhead from the xylene column to the Parex unit. AC9 plus heavy aromatic stream is taken as a side-cut from the Xylene Column and recycle to C7/C9 Transalkylation. A heavy aromatic stream is taken from the bottom of the xylene column and is sent to storage.

The Olefin Hydrogenation Process will saturate the olefins that are analogs of paraffin to the corresponding paraffin. The alkenyl benzene molecules get converted to their corresponding aromatics.

1.4 Olefin Hydrogenation Process

Olefin can cause problems to catalyst and adsorbent in downstream process. The olefin hydrogenation process is used to convert the olefin in feed stream into their hydrogenated products. For decades, the removal of olefin has been traditionally accomplished by using an acid modified clay catalyst to combine the olefin with an aromatics molecule. The reaction products are heavy species, which can be removed by distillation method. The heavy products are then typically disposed in a heavy stream, which has fuel oil value. Even so the former catalytic clay will generate some of hazardous wastes because the catalyst clay life is normally short and cannot be regenerated.

The next generation of technology use nowadays is the regenerated catalyst. It can reduce the hazardous waste disposal, but still producing heavy species also. The latest technology used is a selective hydrogenation catalyst which helps the saturation of olefin to paraffin. This type of catalyst can be regenerated. Besides the hydrogenation reaction has no heavy product, however, a small amount of aromatic loss can be found from the side reactions. The purpose of the olefin saturation unit is not only to remove all of the olefin reactive species present in the charge, but also to maintain the product quality of various units such as the benzene product from the benzene fractionation after extraction process, the charge qualities to the *para*-xylene production unit and to the C7/C9 Transalkylation unit as shown in Figure 1.2.

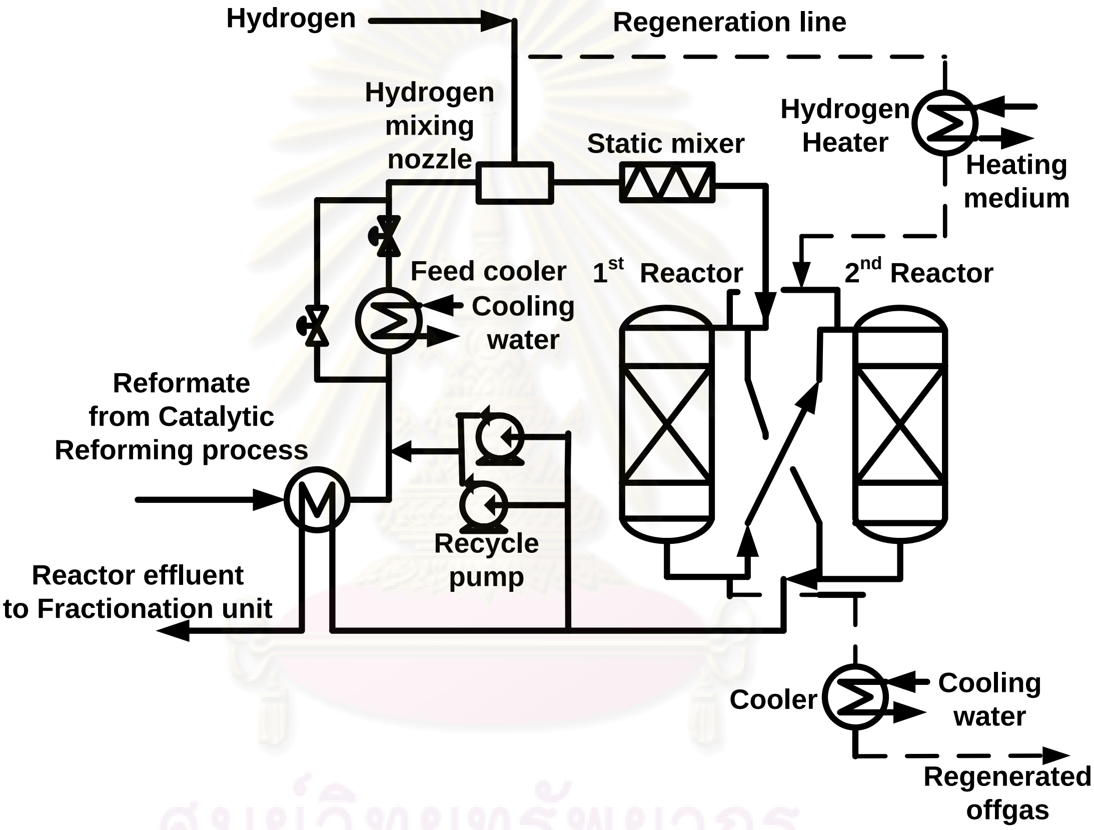


Figure 1.2 Presents the process unit flow scheme.

The olefin hydrogenation process is the three-phase packed bed reactors. The combined feed between reformate from the catalytic reforming process and recycle stream from effluent will be dissolved with hydrogen gas by static mixer to hydrogenate olefin species before flowing through the first and second reactor. The process variables parameters, which affect the catalyst activity, are the combined feed inlet temperature, the hydrogen per hydrocarbon ratio, the reactor pressure, and the liquid hourly space velocity (LHSV). The general operating concept is to maintain all of variable parameter until the trend of olefin conversion is decreased. Then, the reactor inlet temperature (RIT) of combined feed will be increased to improve the catalyst activity to meet the downstream process requirement. By the time that RIT close to the end of run condition, the first reactor or the lead bed will be regenerated while the lag bed will be solely operated reactor.

In the event that the catalyst regeneration is not efficient, the new catalyst replacement is required. The catalyst replacement process time is roughly more than a week to follow many procedures, such the reactor hydrocarbon free, catalyst unloading, catalyst reloading including the reduction of new catalyst. It is possible that the lag reactor may deactivate in the same time of the lead one because it is operated close to end of run conditions also. Consequently, the plant will totally be shut down since the olefin hydrogenation process is the first unit of the aromatics production section.

The major cause of the catalyst decay is the poison from impurities in feed, such as sulfur, chloride, basic nitrogen. The coke formation on the catalyst surface has an effect on catalyst activity also.

1.5 Motivation

There are many technologies for the olefin treating process which are utilized in petrochemical industry. The regenerable catalyst without heavier production is the latest commercial technology, especially providing by the technology licensor of PTT Aromatics and Refining Public Company Limited (PTTAR). This technology is the first one in the world that is utilized for Reformate treating unit.

In the event that the catalyst regeneration is not efficient, the process must be continuous operated without the plant totally shut down since the olefin hydrogenation process is the first unit of the aromatics production section.

The expected additional benefit is to increase the benzene and toluene production by minimizing the aromatics loss, the reduction of hydrogenation reaction severity by change the operation mode is the option.

1.6 Objective

The research objective is to maintain the olefin hydrogenation process reliability in case the catalyst regeneration is not efficient. The aromatics loss minimization, improve the catalyst performance, and operation improvement are also focused.

1.7 Research scopes

- Feed stock and process performance review.
- Single bed operation.
- Process performance improvement.
- Process control improvement
- Catalyst in situ regeneration.

1.8 Benefits

- The process reliability is improved by single bed operation in case the catalyst regeneration is not efficient.
- Aromatics production is increased from minimization of aromatics loss.
- To get the proper operating guideline for operation.
- To know the catalyst activity after regeneration.

CHAPTER II

LITERATURE REVIEWS

Catalytic reforming is one of the most important processes to produce high grade motor gasolines. Besides isomerization and dehydrocyclization reactions, the formation of aromatics by dehydrogenation of naphthenes occurs. Thus, catalytic reformers within refineries are an important source of BTX, aromatics (benzene, toluene, xylenes). Frequently high purity aromatics are recovered from these streams using modern extractive distillation or liquid extraction processes. Reforming process normally produce a small amount of olefins which will impair the quality of the product aromatics and reffinate. Due to the residual content in diolefins and some olefins the reformer streams as well as the benzene and toluene after extractive distillation show a dark, yellowish color expressed by an acid wash color. Aromatics product specification, notably bromine number and acid wash color, have obligated producers to utilize clay treatment and selective hydrogenation to remove trace impurities of diolefins and olefins. The conventional clay treatment is a multiple vessel batch process which periodically requires disposal of the spent clay in a suitable environmental manner, which is costly and environmentally unfriendly [Xiaoxin Zhang, 2002].

The removal or elimination of olefins from reformate is usually required for aromatics production. In most cases, post-treatment with clay or post-hydrogenation is adopted following the reforming unit. However, clay treatment is not an environmentally friendly process, and has low efficiency. In post-hydrogenation, a part of aromatics may be saturated because of the poor selectivity of the catalyst [Liu, Hamby, & Colberg, 1991].

Recently, many different technologies are researched and developed to hydrogenate olefin without aromatics loss such as a conventional sulfide CoMo or NiMo catalysts are used in the selective hydrogenation in commercial plants, however, these kinds of catalysts are only used at a high reaction temperature (300–340˚C) and low LHSV (2–3 h^{-1}) [Xiaoxin Zhang, 2002].

The other is a process which combines the ideal mass transfer property of magnetically stabilized bed (MSB) with the high activity of amorphous nickel alloy catalyst to hydrogenate selectively the olefins in reformate [Xuhong Mu, 2006].

In the other hand hydrogenation of benzene to cyclohexane is one of the most important industrially practiced aromatic compounds hydrogenation reactions. Millions of tones of benzene are hydrogenated to cyclohexane per year, and about 90% of world’s production of cyclohexane is used for manufacturing nylon 6 and nylon 6.6, which are about 90% of all polyamides. Nowadays, almost the whole world’s production capacity of cyclohexane is manufactured by the route of the hydrogenation of benzene. However, despite its apparent simplicity, the hydrogenation reaction of benzene has evolved through many variations and has given rise to many different processes [Constantinos V, 2010].

Owing to environmental and clean-fuel legislation, deep hydrodearomatisation of diesel fuel has been the focus of many recent studies. Supported noble metal catalysts are well known for their high hydrogenation activity for deep hydrodearomatisation at low reaction temperatures and moderate hydrogen pressures, although in general they show low resistance to sulfur poisoning. Due to the low cost and acceptable resistance to sulfur poisoning, Ni-based systems are good alternatives to noble metal hydrogenation catalysts. These catalysts are particularly suited to the production of middle distillates through the hydroconversion of hydrocarbons derived through the Fischer–Tropsch process. Most studies on Ni-based catalysts have been carried out using silica or alumina supports. The use of silica–alumina as a support has received less attention. Recently, Guimon et al. reported that the addition of Al_2O_3 to SiO_2 has a positive effect on the decrease in the coke formation. This was explained in terms of the different interaction between the metal and the support, as shown by X-ray photoelectron spectroscopy and temperature-programmed reduction studies. Among Ni-based catalysts, the Pd–Ni formulation seems to be of special interest. One important aspect of Pd–Ni systems is the very mild deactivation they undergo along the successive reaction experiments. The use of palladium-promoted amorphous silica–alumina supported nickel catalysts for the hydroisomerisation of alkanes has been patented. The lower deactivation of silica-supported Pd–Ni alloys as compared to unsupported ones has been reported for 1,3-butene hydrogenation [V.L. Barrio, 2003].

Supported nickel catalysts have been widely used for hydrogenation reactions of many organic compounds such as nitriles, aromatics and oils. The properties of supports may have important impacts on the catalytic performances of supported metals. In fact, the reducibility and dispersion of supported metals depend on the interactions between the supports and supported metals. In addition, the surface acidic and basic properties may play important roles in determining the catalytic activity and selectivity. Supports with high surface areas and appropriate preparation methods are usually required to obtain the supported nickel catalysts with high reducibility and dispersions. The techniques usually used to prepare supported nickel catalysts include impregnation, deposition–precipitation, sol–gel and co-precipitation. Supported nickel catalysts with high loadings are usually used for industrial hydrogenation processes. It is usually difficult to obtain the supported nickel catalysts with high dispersion and loading of nickel with the conventional impregnation method. The supported nickel catalysts with high dispersion and loading may be prepared by the deposition–precipitation and sol–gel methods, but they usually involve the complicated procedures. Co-precipitation is a simple method, but there are factors such as precursors, precipitating agents, temperature and pH that affect the properties of catalysts prepared. During the preparation of a supported metal catalyst by the co-precipitation method, the step of drying may play a key role in determining the final properties of a catalyst. The direct drying may cause severe agglomerations due to the removal of water with the high surface tension. A solvent with low surface tension may be used to replace water before the drying step so that the agglomeration may be diminished [Shenghua Hu, 2010]

In this research, the catalyst type is the nickel-based catalyst supported with aluminum oxide. Trickle bed reactor with a high liquid-recycle ratio to control the high-rate exothermic reactions that are required special reactor to avoid local hot spots and the corresponding loss of selectivity. The reactor is designed to operate at low temperature 45-110°C and high pressure.

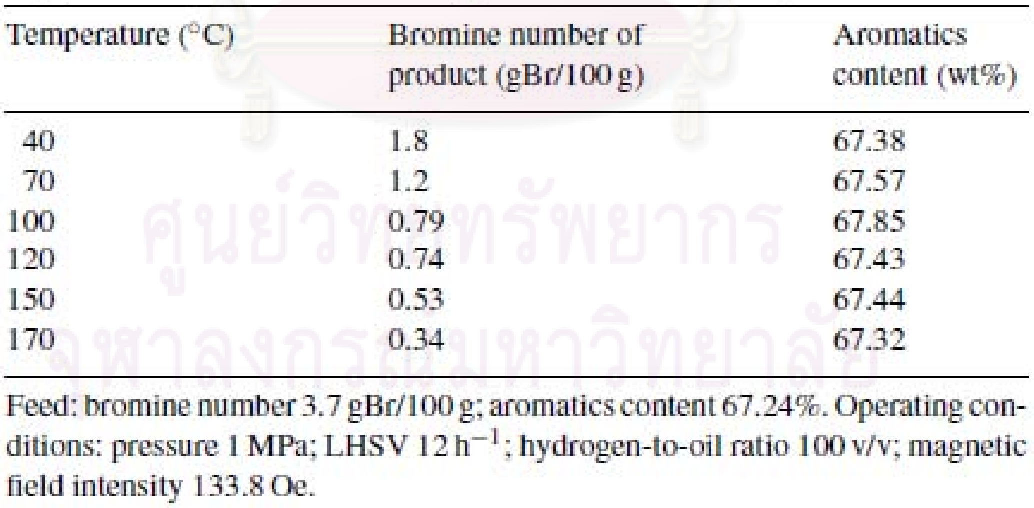
2.1 Effect of operating variables to MSB process

Xuhong Mu was studied the advantages of Magnetically Stabilized Bed (MSB) were combined with the low-temperature activity of amorphous nickel alloy catalyst in developing the MSB selective hydrogenation process for removing olefins in reformate. The effects of operating conditions, such as temperature, pressure, liquid space velocity, and hydrogen-to-oil ratio [Xuhong Mu, 2007].

2.1.1 Effect of temperature

Table 2.1 shows the results of hydrogenation carried out at different temperatures, indicating that the bromine number of the product decreased with increase of temperature. Compared to the reaction temperature of conventional post hydrogenation of 330 ◦C, MSB hydrogenation greatly reduces the reaction temperature, inasmuch as amorphous nickel catalyst is capable of retaining its high activity at lower temperatures. Low temperature implies low coking rate of the catalyst and low energy consumption of the MSB process.

Table 2.1 Dependence of bromine number of product on reaction temperature



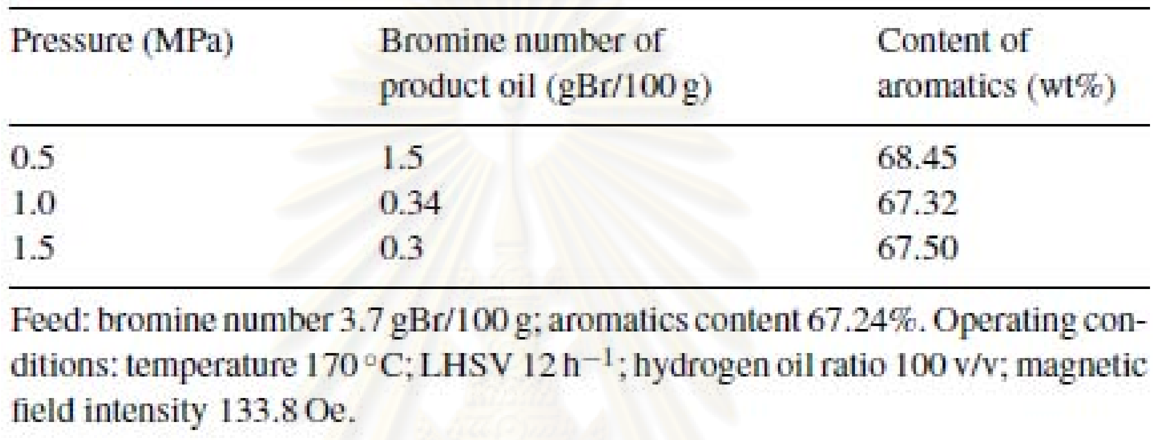
Temperature (°C)	Bromine number of product (gBr/100 g)	Aromatics content (wt%)
40	1.8	67.38
70	1.2	67.57
100	0.79	67.85
120	0.74	67.43
150	0.53	67.44
170	0.34	67.32

Feed: bromine number 3.7 gBr/100 g; aromatics content 67.24%. Operating conditions: pressure 1 MPa; LHSV 12 h^{-1}; hydrogen-to-oil ratio 100 v/v; magnetic field intensity 133.8 Oe.

2.1.2 Effect of pressure

From the viewpoint of reaction equilibrium, increasing pressure is helpful for hydrogenation, though the results in Table 2.2 indicate but slight beneficial effect for pressure higher than 1.0MPa. It can also be seen from Table 2.2 that the aromatic content remains essentially unchanged for the pressure range between 0.5 and 1.5 MPa. Increasing pressure leads to increase of hydrogen concentration the surface of catalyst which is helpful for the hydrogenation reaction. When the pressure is high enough, the overall reaction is controlled by surface reaction and will then be less influenced by pressure.

Table 2.2 Dependence of bromine number of product oil on reaction pressure



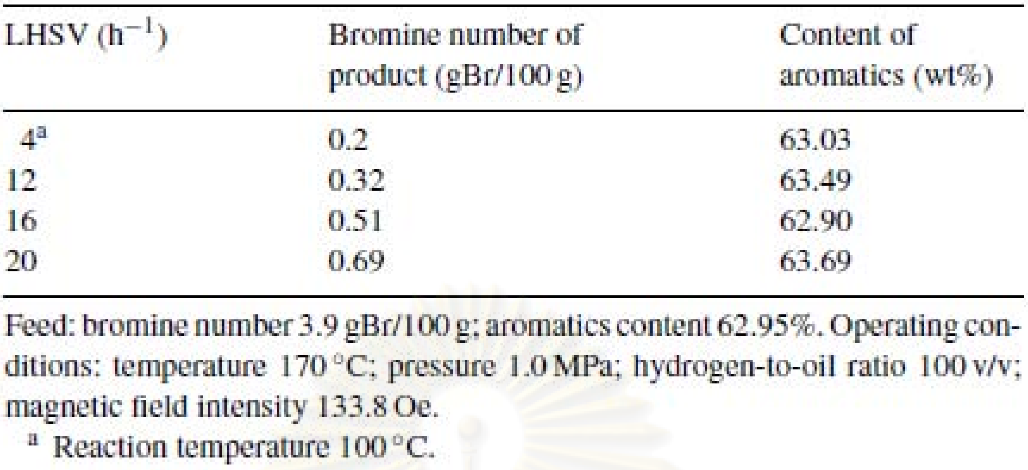
Pressure (MPa)	Bromine number of product oil (gBr/100 g)	Content of aromatics (wt%)
0.5	1.5	68.45
1.0	0.34	67.32
1.5	0.3	67.50

Feed: bromine number 3.7 gBr/100 g; aromatics content 67.24%. Operating conditions: temperature 170 °C; LHSV 12 h^{-1}; hydrogen oil ratio 100 v/v; magnetic field intensity 133.8 Oe.

2.1.3 Effect of liquid space velocity (LHSV)

Table 2.3 shows the effect of liquid space velocity on reaction, indicating that the bromine number of the product increases from 0.2 to 0.51 with the increase of LHSV from 4 to 16 h^{-1}, implying that the quality of product is acceptable only when LHSV is less than 16 h−1. Compared to conventional post-hydrogenation, MSB possesses the advantage of higher space velocity, primarily due to the high activity of the catalyst and the excellent mass transfer of MSB.

Table 2.3 Dependence of bromine number of product on liquid hourly space velocity (LHSV)



LHSV (h^{-1})	Bromine number of product (gBr/100 g)	Content of aromatics (wt%)
4^a	0.2	63.03
12	0.32	63.49
16	0.51	62.90
20	0.69	63.69

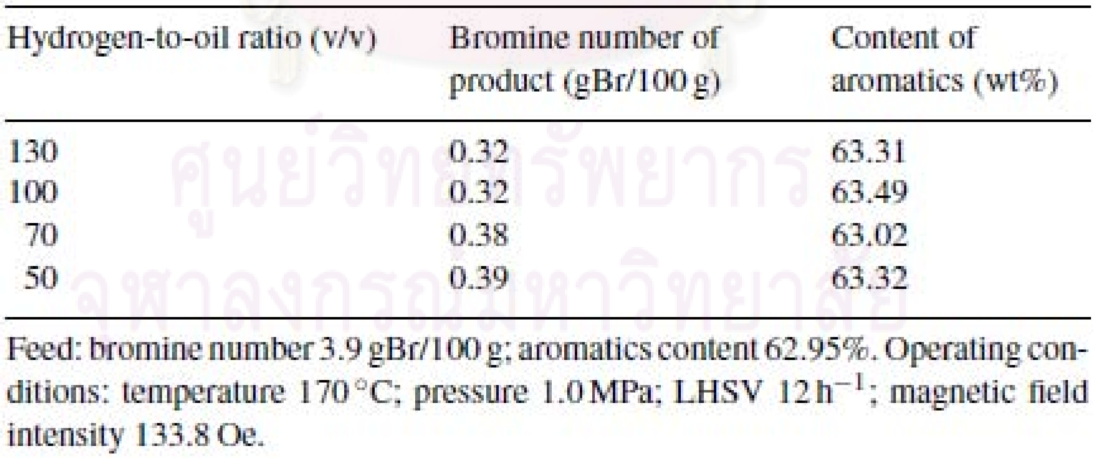
Feed: bromine number 3.9 gBr/100 g; aromatics content 62.95%. Operating conditions: temperature 170 °C; pressure 1.0 MPa; hydrogen-to-oil ratio 100 v/v; magnetic field intensity 133.8 Oe.

[a] Reaction temperature 100 °C.

2.1.4 Effect of hydrogen-to-oil ratio

Table 2.4 shows the effect of hydrogen-to-oil ratio on the reaction is rather insignificant in the range of 50–100 v/v, possibly due to the effective utilization of hydrogen when hydrogen bubbles are broken down to small sizes in the MSB reactor. Lower hydrogen-to-oil ratio implies lower operating cost. [Xuhong Mu, 2006]

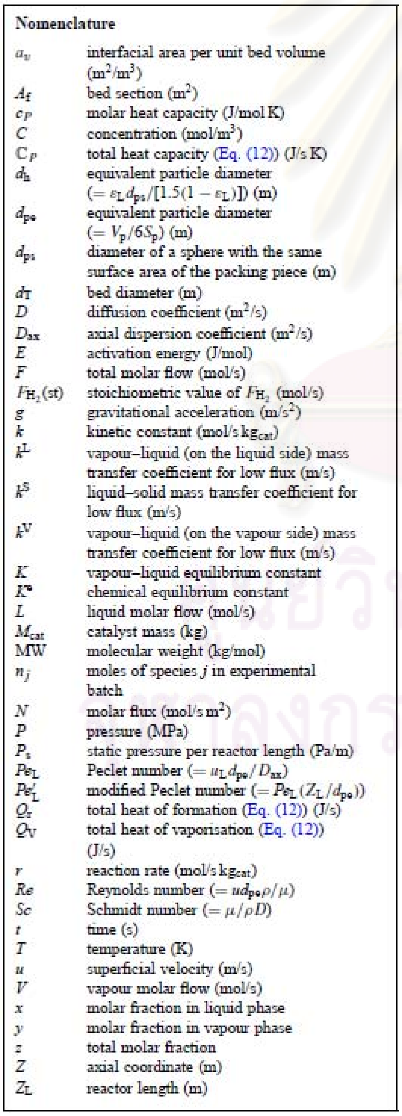
Table 2.4 Dependence of bromine number of product on hydrogen-to-oil ratio



Hydrogen-to-oil ratio (v/v)	Bromine number of product (gBr/100 g)	Content of aromatics (wt%)
130	0.32	63.31
100	0.32	63.49
70	0.38	63.02
50	0.39	63.32

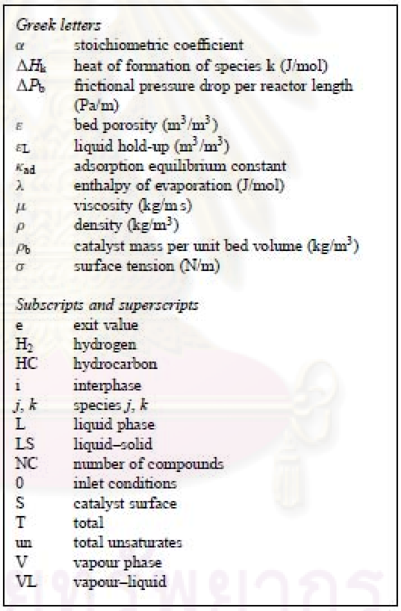
Feed: bromine number 3.9 gBr/100 g; aromatics content 62.95%. Operating conditions: temperature 170 °C; pressure 1.0 MPa; LHSV 12 h^{-1}; magnetic field intensity 133.8 Oe.

S.P. Bressa was study the effect of process and operating variables in the catalytic hydrogenation of unsaturated traces in C3–C4 streams, intended for aerosol propellant use, has been analyzed. The results from catalytic tests carried out on a commercial Pd/Al_2O_3 catalyst have been used to estimate the kinetic parameters of rate expressions. The set of rate expressions is used in a mathematical model of a three-phase fixed-bed catalytic unit operated in up-flow mode. The mathematical model allowed studying the effect that variables such as temperature, pressure, hydrogen mass flow and feed composition will exert on the reactor performance. The volatility of the hydrocarbon mixture is found to be a paramount factor in the process, as H_2 becomes diluted in the vapor phase and, consequently, the amount of H_2 dissolved in the liquid stream and the hydrogenation rates decrease significantly. A temperature rise turned out to be detrimental for the reactor performance, as the increased hydrocarbon volatility overcomes the effect on the kinetic coefficients. This conclusion precludes the usual operating practice of rising temperature to compensate for catalytic activity decay. Instead, increasing the H_2 input and/or the operating pressure were shown to be effective alternatives for this purpose [S.P. Bressa, 2003]



Nomenclature

a_v	interfacial area per unit bed volume (m^2/m^3)
A_t	bed section (m^2)
c_P	molar heat capacity (J/mol K)
C	concentration (mol/m^3)
C_P	total heat capacity (Eq. (12)) (J/s K)
d_h	equivalent particle diameter ($= \varepsilon_L d_{ps}/[1.5(1-\varepsilon_L)]$) (m)
d_{pe}	equivalent particle diameter ($= V_p/6S_p$) (m)
d_{ps}	diameter of a sphere with the same surface area of the packing piece (m)
d_T	bed diameter (m)
D	diffusion coefficient (m^2/s)
D_{ax}	axial dispersion coefficient (m^2/s)
E	activation energy (J/mol)
F	total molar flow (mol/s)
$F_{H_2}(st)$	stoichiometric value of F_{H_2} (mol/s)
g	gravitational acceleration (m/s^2)
k	kinetic constant (mol/s kg_{cat})
k^L	vapour–liquid (on the liquid side) mass transfer coefficient for low flux (m/s)
k^S	liquid–solid mass transfer coefficient for low flux (m/s)
k^V	vapour–liquid (on the vapour side) mass transfer coefficient for low flux (m/s)
K	vapour–liquid equilibrium constant
K^e	chemical equilibrium constant
L	liquid molar flow (mol/s)
M_{cat}	catalyst mass (kg)
MW	molecular weight (kg/mol)
n_j	moles of species j in experimental batch
N	molar flux (mol/s m^2)
P	pressure (MPa)
P_s	static pressure per reactor length (Pa/m)
Pe_L	Peclet number ($= u_L d_{pe}/D_{ax}$)
Pe'_L	modified Peclet number ($= Pe_L(Z_L/d_{pe})$)
Q_r	total heat of formation (Eq. (12)) (J/s)
Q_V	total heat of vaporisation (Eq. (12)) (J/s)
r	reaction rate (mol/s kg_{cat})
Re	Reynolds number ($= u d_{pe}\rho/\mu$)
Sc	Schmidt number ($= \mu/\rho D$)
t	time (s)
T	temperature (K)
u	superficial velocity (m/s)
V	vapour molar flow (mol/s)
x	molar fraction in liquid phase
y	molar fraction in vapour phase
z	total molar fraction
Z	axial coordinate (m)
Z_L	reactor length (m)



Greek letters

α	stoichiometric coefficient
ΔH_k	heat of formation of species k (J/mol)
ΔP_b	frictional pressure drop per reactor length (Pa/m)
ε	bed porosity (m^3/m^3)
ε_L	liquid hold-up (m^3/m^3)
κ_{ad}	adsorption equilibrium constant
λ	enthalpy of evaporation (J/mol)
μ	viscosity (kg/m s)
ρ	density (kg/m^3)
ρ_b	catalyst mass per unit bed volume (kg/m^3)
σ	surface tension (N/m)

Subscripts and superscripts

e	exit value
H_2	hydrogen
HC	hydrocarbon
i	interphase
j, k	species j, k
L	liquid phase
LS	liquid–solid
NC	number of compounds
0	inlet conditions
S	catalyst surface
T	total
un	total unsaturates
V	vapour phase
VL	vapour–liquid

2.2 Effect of operating parameter to Pd/Al_2O_3

2.2.1 H2 input

The H_2 molar flow fed into the bed can be operatively increased from the stoichiometric value needed to hydrogenate the unsaturated. We will analyze here the impact of increasing F^0_{H2}, focusing on the bed length required to achieve the goal of the process, i.e. as a means to reduce the catalyst loading or to compensate for activity losses. However, the final decision on the magnitude of total hydrogen molar flow (F^0_{H2}) should be taken on economic grounds, as bed pressure drop and H_2 recycling should also be considered. Five levels of F^0_{H2} has been tested, ranging from a low value showing a ratio of 1.78 with respect to the stoichiometric value (Case (a) in Table 2.5) up to a four-fold value (Case (e)). Case (b) in Table 2.5 corresponds to the base case.

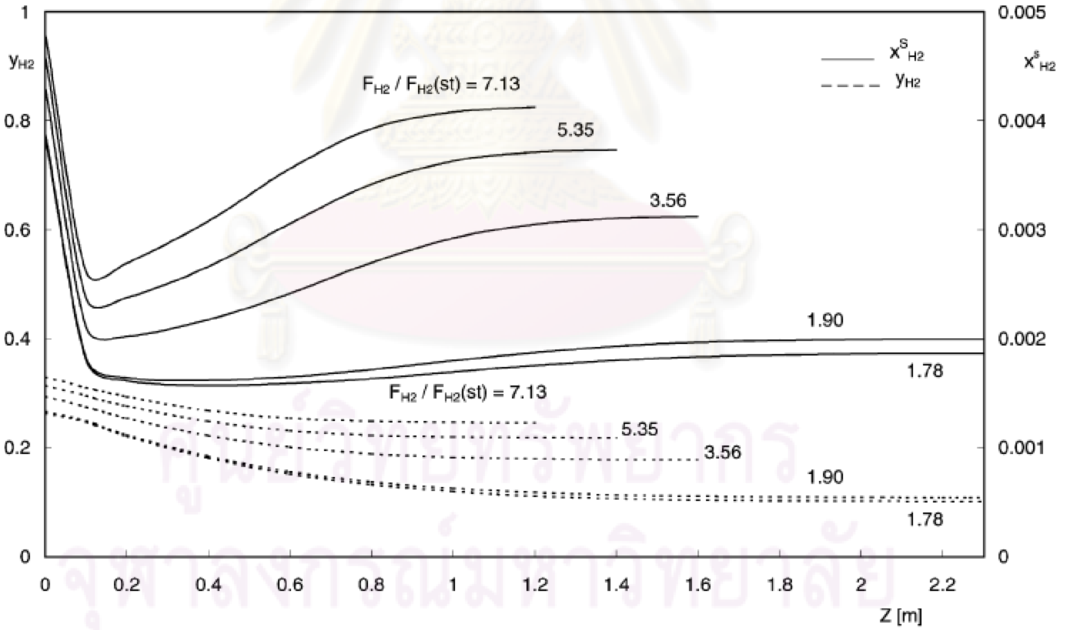
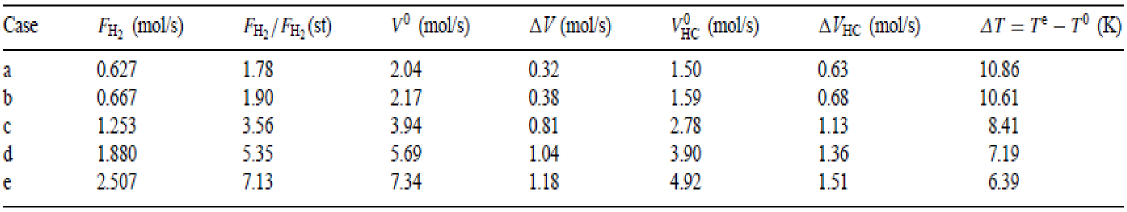


Figure 2.1 Influence of H2 molar flow on the calculated hydrogen mole fraction profiles

Table 2.5 Effect of hydrogen flow rate on reactor performance



Case	F_{H_2} (mol/s)	F_{H_2}/F_{H_2}(st)	V^0 (mol/s)	ΔV (mol/s)	V^0_{HC} (mol/s)	ΔV_{HC} (mol/s)	$\Delta T = T^e - T^0$ (K)
a	0.627	1.78	2.04	0.32	1.50	0.63	10.86
b	0.667	1.90	2.17	0.38	1.59	0.68	10.61
c	1.253	3.56	3.94	0.81	2.78	1.13	8.41
d	1.880	5.35	5.69	1.04	3.90	1.36	7.19
e	2.507	7.13	7.34	1.18	4.92	1.51	6.39

It can be expected that increasing F^0_{H2} will, in some way, increase the H_2 concentration on the catalyst surface, x^S_{H2}. The hydrogenation reactions will become faster and a shorter catalytic bed will be needed. Note that the isomerization reactions are independent of x^S_{H2}. Hence, they will not benefit from higher values of x^S_{H2} and lower amounts of 2-butenes will be produced from 1-butene, saving an important amount of catalyst otherwise needed to accomplish their slow hydrogenation. It is shown in figure 2.1 that x^S_{H2} significantly increases as F^0_{H2} is raised, causing important reductions in bed length, which can be read at the point where each curve ends. By doubling F^0_{H2}, i.e. from Cases (a) to (c), the bed length to obtain 20 ppm of unsaturated at the exit diminishes by 33%. A four-fold increase in F^0_{H2} saves half of the catalytic bed. The increase in x^S_{H2} with F^0_{H2} is primarily caused by higher values of the H_2 vapor mole fraction y_{H2} and, secondarily, by higher values of $(a^{VL}_v\ k^L_{H2})$ derived from higher vapor flow rates (see Table 2.5).

2.2.2 Operating pressure

The direct mean to increase the solubility of H_2 is to raise the operating pressure. The partial pressure of the hydrocarbon mixture at temperature $T^0 = 313.16$ K (base case) is about $P_{HC} = 0.75$ MPa. The difference pressure $(P - P_{HC})$ nearly equals the H_2 partial pressure P_{H2}. An increment from the operating pressure in the base case $P = 1.2$ to 1.5 MPa causes an increment of around 100 % in P_{H2}. Consequently, the equilibrium value molar fraction in liquid phase x^i_{H2} becomes higher in about the same proportion.

As the hydrocarbon vaporization is restrained at higher pressures, the mixture temperature along the bed gets higher at $P = 1.5$ MPa, but causes a lower drop in molar fraction in vapor phase y_{H2}. The changes from bed inlet to exit are ΔV_{HC} =

0.0774 mol/s (1.5 MPa) versus 0.6807 mol/s (1.2 MPa); ΔT = 13.2 K (1.5 MPa) versus 10.6 K (1.2 MPa); y^{e}_{H2}/y^{0}_{H2} = 0.5093 (1.5 MPa) versus 0.4051 (1.2 MPa). The differences just outlined lead to values of x^{S}_{H2} around 100% higher at P = 1.5 MPa, which along with the marginal effect of temperature allows a saving of somewhat more than 50% in the bed length needed to achieve 20 ppm of unsaturated at the bed exit. The profiles of x^{S}_{H2} at 1.2 and 1.5 MPa are compared in figure 2.2. The curve ends mark the necessary bed lengths. The profiles of *trans*-2-butene mole fraction are also given, recalling that this is the last unsaturated to get extinguished.

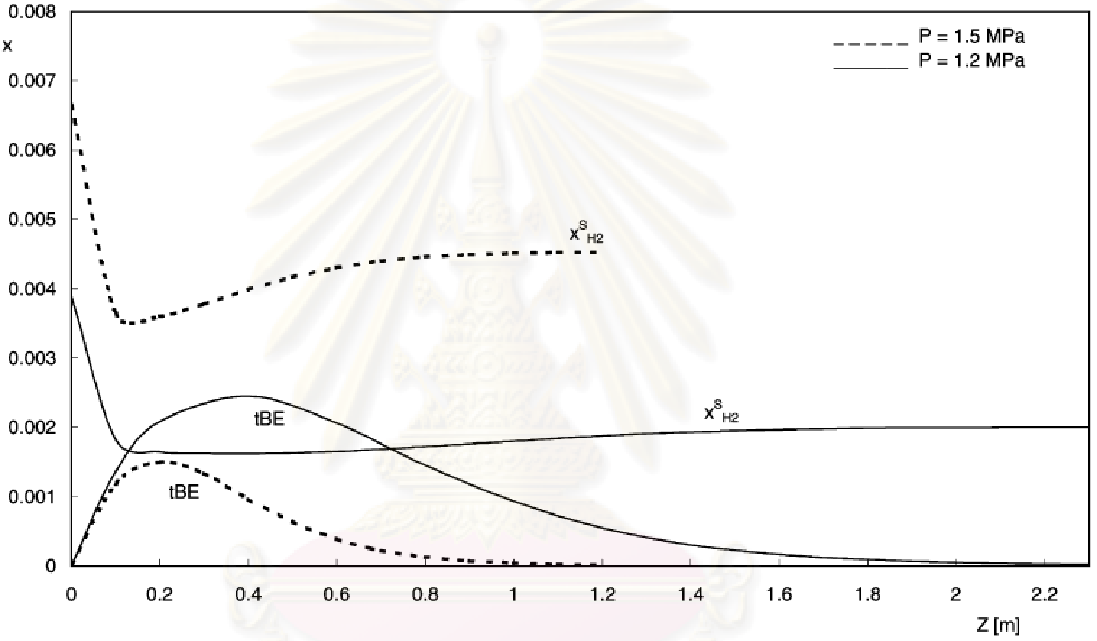


Figure 2.2 Influence of the reactor pressure on calculated hydrogen molar fraction (at liquid-solid interphase). trans-2-butene molar fraction.

2.2.3. Inlet temperature

The conceptual arguments to assess the impact of increasing the thermal level of the mixture have been already discussed: on one hand, an increase in the HC volatility that will make y_{H2} and consequently x^{S}_{H2} decrease and, on the other hand, an increase in the kinetic coefficients. As they show opposite effects on the hydrogenation rates, the net outcome should be quantitatively evaluated. The results can be discussed from Table 2.6, where the inlet temperature was modified by ±10 K from the base-case value, T^{0} = 313.16 K. The unsaturated concentration at the exit increases one order of magnitude for an increment of 10 K. The significant increase of V_{HC} as T^0 increases, not only at the bed inlet, but also along the bed (Table 2.6), causes a significant dilution of H2 in the vapor phase that definitely overwhelms the effect on kinetic coefficients. It becomes interesting to analyze whether catalysts with higher activation energies will still show the same trend with temperature. To this end, it was considered that at $T^0 = 313.16$ K, all hypothetical catalysts will show the same values of the kinetic parameters (those resulting for the material actually tested), but parameterized with an activation energy assumed common for all reactions. The concentration of unsaturated at the exit of a bed with $Z_L = 1.4$ m are plotted in figure 2.3 as a function of T^0 for different values of E. Values of T^0 above 293K (20˚C) are considered, as it was appraised that sub-ambient temperatures will not be convenient. The results for the experimentally tested catalyst and for $E = 0$ are included. The latter is a limit case that just reflects the effect of T^0 on H_2 dilution in the vapor phase.

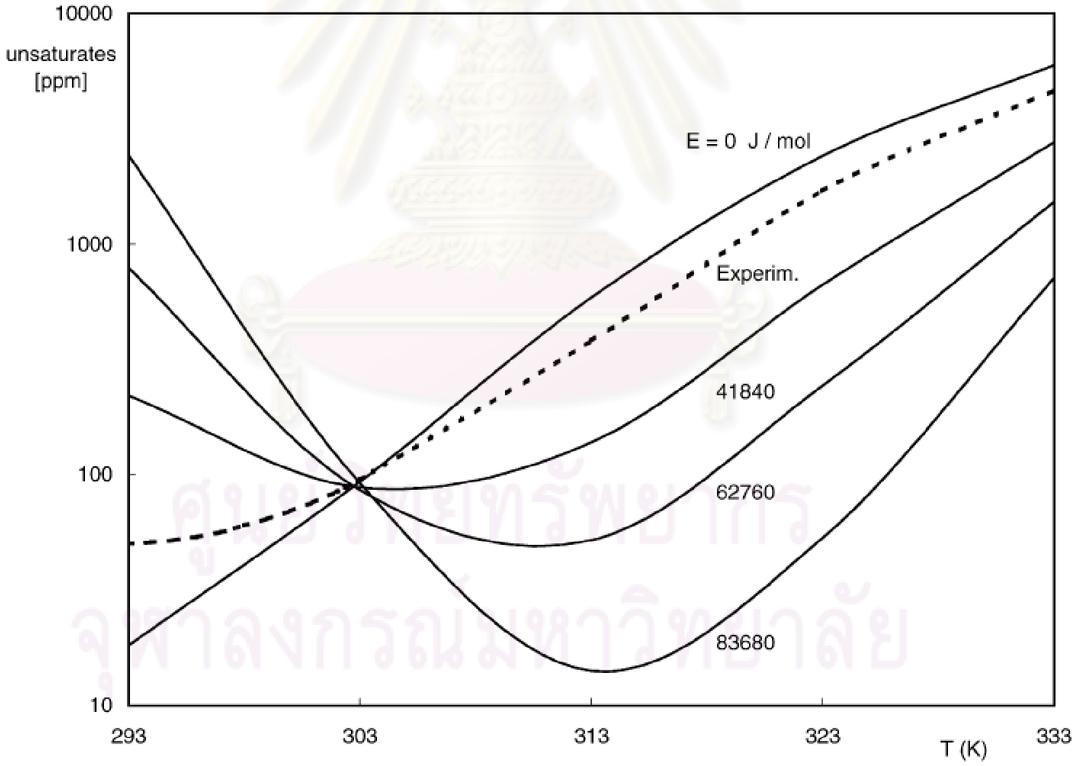
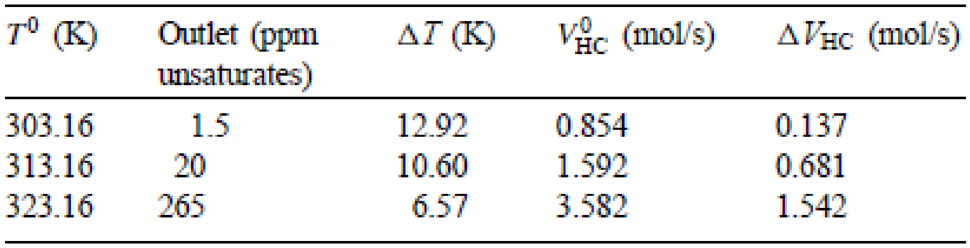


Figure 2.3 Effect of the feed temperature on reactor behavior. Five activation energy level.

Table 2.6 Effect of inlet temperature on reactor performance



T^0 (K)	Outlet (ppm unsaturates)	ΔT (K)	V^0_{HC} (mol/s)	ΔV_{HC} (mol/s)
303.16	1.5	12.92	0.854	0.137
313.16	20	10.60	1.592	0.681
323.16	265	6.57	3.582	1.542

Significant and non-obvious general features were:

- The slow hydrogenation of 2-butenes, especially of *trans*-2-butene, demands around half of the bed length. 2-Butenes can be present in the process stream, but they are always formed by hydrogenation of 1, 3-butadiene and by isomerization of 1-butene.
- Mass transfer limitations on the liquid side of the vapor–liquid interface were most significant for H2 absorption rates.
- The volatility of the hydrocarbon mixture was a paramount factor to dilute H_2 in the vapor phase (hence, to diminish the amount of H_2 dissolved in the liquid stream) and to restrain the temperature rise along the bed, due to the vaporization heat.

These key factors allowed explaining the simulated response of the system to variations in the different operating variables. However, the results could be hardly predicted beforehand, due to the rather complex interplay of the effects. Thus, a temperature rise turned out to be significantly detrimental for the reactor performance at the conditions studied, as the effect of the increased hydrocarbon volatility overcomes the effect on the kinetic coefficients. A parametric analysis revealed that this result is not fortuitous and will stand for different catalysts and operating conditions. The conclusion regarding the effect of temperature precludes the usual operating policy of rising temperature to compensate for catalytic activity decay. Instead, increasing the H2 input and/or the operating pressure were shown to be effective alternatives to improve the reactor performance. The reactor performance was also shown to be sensitive to the composition of the unsaturate pool, as the different compounds present significant differences concerning kinetics, reaction paths and thermal effects. [S.P. Bressa, 2001]

2.3 Sulfur Poisoning of nickel-based catalyst

Deactivation of nickel catalysts by sulfur poisoning is a serious industrial problem and the effect of sulfur on the performance of metal-supported catalysts has been widely studied [Feg-Wen Chang, 2001]. The effect of different components of gasification gas on sulfur poisoning of nickel catalysts were studied. In addition, the sulfur distribution and content of nickel catalyst beds were analyzed to account the poisoning effect of sulfur on the activity of catalysts to decompose tar, ammonia and methane. The desorption behavior of chemisorbed sulfur from the bed materials was monitored by temperature programmed hydrogenation (TPH). It was established that bulk nickel sulfide was active in decomposing ammonia in high-temperature gasification gas-cleaning conditions. The decomposing activity of methane was not affected by bulk nickel sulfide formation, but that of toluene was decreased. The activity of the catalyst regained rapidly when H_2S was removed from the gas. However, the conversion of ammonia was not regained at as high a level as before sulfur addition, most probably due to irreversible sulfur adsorption on the catalyst. The temperature increase could also be used to regenerate the catalyst performance especially in respect to methane and toluene. Sulfur adsorbed on nickel catalysts in different chemical states depends on the process conditions applied. At >900˚C the sulfur adsorbed on the catalyst formed an irreversible monolayer on the catalyst surfaces, while at <900˚C the adsorbed sulfur, probably composed of polysulphides (multilayer sulfur), was desorbed from the catalyst in sulfur-free hydrogen containing atmosphere. However, a monolayer of sulfur still remained on the catalyst after desorption. The enhanced effect of high total pressure on sulfur-poisoning of nickel catalysts could be accounted for the increased amount of sulfur, probably as a mode of polysulphides, adsorbed on the catalyst [Elsevier Science B.V., 1997].

Adsorption studies of H_2S on nickel indicate an increasing reversibility of adsorbed sulfur with increasing temperature. The use of high temperatures during regeneration in reducing atmosphere has a positive effect because of the high heat of chemisorptions. At the steam reforming of methane the reversibility was demonstrated at temperatures of 800 - 900°C by Morita and Inoue, who found that the nickel catalyst regained the initial activity after the removal of sulfur compounds in the feed. However, in industrial scale this normally results in slow regeneration because the rate of diffusion-controlled elution decreases exponentially with time. According to Rostrup-Nielsen, the adsorbed sulfur was easily removed by steaming at temperatures above 600 °C if steaming resulted in formation of sulphates. Some studies by Bartholomew have shown that it might be possible to regenerate the sulfur-poisoned nickel catalysts by removing S from the catalyst as SO_2 by controlled exposure to oxygen (very low O_2 partial pressure), or to species that dissociate to oxygen.

The nickel-sulfur bonds of adsorbed sulfur are significantly stronger than those in bulk nickel sulphides. Due to the strength of the sulfur-metal bond, sulfur adsorption is frequently non-uniform with respect to the catalyst bed, and hence it is very difficult to provide fundamental information on sulfur poisoning. This phenomenon could be explained by the fact that the adsorbed sulfur was probably not totally removed from the catalyst by increasing temperature or even by removing the H_2S from the gas. The activity of the catalysts regained rapidly when H_2S was removed from the gas. At 900°C under 20 bar the regeneration was more rapid than at 800°C. The temperature increase could be used to regenerate the catalyst performance especially in the case of methane and toluene. However, the conversion of ammonia was not regained as high a level as before sulfur addition most probably because all of the sulfur adsorbed on the catalyst was not removed by temperature treatment or even by removing the H_2S from the gas. [Jouko Hepola, 1997]

CHAPTER III

THEORY

3.1 Reaction Chemistry

The hydrogenation reaction of normal- and iso-olefin is the main reaction. The side reactions are the conversion of benzene, toluene and xylene to naphthenic species as follows;

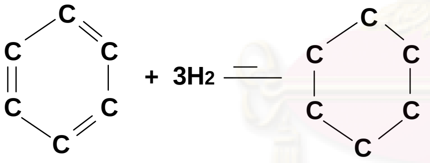
Conversion of normal olefin

$$\mathrm{C\text{-}C\text{-}C{=}C\text{-}C\text{-}C + H2 \rightleftarrows C\text{-}C\text{-}C\text{-}C\text{-}C\text{-}C} \qquad (1)$$

Conversion of iso-olefin

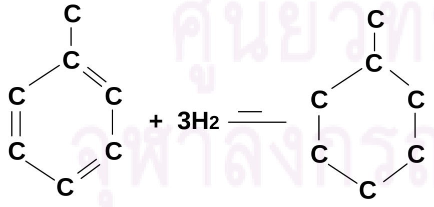
$$\mathrm{C\text{-}C\text{-}C\text{-}\overset{\overset{C}{\|}}{C}\text{-}C + H2 \rightleftarrows C\text{-}C\text{-}\overset{\overset{C}{|}}{C}\text{-}C\text{-}C} \qquad (2)$$

Conversion of benzene



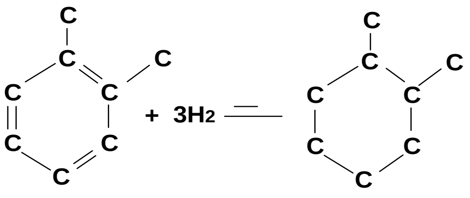
(3)

Conversion of toluene



(4)

Conversion of *meta*-xylene



(5)

Benzene is converted to cyclohexane while toluene is converted to methylcyclohexane. A small amount of xylene may be converted to dimethyl cyclohexane. In a similar fashion, ethyl benzene may be converted to ethyl cyclohexane. The loss of aromatics is easier to interpret by monitoring the appearance of the non-aromatic in the charge and effluent of reactor. The calculation formulas are shown in equation (6), (7) and (8) as follows;

$$\textbf{Benzene loss} = \frac{\text{mole of cyclohexane in effluent} - \text{charge}}{\text{mole of benzene in charge}} \qquad (6)$$

$$\textbf{Toluene loss} = \frac{\text{mole of methyl cyclohexane in effluent} - \text{charge}}{\text{mole of toluene in charge}} \qquad (7)$$

$$\textbf{Xylene loss} = \frac{\text{mole of dimethyl cyclohexane in effluent} - \text{charge}}{\text{mole of xylenes in charge}} \qquad (8)$$

3.2 Deactivation of Catalyst

3.2.1 Sulfur Poisoning of Catalyst

Aromatic feeds normally contain very low levels of sulfur. Typical compounds in the aromatic charge are thiophene and substituted thiophene, methyl, dimethyl and ethyl thiophene. There may also be some very low trace levels of mercaptan as a result of recombination of H_2S and olefins in the upstream units.

The sulfur compounds in the charge are very strongly adsorbed to the surface of the catalyst. Over time the very small levels of sulfur compounds are sufficient to poison the catalyst by occupying the reactive sites.

3.2.2 Deactivation by Fouling

It is possible to foul the catalyst during operation. Under the right conditions olefins may condense on the catalyst to form a heavy condensate that fouls the surface. This is unexpected during normal operation.

If the feed becomes contaminated with oxygen, the olefins in the feed can form active peroxides. When the feed is heated in the unit the active peroxides may decompose and start free radical reactions. Such reactions contribute to formation of polymer that may coat the catalyst. Normally the feed to the unit is sourced directly from upstream fractionation, which is usually sufficient to protect the unit from this type of fouling.

Although it may be possible to reverse fouling by heavy deposits using the hot hydrogen strip, this has not been demonstrated.

3.2.3 Deactivation from Makeup Hydrogen

Trace levels of harmful components may be contained in the hydrogen. H_2S is a frequent contaminant of hydrogen and will deactivate the catalyst in a similar fashion to the sulfur compounds in the charge. H_2S is very strongly adsorbed by the catalyst and should be minimized. Normally the level of H_2S in the hydrogen used by the process is low and the amount of hydrogen used by the process as compared to the catalyst is relatively low. During regeneration the amount of hydrogen passed over the catalyst is significant and so the restriction on H_2S must be more stringent.

Trace levels of HCl contribute an acid function to the catalyst. Acidity may promote polymerization reactions that may lead to fouling of the catalyst.

Carbon Monoxide strongly adsorbs to the catalyst. Accumulation of CO will appear to deactivate the catalyst is a similar fashion to sulfur.

Nitrogen in the form of ammonia in the makeup gas can also contribute to deactivation of the catalyst.

Caustic contamination from the scrubbing of makeup gas can contaminate the catalyst permanently. If caustic washed gas is used, precautions must be taken to ensure no carry-over of caustic reaches the process.

3.2.4 Other Contaminants

Trace metals in the charge can damage the catalyst function. Typical metals checked for in the charge include arsenic, lead, and copper. Any metal contamination should be avoided. Normally the charge is very low in metals.

3.3 Process variable

The operation of the Olefin hydrogenation process is controlled using temperature, pressure, the flow through the reactors and the ratio of H_2 to the reactants. Although sample points are provided in the unit to determine the quality of the product from the olefin hydrogenation unit, an efficient operation is best obtained when the operator monitors the end products after further processing. The design of the unit is to remove as much of the bromine reactive materials in the feed as possible while not saturating aromatics. As was the case with clay treating performed previously it is not normally required to remove all the olefin reactive species present in the charge.

3.3.1 Pressure

In the Olefin hydrogenation unit pressure should be maximized at the reactors to maintain the maximum solubility of the hydrogen in the process liquid.
The goal of the operator should be to maintain the highest pressure in the reactor circuit consistent with the operation of the upstream equipment. Yields are improved with higher pressures that force more of the hydrogen into the liquid phase.

3.3.2 Flow

Normally the flow through the reactor is not adjusted during normal operation. A recycle of product is used to maintain a high velocity through the catalyst bed.

3.3.3 Temperature

As the catalyst ages the temperature of the reactor will need to be increased to maintain the activity of the catalyst. The EOR temperature should not be exceeded the design, as high temperatures may lead to permanent poisoning of the catalyst.
Higher temperatures will cause more hydrogenation of aromatics. As result of this effect, running at the lowest temperature which still makes the product quality acceptable should be the operating goal.

3.3.4 H_2/Reactants

The unit is designed with hydrogen to hydrocarbon ratio set point controller. The purpose of this controller is to maintain the ratio of hydrogen to fresh feed entering the unit.

CHAPTER IV

METHODOLOGY

4.1 Research Methodology

The research is separated into 4 parts. Part 1 is the Feed stock and process performance review, Part 2 is the study to change the operation mode from series to single bed, Part 3 is the process performance improvement by very the variable control parameters, and Part 4 is study of catalyst in situ regeneration as shown in figure 4.1.

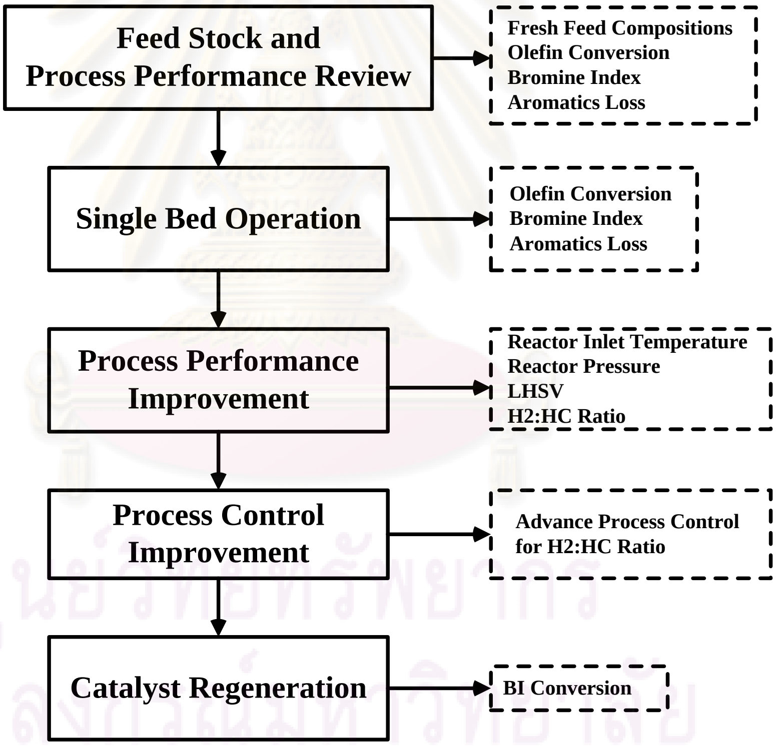


Figure 4.1 Flow diagram of research methodology.

4.2 Materials

The study was done by using olefin hydrogenation reactors in the actual operating conditions with the feed of reformate from catalytic reforming process. Gas Chromatograph is used to analyze the hydrocarbon compositions in both feed and product streams. CA-200 Karl Fischer Moisture meter equipped with Bromine Index measurement probe was used to measure the bromine index.

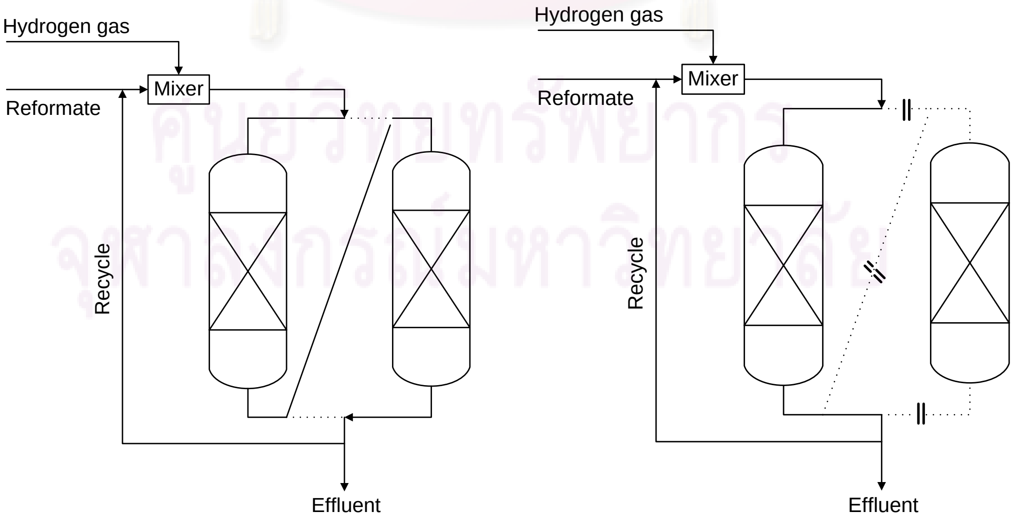
4.3 Experiment

Part 1: Feed stock and Process Performance Review

The fresh feed characteristic and currently process performance of olefin hydrogenation process such olefin conversion and aromatics loss was analyzed to understand the consequences which are affect to downstream process.

Part 2: Single Bed Operation

The research was to alter the operation mode of olefin hydrogenation process from a series to a single bed operation at constant reactor inlet temperature, reactor pressure, and combined feed rate as shown in figure 4.2a and 4.2b.



(a) (b)

Figure 4.2 Schematic diagram of Olefin hydrogenation process in series (a) and single (b) operation.

The olefin conversion, aromatic loss calculation, and bromine index in necessary streams was analyzed and calculated to monitor the process performance and product qualities. The process control variable was adjusted to maximize the catalyst utilization after the single bed operation is stable conditions and ensure that is no effect to downstream process. At the end of run conditions, the catalyst was regenerated and evaluated the catalyst performance compare with fresh catalyst.

Part 3: Process Performance Improvement

The variable parameters such as temperature, pressure and the flow through the reactor were varied and studied effect on the catalyst performance.

Part 4: Catalyst regeneration

This part is study the catalyst performances after regeneration compare with before. The regeneration is following the provided procedure from licensor. The hydrogen used for the strip is 99.9% purity or electrolytic grade at a GHSV of 120; equivalent a flow rate of 4400 Nm3/hr, 300°C with 48 hours holding.

Part 5: Process Control Improvement

This part is study to improve the hydrogen-to-hydrocarbon logical control from regulatory control to advance process control to maximize the hydrogenation reaction all the time.

Part 5: Operating Window Development

The objective of Operating Window to assure the all of condition is practical. Including identify plant limitations in order to keep the plant running safely and smoothly as well as maintaining reliability and integrity of the plant.

CHAPTER V

RESULTS AND DISCUSSIONS

5.1 Feed Stock and Process Performance Review

The fresh feed characteristic and currently process performance of Olefin hydrogenation process need to be analyzed to understand the consequences which are affected on downstream process.

5.1.1 Fresh Feed Compositions

Fresh feed of Olefin Hydrogenation unit is from the Catalytic Reforming process that converts naphthenic to aromatics. The fresh feed composition is analyzed with gas chromatography method (ASTM D6293). The composition is consist of 90 wt% aromatics, 10 wt% paraffin, 1 wt% olefin, and 0.3 wt% naphthenic hydrocarbon as shown in figure 5.1. Amount of olefin content depends on the feed stock quality and reaction severity of reforming catalyst.

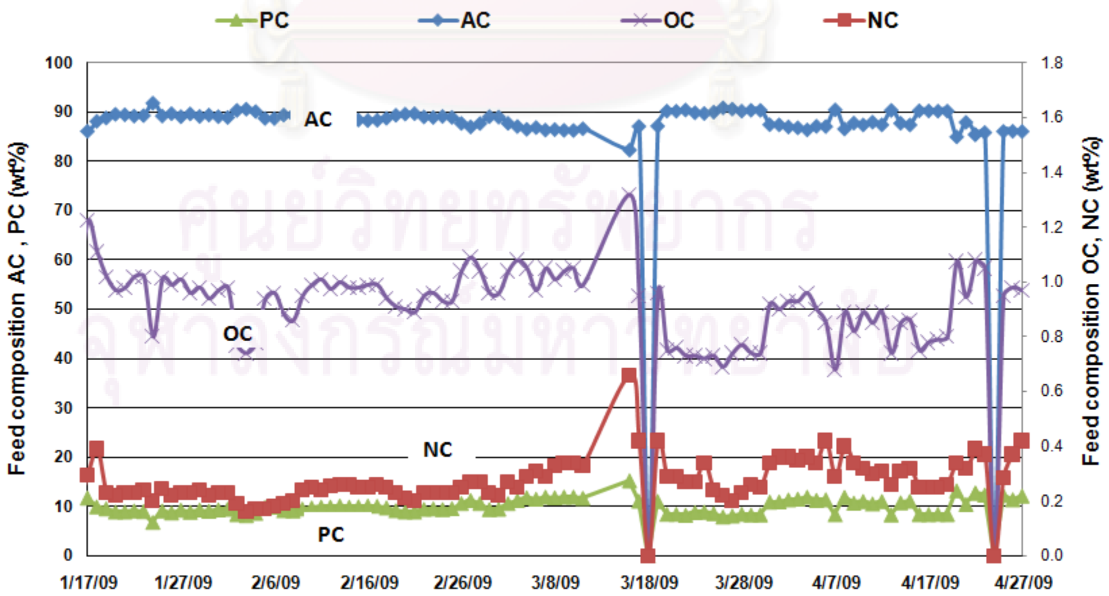


Figure 5.1 Olefin hydrogenation fresh feed compositions.

Normally, feed composition is changed every couple of week or a week depending on plant production plan. More than 4 sources of raw material are blended with different blending ratio to minimize the raw material cost. So the Olefin Hydrogenation reactor fresh feed compositions are varied with upstream feed source.

5.1.2 Olefin Components in Fresh Feed

The olefin components in reactor charge consist of olefin carbon atom number 5, 6 and 7 (OC5, OC6, and OC7) as shown in figure 5.2. Amount of each olefin species is rather fluctuated due to vary of feed stock.

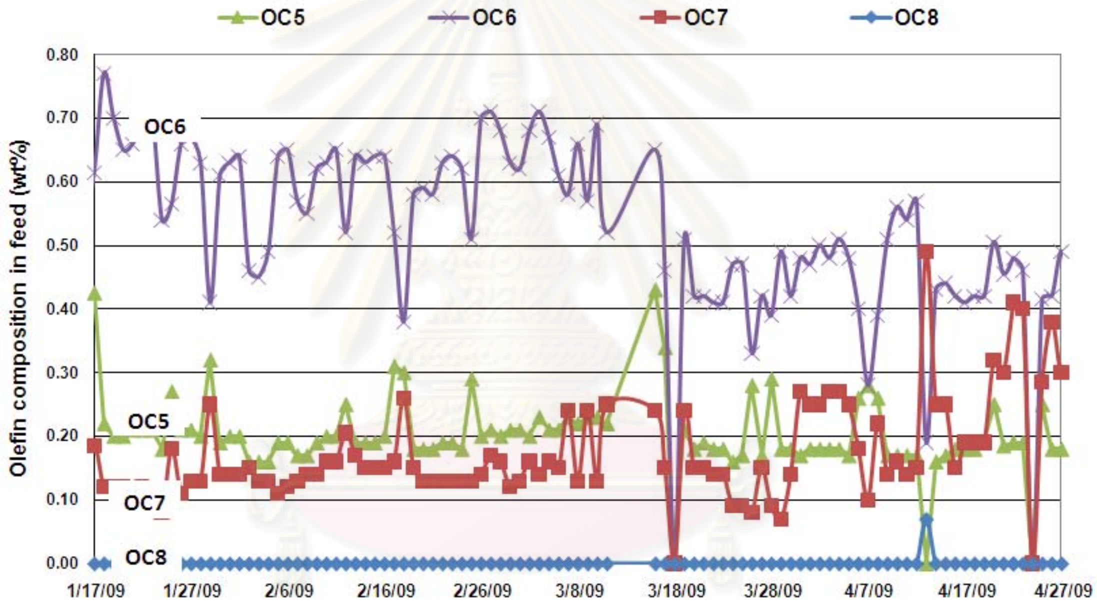


Figure 5.2 Olefin components in fresh feed.

5.1.3 Olefin Conversion

Total olefin conversion across two reactors is more than 97 wt%. Total olefin in feed stream is reduced from 1 wt% to less than 0.05 wt% as shown in figure 5.3 by selective hydrogenation reaction.

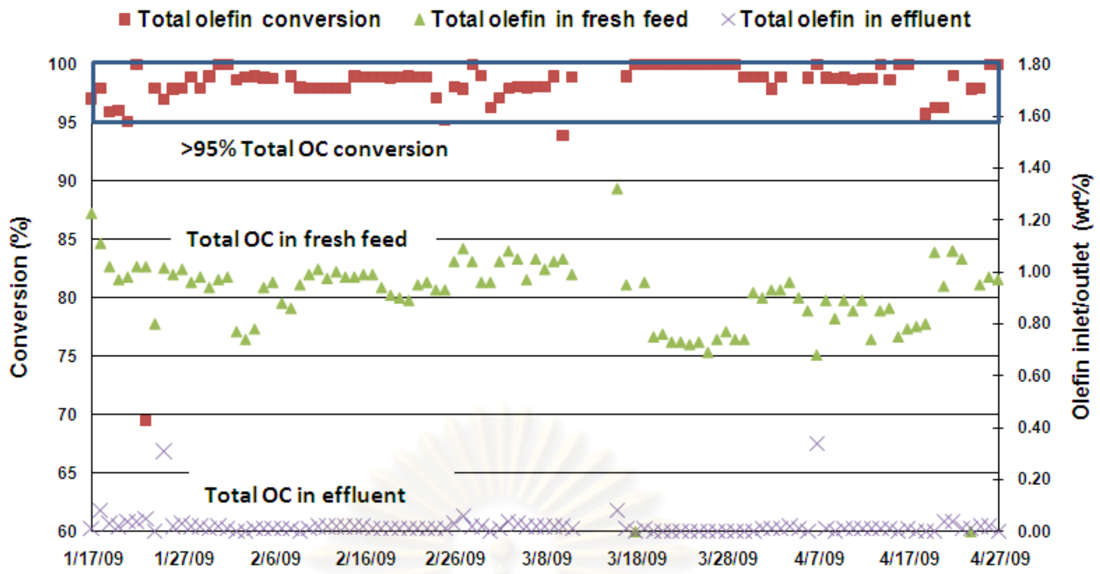


Figure 5.3 Total olefin conversion.

The OC5 conversion is approximate 100 wt% conversion, OC6 conversion is around 97.5-100 wt% while the OC7 conversion is mostly in range of 90-97 wt% as shown in figure 5.4, 5.5 and 5.6. That means the lighter olefin species is easier to hydrogenate than heavier.

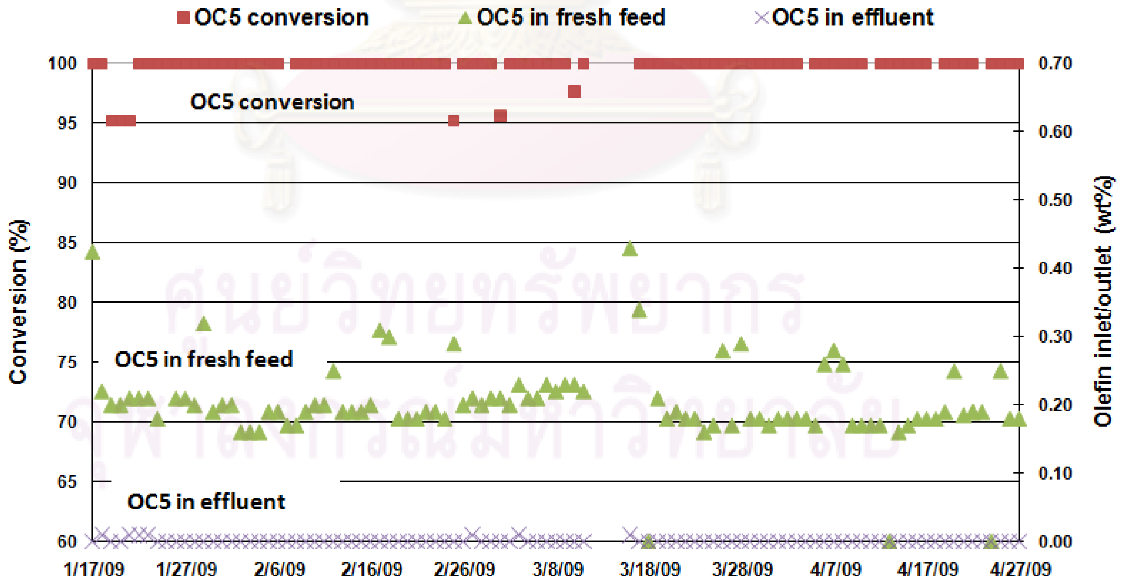


Figure 5.4 Olefin OC5 conversion.

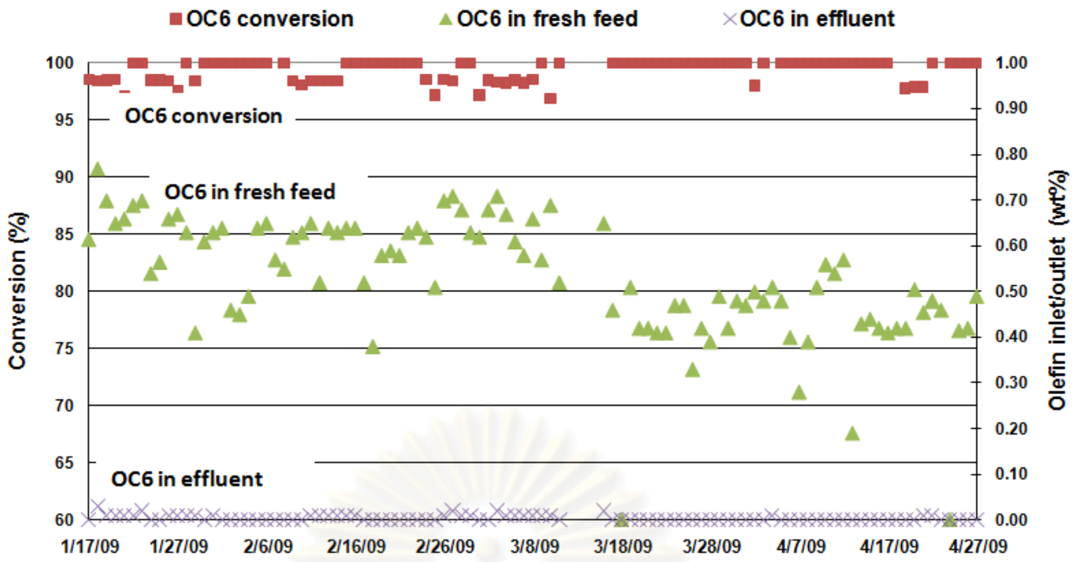


Figure 5.5 Olefin OC6 conversion.

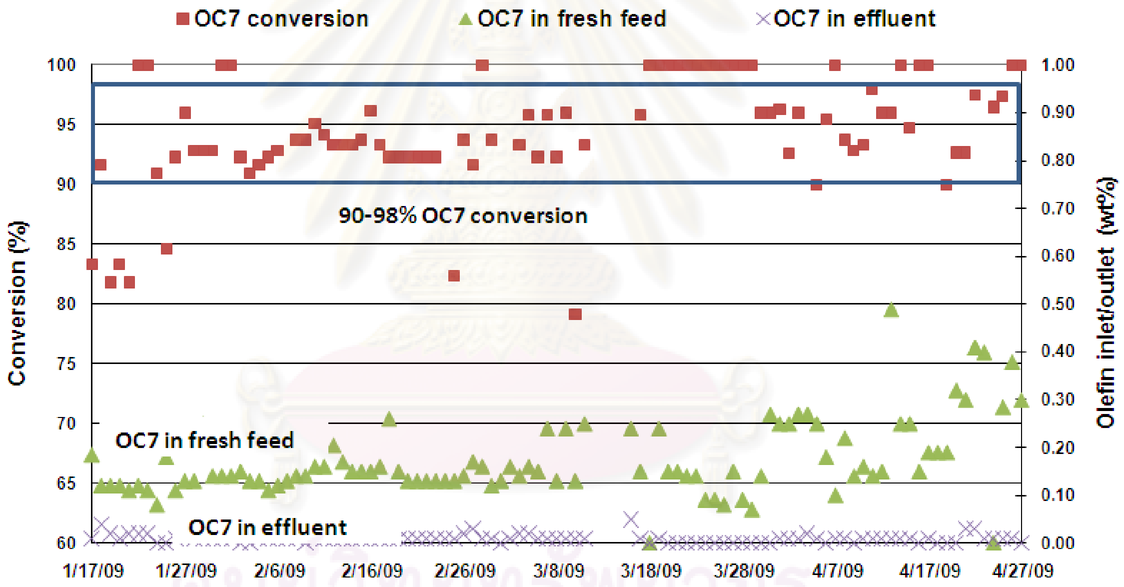


Figure 5.6 Olefin OC7 conversion.

5.1.4 Bromine Index

Amount of olefin in effluent stream is very small level. To monitor the process performance, so the ASTM D 1492 or D 2740 (Appendix B.) is used to measure bromine index (BI) that represent to trace amount of olefin. High concentrations of bromine reactive species are undesirable for some of the downstream units and products and such as the Olefin Hydrogenation unit is designed to hydrogenate these species.

The Bromine index in fresh feed is around 2,500-3,500 mg Br/100g sample. Olefins species are hydrogenated to their hydrogenated product through the first and second reactor (lead and lag reactor). Bromine index of outlet lead reactor is around 150-300 mg Br/100g sample then it will be reduced in lag reactor to less than 100 mg Br/100g sample as shown figure 5.7.

Result is shown 2,350 -3,200 mg/100g of BI is converted in lead reactor that is approximate 91-94% comparing with BI in feed. For the lag reactor, 50-200 mg/100g of BI is converted that is approximate 2-6% comparing with BI in feed so the single bed operation concept is very high possibility to apply for the Olefin Hydrogenation process.

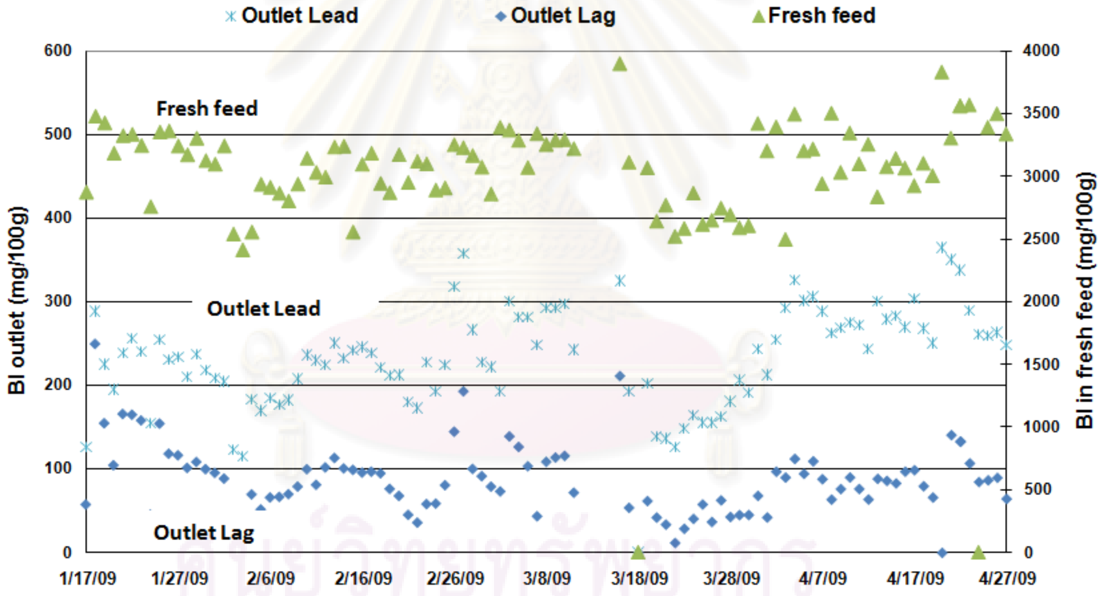


Figure 5.7 Bromine Index in fresh feed, outlet lead and outlet lag reactor.

The C7/C9 Transalkylation unit is limited the Bromine index in charge less than 150 mg Br/100g sample. Most of olefin is from OC7 in Olefin Hydrogenation effluent stream that is co-boiled with toluene will be presented in C7/C9 Transalkylation unit feed follow Figure 1.1 Simplify block flow diagram of BTX production.

Amount of Bromine index in the charge of C7/C9 Transalkylation unit is around 30-50 mg Br/100g sample that is rather small when compare with feed specification 150 mg/100g as shown in figure 5.8.

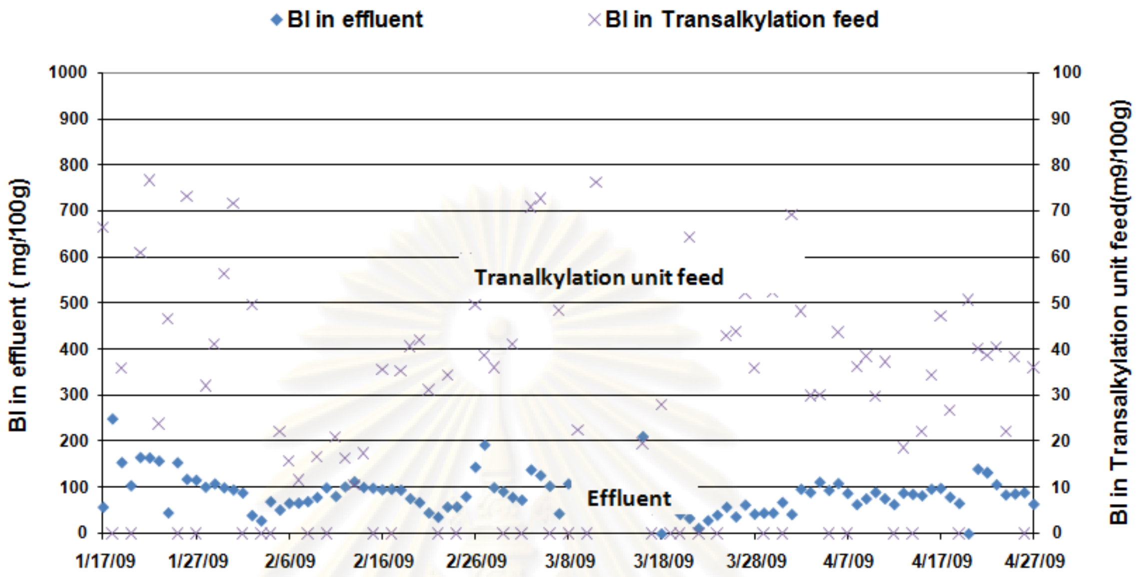


Figure 5.8 Bromine index in C7/C9 Transalkylation unit feed.

For the *para*-xylene production unit, results of BI in unit charge are normally less than 10 mg Br/100g sample. BI in *para*-xylene production unit charge will be absorbed in the molecular sieve adsorbent of this process that leads to deficiency of PX production. The design of unit charge quality allows less than 20 mg Br/100g sample. However, amount of bromine index in Olefin Hydrogenation effluent stream has no major effect to *para*-xylene production unit as shown in figure 5.9 because the quantity of olefin OC8 molecules in charge of the Olefin Hydrogenation process is very small.

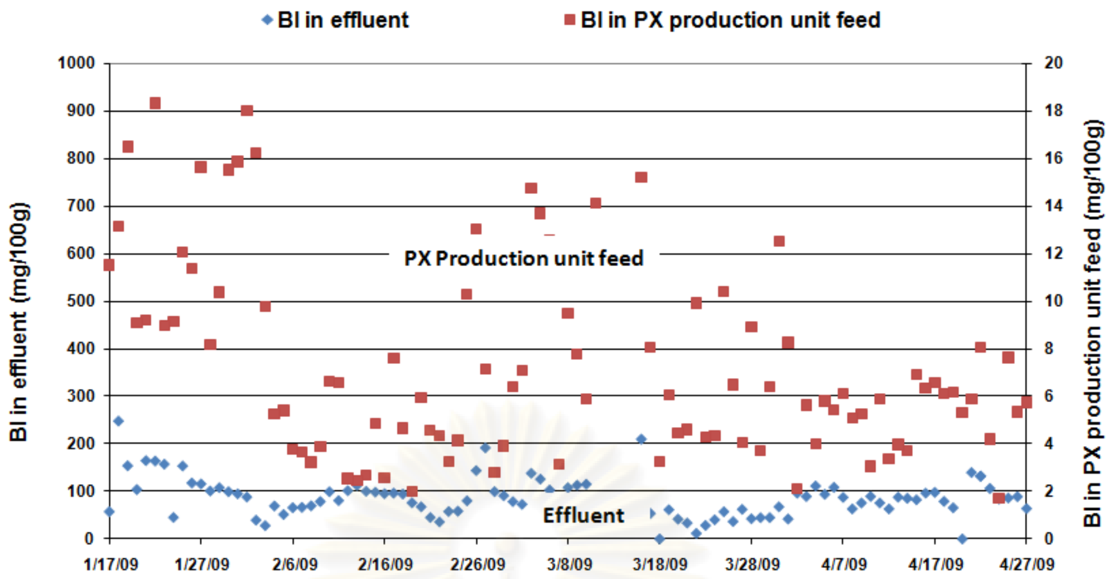


Figure 5.9 Bromine index in *para*-xylene production.

Olefin OC8 concentration that is presented in *para*-Xylene production unit charge can be generated by thermal cracking reaction in column bottom section of Xylene column. Xylene column is a part of Aromatics Fractionation unit.

5.1.5 Aromatics Loss

The benzene and toluene loss are around 0.25-0.5 and 0.05-0.1 mol% respectively as shown in figure 5.10. The xylenes loss is very small, it can be negligible. Maximum allowance of benzene and toluene loss is 0.5 and 0.25 mol%, respectively. Benzene is hydrogenated to cyclohexane, toluene is hydrogenated to methylcyclohexane, and xylene is hydrogenated to dimethylcyclohexane. The aromatics loss should be minimize to maximize the aromatics production. In this case the aromatics loss is rather high so the opportunity for optimization is high possibility.

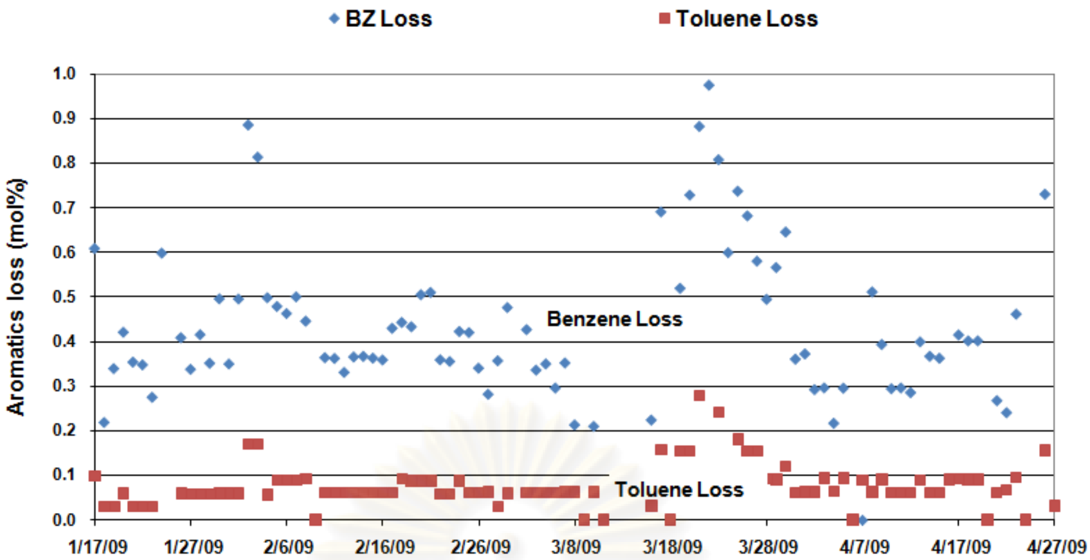


Figure 5.10 Benzene and Toluene loss.

5.2 Single Bed Operation

The study is to change the reactor operation mode from a series to single bed operation, which is relatively different from original operating design. The plant reliability is expected to be improved in the single bed operation by preventing catalyst deactivation in both reactors at the same time. The catalyst deactivations normally cause by the feed contaminants such sulfur, nitrogen, chloride and heavy metals. Particularly, the sulfur compounds have a very high potential to permanently absorb on catalyst at high operating temperature, especially at the end of run conditions.

In single bed operation, the amount of catalyst was decreased by half comparing to the series operation. The liquid hourly space velocity (LHSV) is directly twice increased. The hydrogenation reaction severity is expected to be decreased, which is affected on the olefin and aromatic conversion while the effluent qualities still meet the charge requirement of the downstream processes.

5.2.1 Olefin Conversion

For the series operation, most of olefin is hydrogenated to saturated hydrocarbon. The single operation shows a significant change of total olefin conversion from 95-99 wt% to 85-92 wt% within 6 months as shown in figure 5.11. Higher amount of olefin content in feed is affected on lower olefin conversion according to the constant catalyst activity.

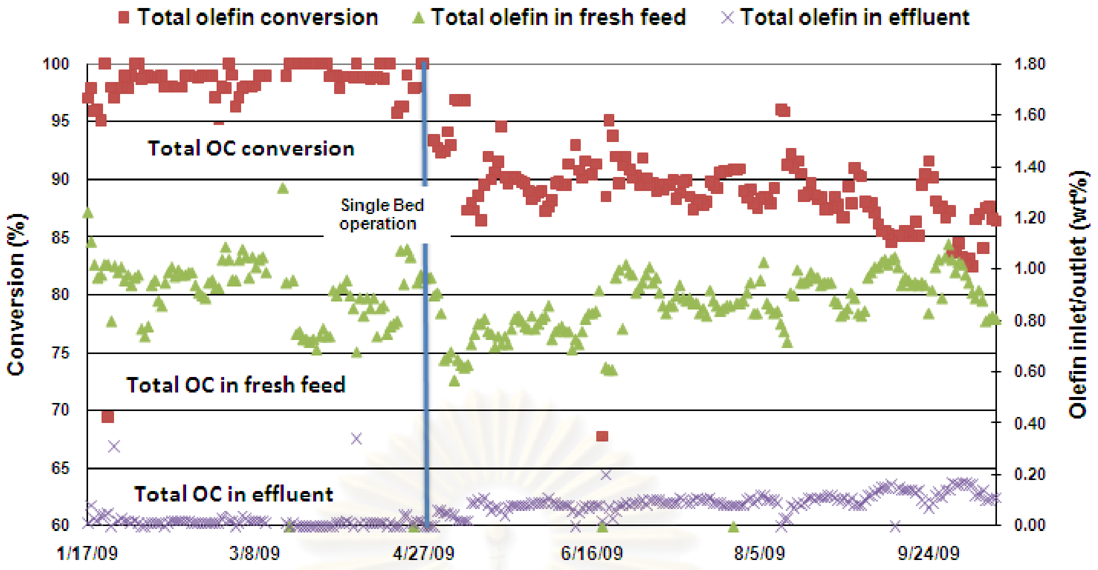


Figure 5.11 Total olefin conversion.

The OC5 conversion is decreased from 100 wt% to 92-96 wt%, OC6 conversion is decreased from 97.5-100 wt% to 83-97 wt% and OC7 conversion is decreased from 90-97 wt% to 75-85 wt% as shown in figure 5.12-14.

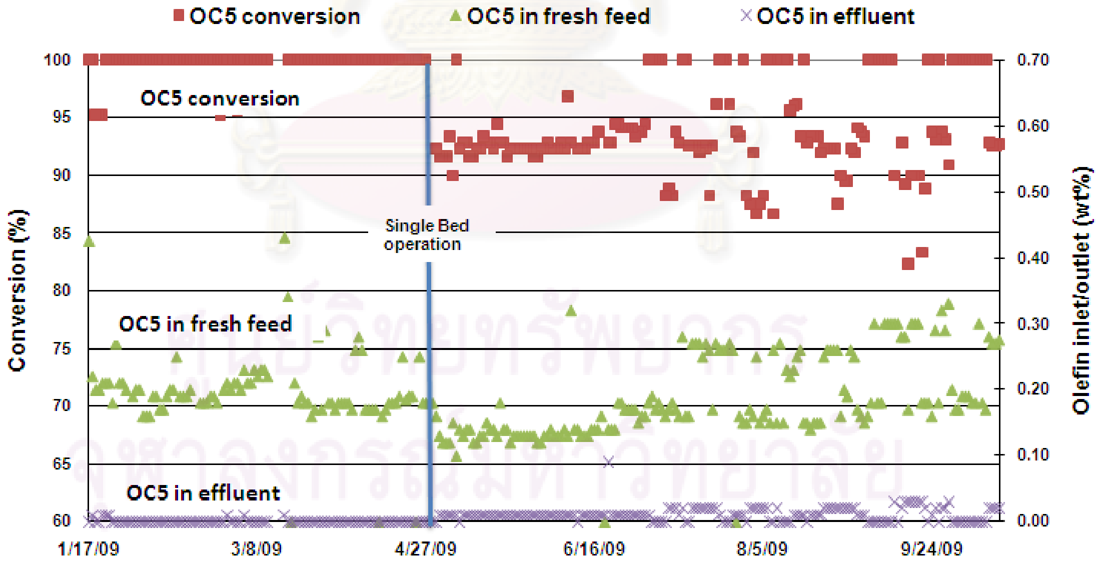


Figure 5.12 Olefin OC5 conversion.

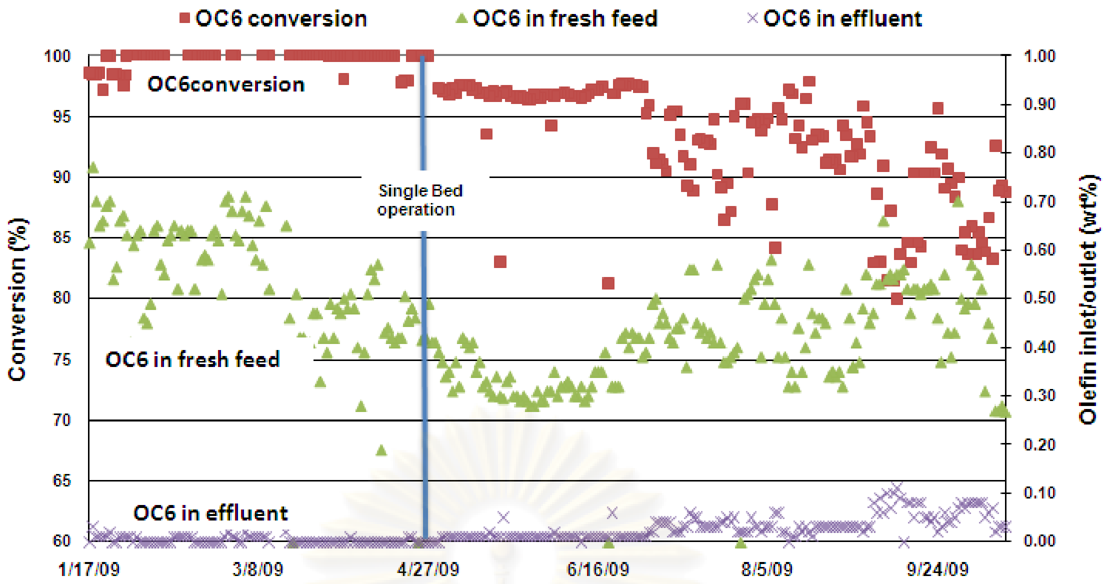


Figure 5.13 Olefin OC6conversion.

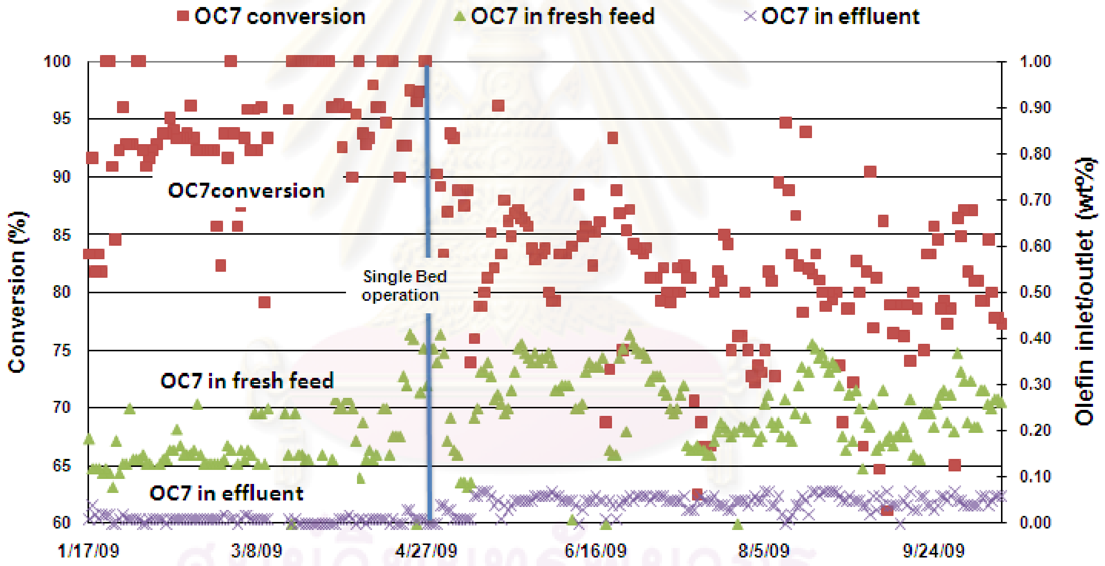


Figure 5.14 Olefin OC7 conversion.

The lighter olefin species are easier to convert than the heavier ones as same as the previous experiment, such as the conversion of olefin C5 and C6 are higher than the conversion of olefin C7 as shown in figure 5.12-14.

5.2.2 Bromine Index

The bromine index of effluent reactor is increased from 50-200 mg Br/100g sample to 200-500 mg Br/100g sample as shown in figure 5.15. Apparently, this will lead to the increase of the amount of BI in the charge of C7/C9 Transalkylation unit from 20-60 to 30-80 mg Br/100g sample as shown in figure 5.16, while the design of unit charge quality allows less than 150 mg Br/100g sample. This is due to the unconverted olefin C7 molecules and their co-boiled with toluene will be presented in the C7/C9 Tranalkylation charge.

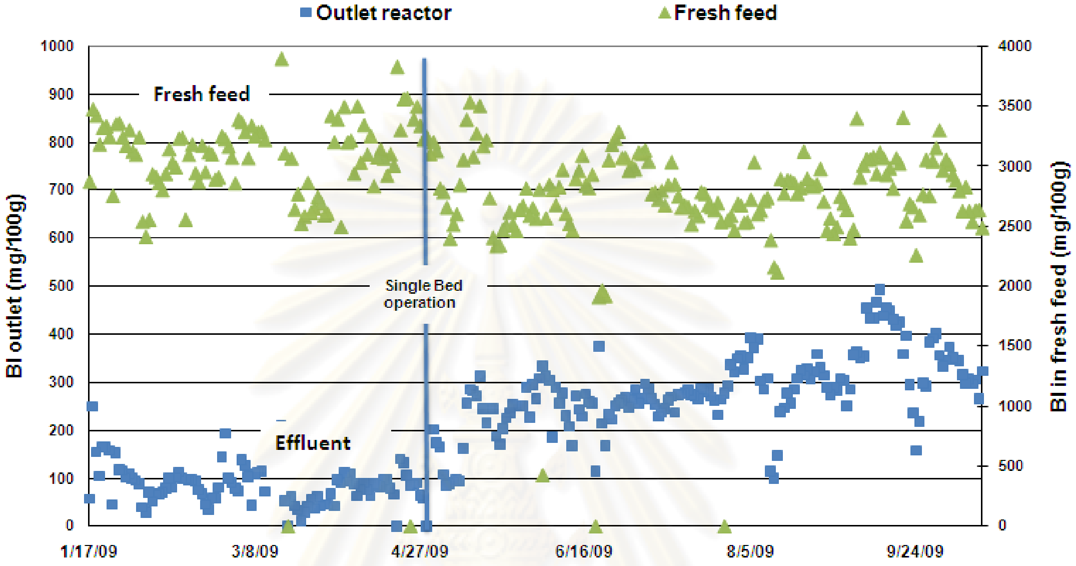


Figure 5.15 Bromine index in fresh feed and effluent.

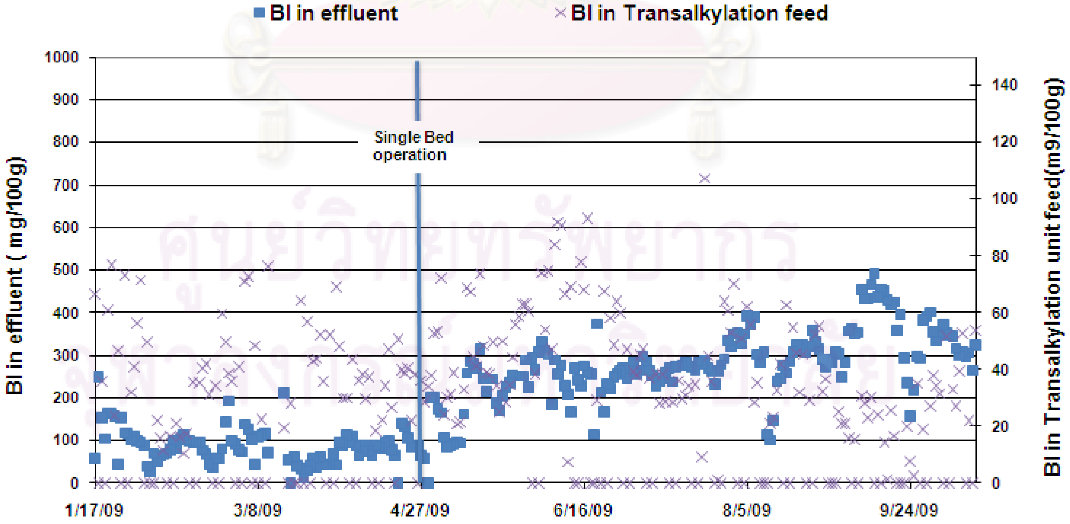


Figure 5.16 Bromine index in C7/C9 Transalkylation unit.

For the *para*-xylene production unit, results of BI in unit charge are normally less than 10 mg Br/100g sample in both of series and single mode as shown in figure 5.17. The design of unit charge quality allows less than 20 mg Br/100g sample. However, the single and series operation modes have no significant effect to *para*-Xylene production unit because the quantity of olefin C8 molecules in charge of the olefin hydrogenation process is very small, so the olefin C8 species do not significant change in feed of *para*-Xylene production unit, although the single operation is applied.

The olefin OC8 species, which have same boiling point with mixed xylene can be generated within the bottom section of Xylene distillation column. The xylene column bottom temperature is controlled around 345-350°C to minimize the thermal cracking reaction of heavy aromatic materials, which are the bottom product.

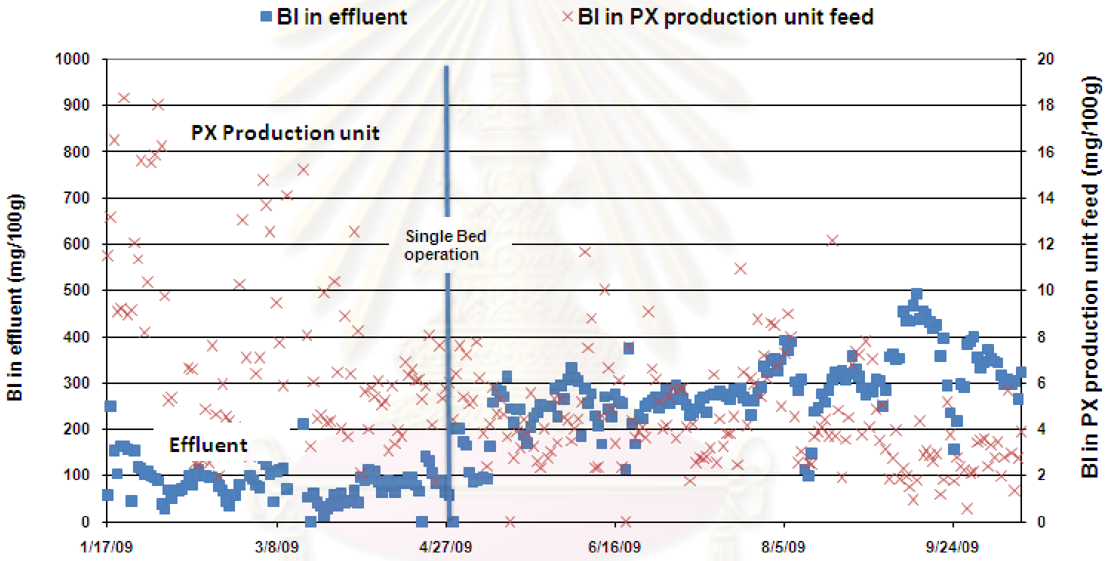


Figure 5.17 Bromine index in *para*-xylene production unit.

The reactor effluent stream is sent to distillation column to separate benzene and co-boiling point materials includes lighter to overhead product. The overhead product is fed to Extraction unit to separate non-aromatics from aromatics species by solvent. Non-aromatic from Extraction unit is called "Raffinate" that is contained with paraffin PC5-6 and olefin OC5-6. The aromatic stream is called "Extract" that is contained with 90 wt% benzene, 10wt% toluene.

Most of the unconverted olefin present in the Raffinate stream, which is normally the non aromatic species from the Extraction unit. The BI in Raffinate is increased from 1,000-1,500 to 1,500-3,000 mg Br/100g sample as shown in figure 5.18. In practice, olefin in Raffinate can be sold in the light naphtha's price. The benzene form Extraction unit is sent to the benzene fractionation to be purified before run down to product tank.

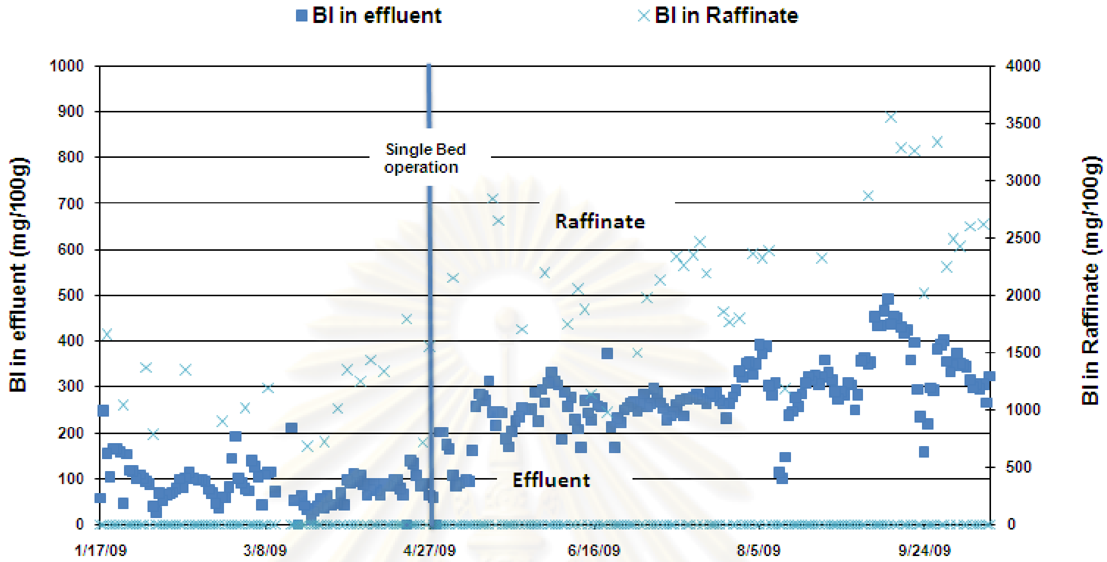


Figure 5.18 Bromine index in Raffinate product.

5.2.3 Aromatic Loss

In terms of benzene loss, the lost is reduced from 0.25-0.5 mol% to 0.2-0.3 mol% leading to the increase in benzene productivity. Toluene loss is reduced from 0.05-0.1 mol% to 0.03-0.07 mol% as shown in figure 5.19. The xylene loss is very small; hence, it can be negligible. This may imply that the second reactor is not necessary for this period. Although olefin O C5-7 conversion is decreased, but bromine index in C7/C9 Transalkylation and *para*-xylene production unit are still in control within the feed specification.

In the case that the reactor fresh feed is 3,408 metric tons per day, the benefit will be improved around ***0.43 million US$ per year*** *(Appendix C)*. Decrease of benzene loss is directly increased of benzene production. For the same reason, decrease in toluene loss essentially consequences to increase the PX production because toluene is normally transformed to xylene species in the C7/C9 Transalkylation unit.

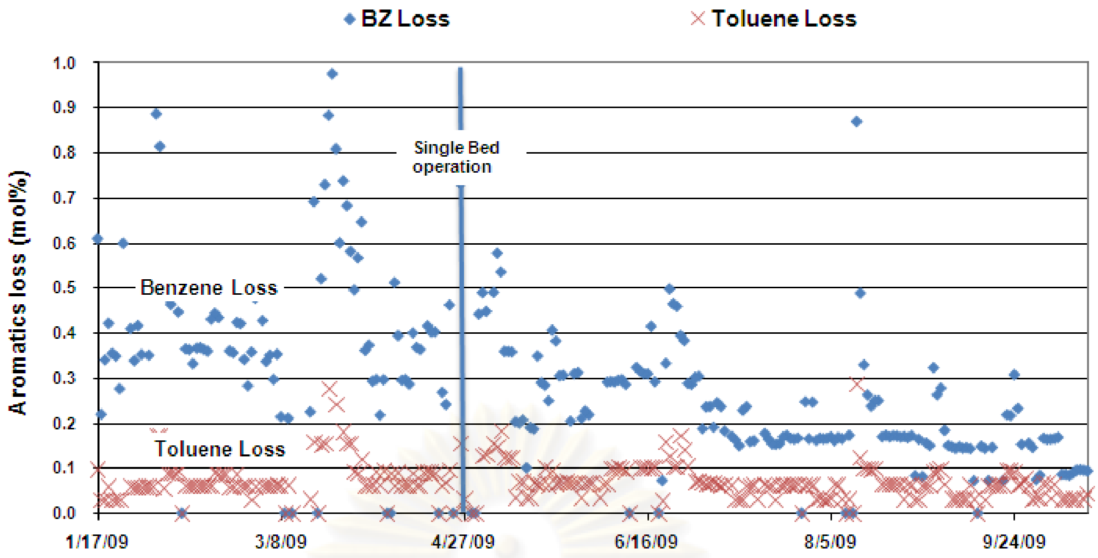


Figure 5.19 Benzene and toluene loss.

5.3 Process Performance Improvement

The operation of the Olefin Hydrogenation Process is controlled using temperature, pressure and the flow through the reactor. Although sample points are provided in the unit to determine the quality of the product from the olefin reduction unit, an efficient operation is best obtained when the operator monitors the end products after further processing. The design of the Olefin Hydrogenation Process is to remove as much of the bromine reactive materials in the feed as possible while not saturating aromatics. This experiment is designed to study the effect of each variable parameter, which is to the olefin conversion, aromatics loss, and bromine index in downstream feed.

5.3.1 Effect of Reactor Inlet Temperature (RIT)

Test 1: An increase of RIT causes more hydrogenation of olefin. Increase of RIT from 70°C to 72°C results in increase of OC5 conversion from 82.5 to 85.71 mol% as shown in table 5.1 and Test 1 in figure 5.20. For OC6 and OC7 conversion, they are increased also, but the highest conversion is OC5, while the lowest conversion is OC7.

The hydrogenation reaction is an exothermal reaction. Higher conversion of olefin should lead to higher reactor different temperatures. In this case, the reactor different temperature is not significant changed because the RIT may not be sufficient to affect the reactor different temperature as shown in Test 1 of figure 5.21.

H2:HC ratio is increased from 4.95 to 5.38 Nm^3/MT of fresh feed as shown in table 5.1 and Test 1 in figure 5.22. The higher hydrogenation reaction is required more hydrogen to hydrogenate olefin species in reactor charge.

Bromine index in C7/C9 Transalkylation unit is decreased from 75.86 to 65.93 mg/100g sample as shown in table 5.1 and Test 1 in figure 5.23. The decreasing of BI is due to the higher OC7 conversion.

The benzene loss is increased from 0.06 to 0.08 mol% due to higher hydrogenation severity as shown in table 5.1 and Test 1 in figure 5.24 while toluene and xylene loss are maintained because benzene is easier to hydrogenate than toluene and xylene.

Table 5.1 Result of RIT increasing from 70°C to 72°C at constant reactor pressure and LHSV.

Parameter	Unit	Test 1			
RIT	°C	70.00	70.40	71.72	72.00
OC5 Conversion	Mole%	82.50	82.01	81.62	85.71
OC6 Conversion	Mole%	79.00	80.09	79.96	80.49
OC7 Conversion	Mole%	60.50	61.75	62.10	63.64
Total OC Conversion	Mole%	73.64	74.45	75.56	76.47
Reactor ΔT	°C	3.44	3.42	3.40	3.40
H2:HC ratio	Nm3/MT	4.95	4.87	5.03	5.38
BI in C7/C9 Transalkylation Feed	mg/100g	75.86	81.26	74.90	65.93
Benzene Loss	Mole%	0.06	0.02	0.03	0.08
Toluene Loss	Mole%	0.03	0.03	0.04	0.03
Xylene Loss	Mole%	0.00	0.00	0.00	0.00

Test 2: Increase of RIT from 72°C to 77°C results in increase of OC5 conversion from 82.76 to 85.80 mol% as shown in table 5.2 and Test 2 in figure 5.20. The OC6 and OC7 conversion are increased but the highest conversion is OC5, while the lowest conversion is OC7 as same as previous experiment.

Reactor different temperature is slightly increased from 3.5°C to 3.66°C according to higher reaction severity.

H2:HC ratio is increased from 4.91 to 5.7 Nm^3/MT of fresh feed as shown in table 5.2 and Test 2 in figure 5.22. The higher hydrogenation reaction is required more hydrogen to hydrogenate olefin species in reactor charge.

Bromine index in C7/C9 Transalkylation unit is significantly decreased from 72.2 to 40.25 mg/100g sample as shown in table 5.2 and test 2 in figure 5.23. The decreasing of BI is from the higher OC7 conversion.

The benzene loss is increased from 0.05 to 0.08 mol% due to higher hydrogenation severity as shown in table 5.2 and Test 2 in figure 5.24 while toluene and xylene loss are maintained as same as previous experiment.

Table 5.2 Result of RIT increasing from 72°C to 77°C at constant reactor pressure and LHSV.

Parameter	**Unit**	**Test 2**				
RIT	°C	71.95	73.63	74.95	75.57	76.95
OC5 Conversion	Mole%	82.76	85.19	85.56	84.80	85.80
OC6 Conversion	Mole%	79.07	80.95	80.26	79.12	80.00
OC7 Conversion	Mole%	62.86	63.89	62.54	63.82	63.64
Total OC Conversion	Mole%	74.77	76.19	75.02	74.83	76.47
Reactor ΔT	°C	3.50	3.58	3.58	3.61	3.66
H2:HC ratio	Nm3/MT	4.91	5.05	5.40	5.52	5.70
BI in C7/C9 Transalkylation Feed	mg/100g	72.21	61.16	53.74	46.31	40.25
Benzene Loss	Mole%	0.05	0.05	0.05	0.03	0.08
Toluene Loss	Mole%	0.04	0.04	0.04	0.03	0.03
Xylene Loss	Mole%	0.00	0.00	0.00	0.00	0.00

Test 3: According to OC7 conversion is decreased to 55 mole% that is effect from catalyst deactivated, BI in C7/C9 Transalkylation unit feed is increased to 100 mg/100g sample as shown in Test 3 of figure 5.20 and 5.23. The Transalkylation unit feed specification is controlled less than 150 mg/100g sample. The catalyst is decided to be regenerated to ensure that it can be regenerated as supplier guarantee.

Although the olefin conversion is rather low but RIT still does not reach the end of run condition at 110°C of effluent. RIT is allowed to increase as much to 100°C as shown in Test 3 to utilize the catalyst before regeneration.

Test 3: Increase of RIT from 78°C to 100°C results in increase of OC5 conversion from 83.61 to 90.32 mol%, OC6 conversion is increased from 78.26 to 89.8 mole%, and OC7 conversion is increased from 59.88 to 76.92 mole% as shown in table 5.3 and Test 3 in figure 5.20. Reactor difference temperature is increased from 3.74°C to 4.46°C according to higher reaction severity.

H2:HC ratio is increased from 5.29 to 6.25 Nm^3/MT of fresh feed as shown in table 5.3 and Test 3 in figure 5.22.

Bromine index in C7/C9 Transalkylation unit is significantly decreased from 94.69 to 88.05 mg/100g sample as shown in table 5.3 and Test 3 in figure 5.23. The decreasing of BI is from the higher OC7 conversion.

The benzene loss is increased from 0.02 to 0.24 mol%, toluene loss is increased from 0.04 to 0.1 mole% due to higher hydrogenation severity while xylene loss is still maintained.

Table 5.3 Result of RIT increasing from 78°C to 100°C at constant reactor pressure and LHSV.

Parameter	Unit	Test 3					
RIT	°C	78.05	81.00	87.25	92.89	98.37	100.00
OC5 Conversion	Mole%	83.61	82.76	83.33	86.21	89.66	90.32
OC6 Conversion	Mole%	78.26	78.72	81.25	84.78	86.00	89.80
OC7 Conversion	Mole%	59.88	60.61	63.64	67.65	70.00	76.92
Total OC Conversion	Mole%	74.89	74.77	76.11	80.18	81.82	85.95
Reactor ΔT	°C	3.74	3.93	4.39	4.36	4.44	4.46
H2:HC ratio	Nm3/MT	5.29	5.50	5.74	5.60	5.50	6.25
BI in C7/C9 Transalkylation							
Feed	mg/100g	94.69	80.37	66.05	89.82	87.08	88.05
Benzene Loss	Mole%	0.06	0.06	0.08	0.10	0.11	0.24
Toluene Loss	Mole%	0.04	0.04	0.03	0.05	0.07	0.10
Xylene Loss	Mole%	0.00	0.00	0.00	0.00	0.00	0.00

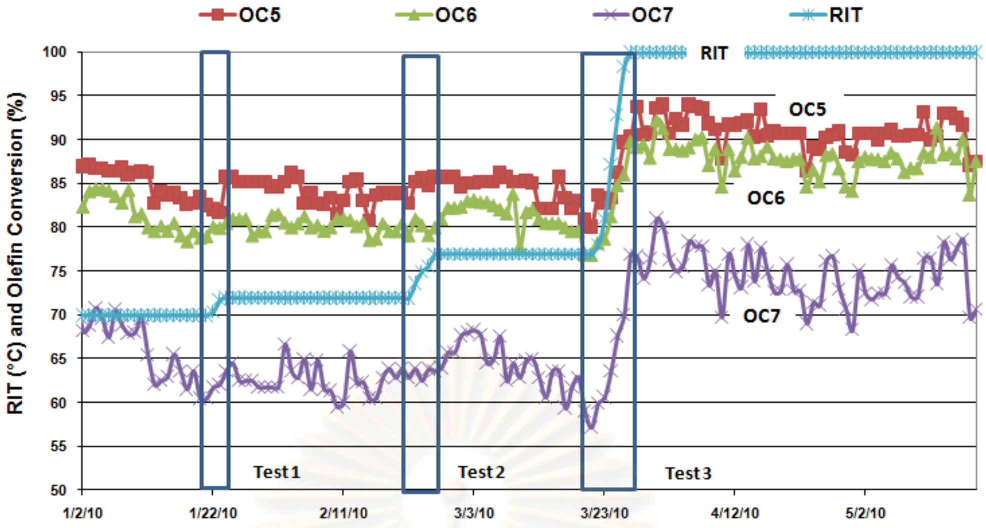


Figure 5.20 Reactor inlet temperature and olefin conversion at constant reactor pressure and LHSV.

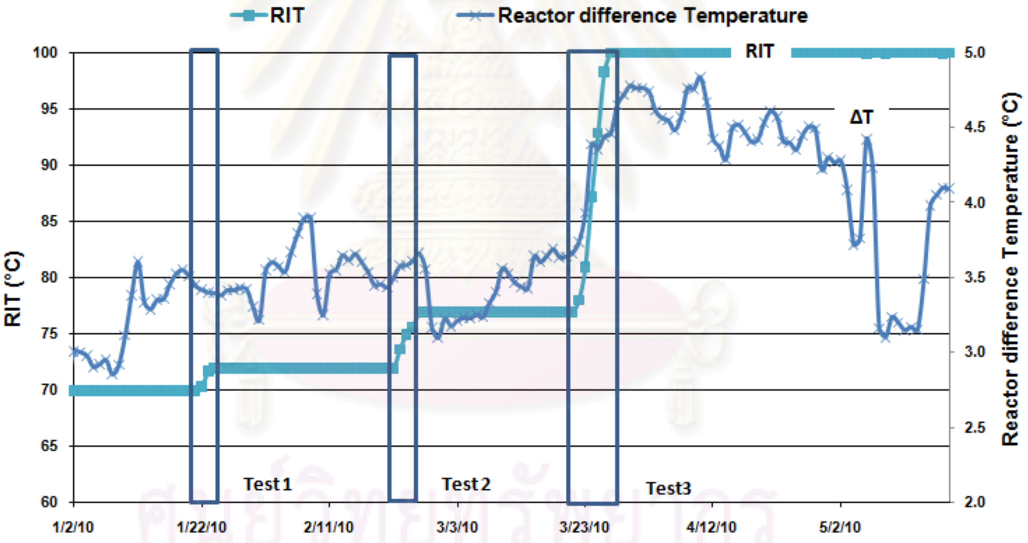


Figure 5.21 Reactor inlet temperature and reactor difference temperature at constant reactor pressure and LHSV.

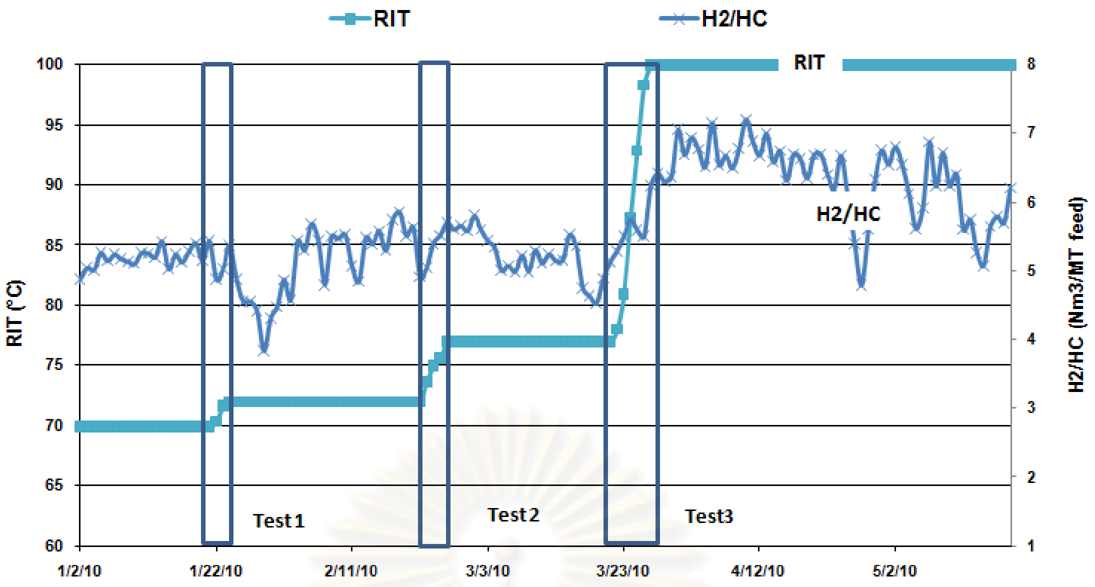


Figure 5.22 Reactor inlet temperature and H2:HC ratio at constant reactor pressure and LHSV.

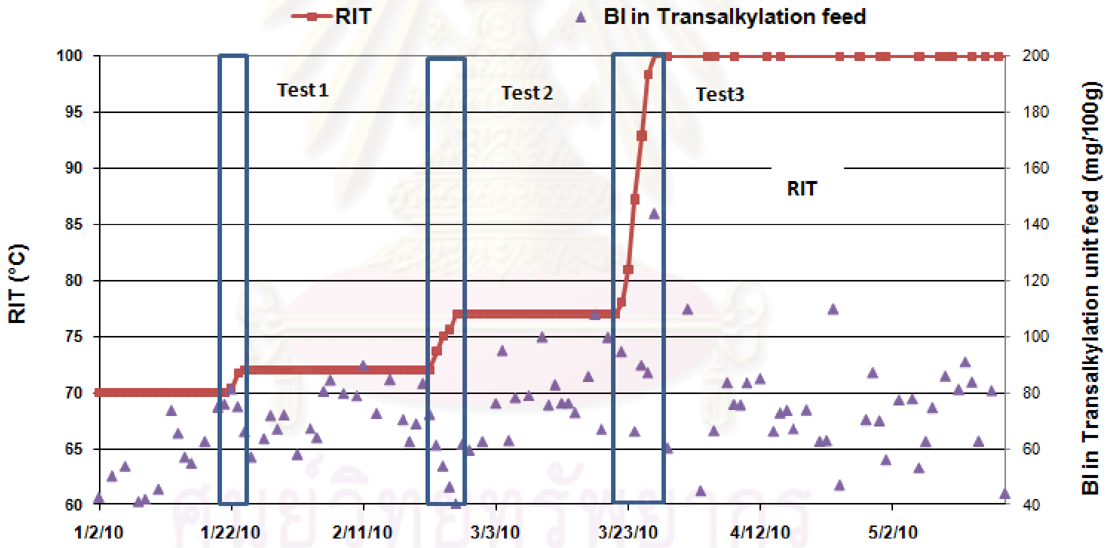


Figure 5.23 Reactor inlet temperature and BI in C7/C9 Transalkyation unit feed at constant reactor pressure and LHSV.

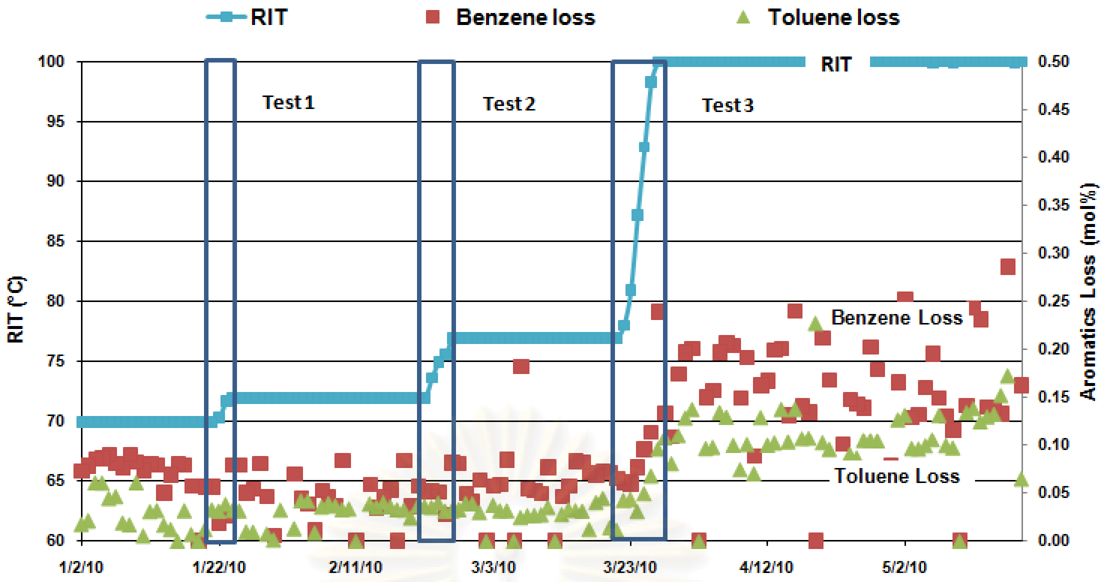


Figure 5.24 Reactor inlet temperature and aromatics loss at constant reactor pressure and LHSV.

As result of experiment, running at the higher RIT leads to higher olefin OC5, OC6 and OC7 conversion. The higher reaction severity causes higher reactor difference temperature and consumed more hydrogen. Although increase of RIT accelerates the hydrogenation reaction, but the excess RIT is affected to higher aromatics loss also.

The reactor should be operated at lowest temperature, which still makes the product quality acceptable. This should be the operating goal because excess temperature cause of more aromatics loss and increase the potential of catalyst deactivation rate.

5.3.2 Effect of Reactor Pressure

The reactor pressure is increased from 22 barg to 25 barg. Olefin conversion is not improved as expectation as shown in figure 5.25. Theoretically, higher pressure leads to higher solubility of the hydrogen in the process liquid so the hydrogenation severity should be increased. Increases 3 barg of pressure may not be sufficient to observe the catalyst activity improvement. Increases pressure is affected on higher hydrogen gas control valve opening; the valve opening is increased from 55 to 80% which is rather high comparing with normal operation, so the pressure should not increase more to maintain the controllability of valve in case the process is more required hydrogen.

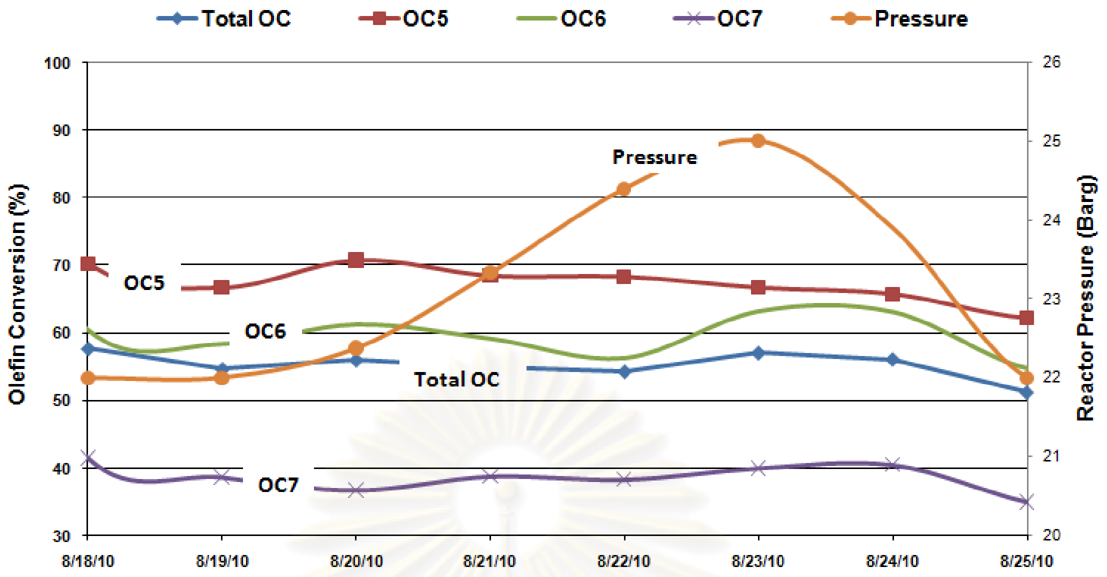


Figure 5.25 Reactor pressure and olefin conversion at constant RIT and LHSV.

5.3.3 Effect of Liquid Hourly Space Velocity (LHSV)

Decrease of LHSV results in slight increase of OC5 and OC6 conversion, while OC7 conversion is rather fluctuating as shown in figure 5.26. Benzene loss is increased from 0.07 to 0.085 mole% while toluene is maintained as shown in figure 5.27. Lower LHSV leads higher residence time in reactor, but lower selectivity which shows the increased of benzene loss.

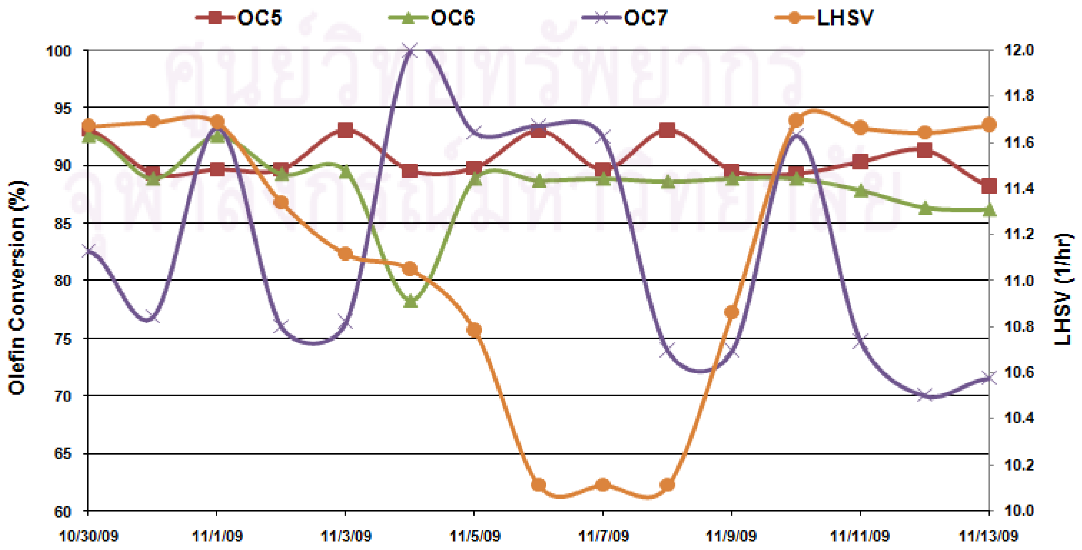


Figure 5.26 Decrease of LHSV and olefin conversion at constant RIT and pressure.

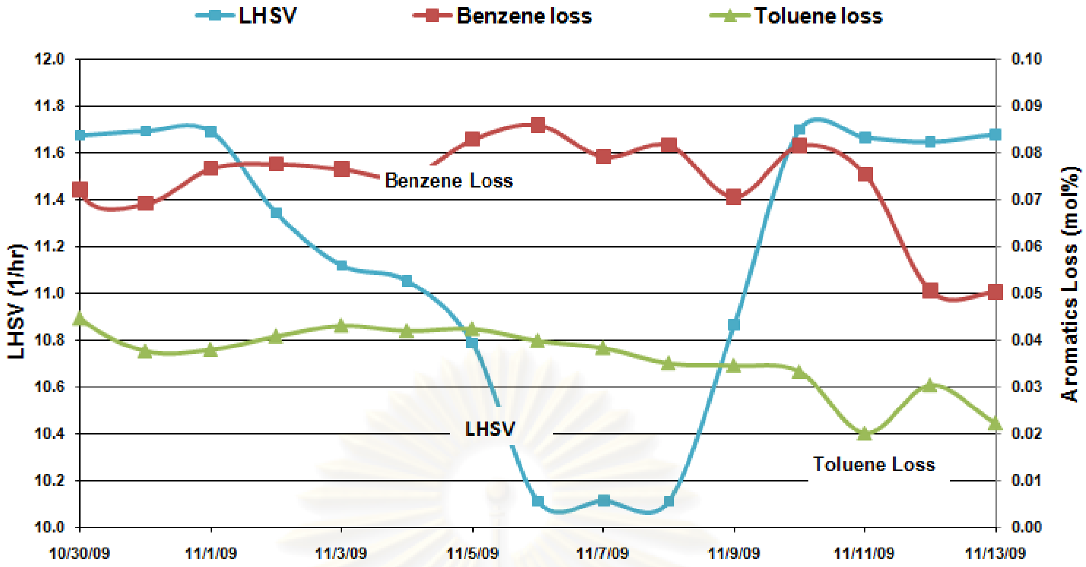


Figure 5.27 Decrease of LHSV and aromatics loss at constant RIT and pressure.

Increase of LHSV causes decreases in OC5, OC6 and OC7 conversion as shown in figure 5.28. Benzene and toluene loss are decreased from 0.08 mole% to no loss as shown in figure 5.29. Higher LHSV leads to reduce of residence time in reactor.

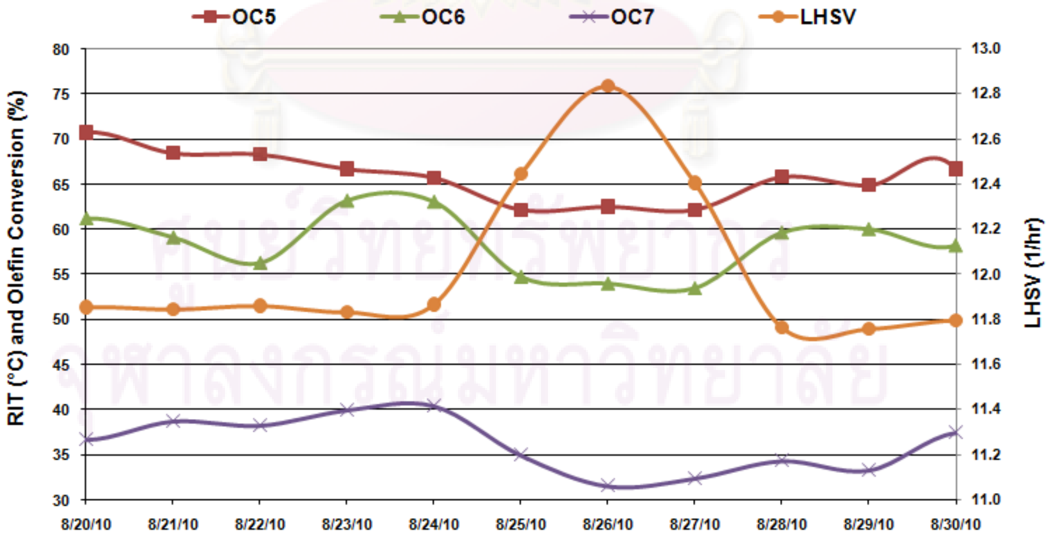


Figure 5.28 Increase of LHSV and olefin conversion at constant RIT and pressure.

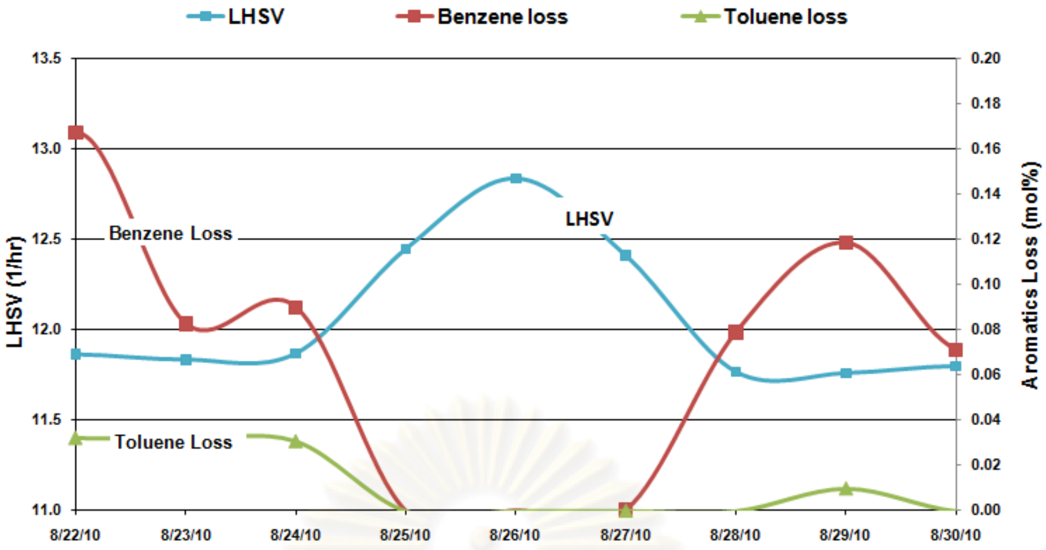


Figure 5.29 Increase of LHSV and aromatics loss at constant RIT and pressure.

Refer to the experiment result of LHSV adjustment; it should not be adjusted during normal operation. A recycle of product is used to maintain a high velocity through the catalyst bed. Normally, the WHSV through the beds is 11.77/hr. Reduction in WHSV leads to poor selectivity and additional aromatic saturation.

5.3.4 Effect of Hydrogen to Hydrocarbon Ratio (H_2:HC)

As result of experiment, running at higher hydrogenation reaction severity is required more H_2:HC ratio as shown in figure 5.22. To maximize the catalyst performance, the H_2:HC ratio should be maximized while the aromatics loss is not higher than control value. Especially, start of run condition because the reaction severity is very high.

5.4 Process Control Improvement

The original control of hydrogen make up gas flow rate to olefin hydrogenation reactor is a basic regulatory controller. The set point of H_2:HC ratio is daily calculated and manual input the set point value by panel operator. This method is suitable for stable olefin concentration in reactor charge. In case the olefin concentration in charge is frequently changed, the set point is not easy to control to meet the stoichiometry of hydrogen consumption. For the same result, Panel operator needs to control the reactor level by trial the set point to maintain interface level of reactor on top section between 20-80%, that is ensure the hydrogen consumption is proper for the reaction requirement. If reactor level more than 100% , result of insufficient H_2. Affect to reactor liquid full. If level less than 0%, result of excess H_2. Affect to reactor dry. Both of results are leading to higher olefin content in feed of downstream process such as C7/C9 Transalkylation and PX-Production unit. Figure 5.30 is shown the fluctuation of reactor level control by manual input setpoint of H_2:HC ratio control.

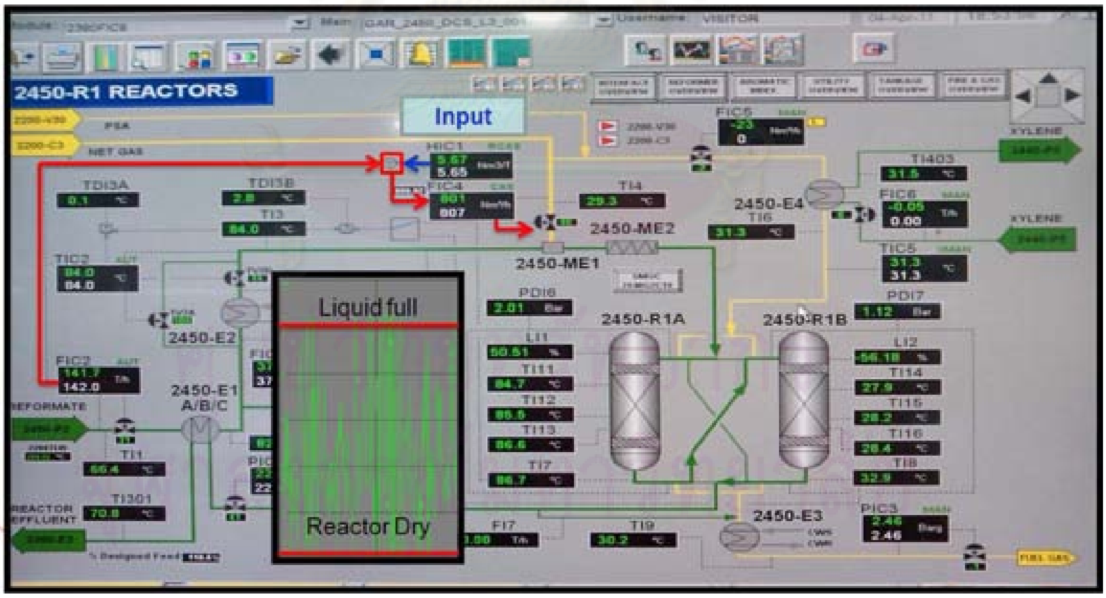


Figure 5.30 The Original process control for olefin hydrogenation process.

The advance process control was applied to control the H_2:HC ratio by using reactor level control instead of manual input the set point. The reactor level is significantly improved as shown in figure 5.31. As the result of improvement, the reactor will not risk to liquid full or reactor dry due to improper H_2:HC ratio control. The hydrogenation reaction is maximized the performance all the time.

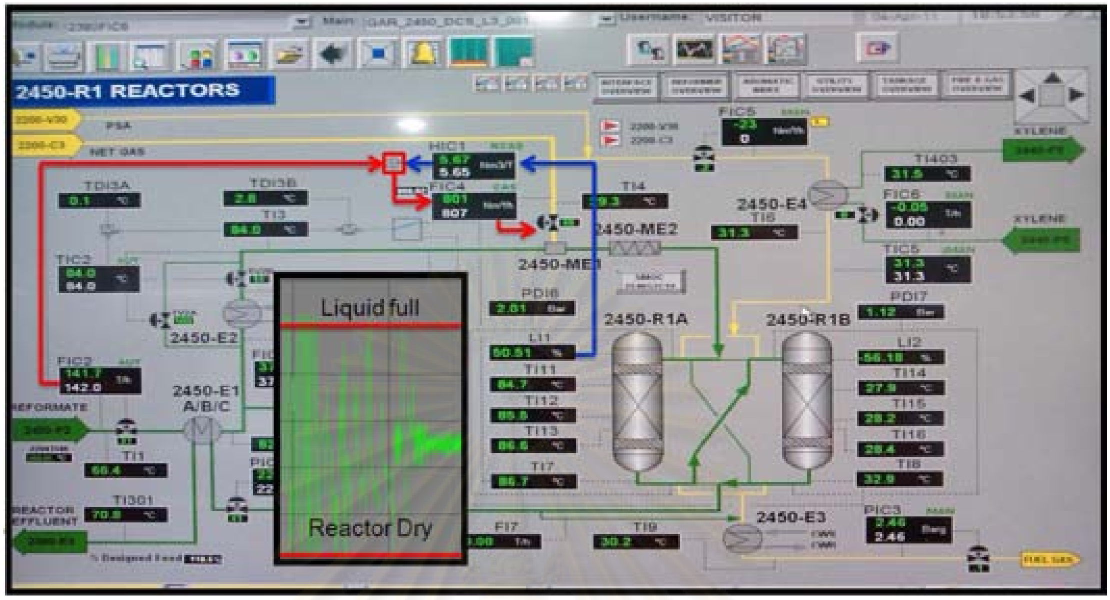


Figure 5.31 The advance process control for olefin hydrogenation process.

5.5 Catalyst Regeneration

When the catalyst in an Olefin Hydrogenation reactor has become deactivated by polymer deposition or by temporary poisons, the catalyst can be partially restored to fresh using regeneration. For the most part, regeneration physically desorbs contaminants such as H_2S, organic sulfur, oxygenates, and organic heavies. The hydrogen used for the strip must be 99.9% purity or electrolytic grade at a GHSV of 120; equivalent a flow rate of 4400 Nm^3/hr, 300°C with 48 hours holding.

Before the reactor A was regenerated, BI conversion is around 60 wt% as shown in figure 5.30. Reactor B is a single serviced during the reactor A is regenerated. For the reactor B, the BI conversion is around 80 -95 wt% that means the nitrogen preservation for one year is efficient.

During the regeneration some of liquid hydrocarbon was found after regeneration gas cooler (Figure 1.2). The purge gas is analyzed for the H_2S, HCl, and NH_3 by draeger tube. Only HCl is found around 50-100 ppm vol that mean the chloride is temporary absorbed on catalyst surface while H_2S and NH_3 are not found.

When the regeneration activity is completed, reactor A is serviced as lead and reactor B is lag at start of run temperature °C4.5 BI conversion of reactor A is rapidly decreased from 90 to 70 wt% within 20 days. At the same time BI conversion in reactor B is rapidly increased from 2 to 15 wt% because unconverted olefin in outlet lead stream is hydrogenated in reactor B. After the reactor A is operated in single bed mode, BI conversion is slightly decreased and maintained around 50 -55 wt% as shown in Figure 5.30.

According to experimental result the in situ regeneration is not efficient because of catalyst activity is not recovery. The possible causes may come from the lower required temperature of decoking, poor distribution of hot hydrogen flow, and sulfur poison is not removed. Catalyst activity is decreased until close to before regeneration condition within 20 days. However, the benefit that we can take is operating temperature. The catalyst can be operated at lower temperature than before.

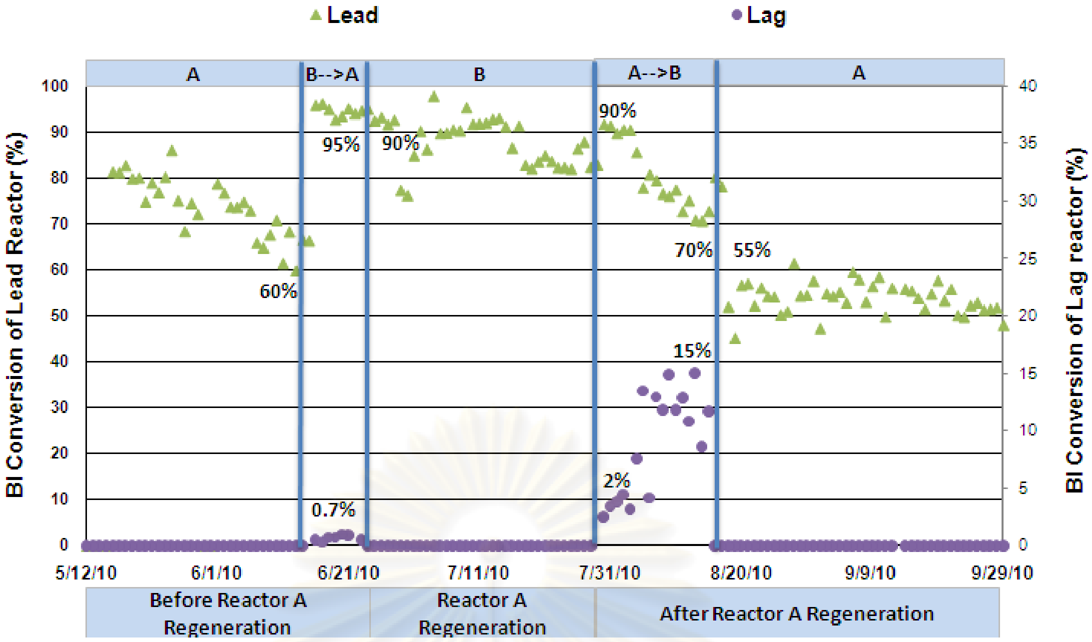


Figure 5.32 BI conversion of lead and lag reactor.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

In this chapter, section 6.1 provides the conclusions obtained from the experimental results Olefin hydrogenation process improvement and aromatics loss minimization in BTX production industry. Additionally, recommendations for further study are given in section 6.2.

6.1 Conclusions

The lighter olefin and aromatic species are easier to hydrogenate than heavier. Olefin C7 in effluent stream is a major effect on amount of bromine index in C7/C9 Transalkylation feed, while the bromine index in para-Xylene production unit is related with xylene column bottom temperature control more than the olefin hydrogenation catalyst activity.

The olefin hydrogenation process can be operated in the single bed operation to improve the plant reliability in the event that the catalyst regeneration is not efficient or catalyst deactivation in both reactors at the same time. This methodology can be applied without any impact to the downstream processes such the C 7/C9 Tranalkylation unit and *para*-Xylene production unit feed. The single bed operation also minimizes the aromatic loss from the side reactions resulting in the increase in benzene and xylene production and return benefit around 0.43 million US$ per year.

As the catalyst ages, the temperature of the reactor needs to be increased to maintain the catalyst activity. Higher temperatures cause more hydrogenation of olefin and aromatics. As the result, running at the lowest temperature, which still makes the product quality acceptable should be the operating goal.

The liquid hourly space velocity should be maintained at original design 11.72 hr^{-1}. A decrease of LHSV results in lower catalyst selectivity that leads to higher aromatics loss, while higher LHSV leads to lower activity. The reactor pressure should be controlled at original design 22 barg to maintain in the system consistent with the operation of the upstream equipment.

The advance process control is significantly improve the H_2:HC ration control.

The in situ regeneration is not efficient for existing equipment and regeneration condition. Catalyst activity is back to before regeneration condition within 20 days, but reactor inlet temperature can be operated at start of run condition.

6.2 Recommendations

1. The ex situ regeneration should to be study to minimize the operating cost due to the catalyst price is very expensive.
2. For the future project "Install olefin Hydrogenation Process for Aromatics I" should be study the possibility of in situ regeneration and review the equipment design.

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APPENDICS

APPENDIX A

CALCULATION METHOD

Olefin Conversion

$$\text{OC conversion (mole\%)} = \frac{Mole\ of\ OCin - Mole\ of\ OCout}{Mole\ of\ OCin} \times 100$$

Liquid Hourly Space velocity (LHSV)

$$\text{LHSV } (\frac{1}{\text{hr}}) = \frac{Liquid\ charge\ flow\ rate\ (\frac{m3}{hr})}{Catalyst\ volume\ (m3)}$$

Hydrogen-to-Hydrocarbon Ratio (H2:HC)

$$H2{:}HC\ (\frac{Nm3}{MT}) = \frac{Hydrogen\ gas\ flow\ rate\ (Nm3/hr)}{Fresh\ feed\ floe\ rate\ (MT)}$$

Hydrogen-to-Hydrocarbon Mole Ratio (H2:HC)

$$H2{:}HC = \frac{Hydrogen\ gas\ flow\ rate\ \left(\frac{Nm3}{hr}\right) \times Mole\ fraction\ hydrogen}{22.414(359) \times Fresh\ feed\ flow\ rate\ \left(\frac{kg}{hr}\right) \times \frac{1}{Avg.MW\ of\ fresh\ feed}}$$

Aromatics Loss

$$\text{Bz Loss} = \frac{Mole\ of\ cyclohexane\ in\ effluent - Mole\ of\ cyclohexane\ in\ fresh\ feed}{Mole\ of\ benzene\ in\ fresh\ feed}$$

$$\text{Toluene Loss} = \frac{Mole\ of\ methylcyclohexane\ in\ effluent - Mole\ of\ methylcyclohexane\ in\ fresh\ feed}{Mole\ of\ toluene\ in\ fresh\ feed}$$

$$\text{Xylene Loss} = \frac{Mole\ of\ dimethylcyclohexane\ in\ effluent - Mole\ of\ dimethylcyclohexane\ in\ fresh\ feed}{Mole\ of\ xylenes\ in\ fresh\ feed}$$

APPENDIX B

ANALYTICAL PROCEDURES

1. Fresh Feed

The relative density of the feed is used in the calculation of the flow rate of the feed. ASTM D 4052 is a method using a digital density meter that measures the frequency of a vibrating tube. The frequency of the vibration and the volume of the tube are used to determine the density of the fluid. Other methods are available that produce equivalent results.

UOP 744 or ASTM D 2360, Aromatics in Hydrocarbons by Gas Chromatography, will give the breakdown of the aromatics in the feed stream. The majority of the feed will be aromatics. Normally for the charge to the Olefin Hydrogenation unit, this analysis is not overly useful as gross changes in the composition of aromatics across the unit are not expected. These methods provide a backup for the non-aromatic production across the unit. In the most technically accurate definition, it is not certain that benzene measured with this technique will be accurate as some of the non-aromatics normally found in the aromatics streams can co-elute with the benzene and elevate the benzene concentration erroneously. In the feed of the Olefin Hydrogenation unit the non-aromatic material may be light enough that this interference will not exist.

UOP 690 is used to measure octane and lower boiling hydrocarbons in olefin-free gasoline. ASTM D 5134 is Standard Test Method for Detailed Analysis of Petroleum Naphthas through n-Nonane by Capillary Gas Chromatography. Either of these methods can be used to track the non-aromatic species of interest. Cyclohexane is followed to determine the hydrogenation of benzene. Methyl cyclohexane will indicate the hydrogenation of toluene. Dimethyl cyclohexane and ethyl cyclohexane are indicators of C8 aromatic hydrogenation.

UOP 304, ASTM D 1492 or D 5776 can measure bromine index. High concentrations of bromine reactive species are undesirable for some of the downstream units and products and as such the Olefin Hydrogenation unit unit is designed to hydrogenate these species. In each of these methods bromination of the double bonds of the olefins and alkenyl-benzene is measured by titration. ASTM D 848 is used for acid wash color, which has been generally superseded by bromine index. It is worth noting no good correlation exists between Bromine index and acid wash color.

Chlorides in the feed are measured by UOP 395. Both organic and inorganic chlorides are measured. Chlorides generally do not cause a problem for the catalyst but high levels may promote polymerization which could lead to the permanent deactivation of the catalyst.

ASTM D 5453, D 6212, D 6313, D 6428, and D4045 are several methods available for determining sulfur. As the catalyst deactivates by the adsorption of sulfur, the better the sulfur entering and exiting the unit is tracked the easier it should be to predict the deactivation rate of the catalyst. Most of these methods may quantify the sulfur to below 1 wt ppm. In most of these methods sulfur compounds are converted to either H2S or SO2 which are subsequently detected.

Nitrogen in the charge is measured by ASTM D 6069 or D 6366. Some adsorption of nitrogen can occur but it is not considered the prime mechanism for catalyst deactivation.

Basic nitrogen in the charge is measured by UOP 313. Basic nitrogen is a very sensitive measure of nitrogen.

UOP 906 is used to measure trace metal contamination of the charge. Nickel metal is the catalyst in the UORP unit. Contamination of the nickel by other metals could render the nickel inactive.

Any unusual color should also be noted. Color is a good indication of contamination of small quantities of very heavy material that will not appear in GC analysis or in the distillation.

Finally visual appearance is used to judge if there is any gross contamination of the unit. If debris or cloudiness is seen in the sample the feed must be further examined to determine the nature of the contamination.

2. Hydrogen Gas

Purity is most important here. The best performance in the unit corresponds to the highest solubility of the gas in the reactor. For given hydrogen ratio required for the operation higher hydrogen purity will reduce the quantity of other gases that need to dissolve in the system. It is also important to monitor the hydrogen gas for possible catalyst contaminants. The detailed compositions for these streams can be used to calculate stream gravity that can be used in mass balance calculations and the calculation of the hydrogen to hydrocarbon molar ratio.
Composition is measured by UOP 539, which is a GC method. The results of UOP 539 can also be used to calculate the gravity of the streams by using the method outlined in UOP 948.

H_2S is strongly adsorbed to the nickel and may not completely desorb during regeneration. Normally the quantity of H_2S in the hydrogen gas stream is low enough that the accumulation of H_2S on the catalyst is not significant. Normally this is measured at the hydrogen gas source but should be reported with the data from this unit. H2S is normally measured using a hand held detection tube. Care has to be taken to avoid getting erroneously high or low readings. Since the detection tubes are designed to read the atmosphere of an enclosed space the normal method for using them for a process stream is to create an enclosed space around the sample point typically with a plastic bag or a similar device. The pump and the tube are used inside the enclosed space after it is purged with the sample gas.

HCl can be detrimental as it can promote polymerization on the catalyst. This is measured in a similar fashion to H2S by the use of gas detection tubes.

Water is another contaminant that may attenuate the catalyst function but this is not expected. Moisture in the makeup gas and recycle gas is measured using gas detection tubes also. This is not a normal component, but checks should be made occasionally.

Ammonia in the hydrogen gas can react with HCl and cause fouling. Ammonia in the makeup gas is measured using gas detection tubes. This is not a normal component but checks should be made occasionally.

The impact of CO and CO2 can strongly adsorb to the catalyst and compete with the hydrocarbons which will increase the required temperature. UOP 603 is a method for measuring these compounds.

3. Effluent

Provisions are made to allow sampling of the liquid of the product. The product contains small quantities of very volatile components and as such this sample needs to be handled with pressurized equipment in order to get representative results. Although samples and normally collected in pressurized cylinders there are a variety of techniques for transferring a pressurized sample to the analytical instruments including pressurized syringes and sample loops. Use of non-pressurized equipment can lead to small errors.

Analysis of the product closely matches the analysis of the liquid charge.
Bromine index and the composition of the product are the normally significant analysis for the operation of the unit. Since it is the purpose of the unit to reduce the Bromine Index of the charge this is normally tracked closely. Analysis of the product composition provides information on the possible aromatic losses that can occur. An increase in non-aromatic fraction is closely followed.

Analysis of the trace contaminants may provide an indication of the rate that the catalyst is accumulating the particular poisons.

4. Regeneration Gas

Analysis of the regeneration gas is very similar to the hydrogen gas. During regeneration the quantity of gas that the catalyst is exposed to is much higher than during normal operation and as a result contamination of the gas will have a more significant impact. CO and CO2 must be limited. H2S in the regeneration gas would defeat the purpose of the regeneration.

APPENDIX C

BENEFIT CALCULATION

Basis:

- Fresh feed = 142 T/hr
- Benzene in feed 15.12 mol%
- Toluene in feed 31.16 mol%

Additional Information

- Benzene loss is decreased from 0.5 to 0.3 mol% of Benzene in fresh feed
- Toluene loss is decreased from 0.1 to 0.07 mol% of Toluene in fresh feed
- Benzene price is 1,000 USD/ton
- Toluene price is 1,300 USD/ton (equivalent with xylene)
- MW benzene is 78.11
- MW toluene is 92.14

Benzene Loss

Series Operation

Cyclohexane generate (mol%)= Bz loss (mol%) x Bz in fresh feed (mole%)
= 0.5 x 15.12
= 0.076 mol%

Mole of cyclohexane generate = mole of benzene loss
Benzene loss = 0.076 x 78.11 / 100
= 0.059 wt%
= 0.059 x 142 / 100
= 0.084 T/hr

Single Operation

Cyclohexane generate (mol%)= Bz loss (mol%) x Bz in fresh feed (mole%)
= 0.3 x 15.12
= 0.045 mol%

Mole of cyclohexane generate = mole of benzene loss
Benzene loss = 0.045 x 78.11 / 100
= 0.035 wt%
= 0.035 x 142 / 100
= 0.05 T/hr

Benzene loss reduction = 0.084-0.045
= 0.34 T/hr

Benefit = 0.034 x 24 x 365 x 1000
= **293,820** USD/year

Toluene Loss

Series Operation

Methylcyclohexane generate (mol%) = Tol loss (mol%) x Tol in fresh feed (mole%)
= 0.1 x 31.16
= 0.031 mol%

Mole of cyclohexane generate = mole of benzene loss
Benzene loss = 0.031 x 92.14 / 100
= 0.029 wt%
= 0.029 x 142 / 100
= 0.041 T/hr

Single Operation

Methlycyclohexane generate (mol%) = Tol loss (mol%) x Tol in fresh feed (mole%)
= 0.07 x 31.16
= 0.022 mol%

Mole of methylcyclohexane generate = mole of benzene loss
Benzene loss = 0.022 x 92.14 / 100
= 0.02 wt%
= 0.02 x 142 / 100
= 0.029 T/hr

Toluene loss reduction = 0.041-0.029
= 0.012 T/hr

Benefit = 0.012 x 24 x 365 x 1300
= **139,284** USD/year

Total benefit = 293,820 + 139,284
= **433,104** USD/year

VITA

Mr. Tawath intorn was born on March 3rd, 1984 in Samutprakan province, Thailand. He finished high school from Satree Samutprakan School in 2002. He received the bachelor's degree of Chemical Engineering from Faculty of Engineering, Suranaree University of Technology in 2006. He works at PTT Aromatics and Refining Public Company Limited in 2007. He started his master's study at Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University in June, 2009.

LIST OF PUBLICATIONS

Proceeding

Tawath Intorn and Bunjerd Jongsomjit, "Olefin Hydrogenation Process Reliability Improvement and Aromatic Loss Minimization in BTX Production Industry" Proceeding of the 17th Regional Symposium on Chemical Engineering, Bangkok, Thailand, November, 2010.

150 mg Br/100g sample. This is due to the unconverted olefin C7 molecules and their same boiling point with aromatic C7 molecules will be presented in the C7/C9 tranalkylation charge.

For the *para*-xylene production unit, results of BI in unit charge are normally less than 5 mg Br/100g sample in both of operating mode. BI in charge will be absorbed in the molecular sieve adsorbent of this process. The design of unit charge quality allows less than 20 mg Br/100g sample. However, the single and series operation modes have no significant effect to *para*-xylene production unit because the quantity of olefin C8 molecules in charge of the olefin hydrogenation process is very small so the olefin C8 species do not significant change in feed of *para*-xylene production unit, although the single operation is applied.

Most of the unconverted olefin present in the raffinate stream, which is normally the non aromatic species from the extraction unit. The BI is increased from 1,000-1,800 to 1,500-3,000 mg Br/100g sample. In practice, olefin in raffinate can be sold in the light naphtha's price. The benzene form extraction unit is sent to the benzene fractionation to be purified before run down to product tank, BI in benzene product slightly increases from 1-3 mg Br/100g sample to 2-4 mg Br/100g sample which still meets the purchasing specification that is less than 10 mg Br/100 g sample.

Conclusions

The olefin hydrogenation process can be operated in the single bed operation to improve the plant reliability in the event that the catalyst regeneration is not efficient or catalyst deactivation in both reactors at the same time. This methodology can be applied without any impact to the downstream processes such the benzene production unit, C7/C9 tranalkylation unit and *para*-xylene production unit. The single bed operation also minimizes the aromatic loss from the side reactions resulting in the increase in benzene and xylene production. The results in current work can be applied to the subsidiaries aromatic plant in the future.

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