SIMULATION STUDY OF REACTIVE DISTILLATION USING ASPEN PLUS FOR THE PRODUCTION OF MTBE

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ABSTRACT

Methyl tertiary butyl ether (MTBE) is a chemical compound that widely used as an octane enhancer in gasoline blending in order to improve hydrocarbon efficiency. It has a low vapor pressure and can be blended with other fuels without phase separation. It has the desirable octane characteristics. In the oxygenate group, MTBE is attractive for a variety of technical reasons. MTBE is produced via direct addition of methanol to isobutylene using sulphonated ion exchange resin as catalysts. There are several of ways that can be used to produce MTBE such as conventional method. This process involves reactor and separate distillation column units. Another method for the production of MTBE is introduced by Smith in the 1980. It is a combination of reactor and distillation column in the one system and improvement of conventional method. Main objective of this research are to develop a simulation model of reactive distillation for production of MTBE using Aspen Plus as a modeling platform. This research also study on the effect that affected the design and operating condition of the column. It started with finding the mathematical models that suitable for the simulation and substitute in the simulation software which is ASPEN Plus. Analysis and observation has been performed after the simulation converges and complete. Based on the result that obtained from simulation, main factors that can affect the conversion in MTBE production was majorly from Isobutylene condition. Manipulation of the inlet temperature in the both stream does not affect the condition of the column. Changes of Isobutylene feed composition contribute a lot in the increment of the conversion of methanol. Conversion of the process increase from 75.8% until 94% when feed composition of Isobutylene changing from 0.25 until 0.57.

ABSTRAK

Metal *tert*-Butil Eter (MTBE) adalah sebatian kima yang digunakan secara meluas dalam meningkatkan nilai Oktana dalam campuran petrol dalam rangka meningkatkan kecekapan pembakaran hidrokarbon. MTBE memiliki tekanan stim yang rendah dan ia dapat dicampurkan dengan bahan pembakar yang lain tanpa perbezaan fasa. Berbanding dengan semua bahan pembakar yang laen, MTBE mempunyai pelbagai kebaikan. MTBE dihasilkan melalui penambahan langsung diantara metanol dengan isobutilen menggunakan resin pertukaran ion sulfonasi sebagai pemangkin. Penghasilan MTBE melalui cara lama melibatkan dua proses utama dalam satu pengeluaran. Ia melibatkan logi tindak balas dan unit penyulingan yang berasingan. Namun begitu, pada tahun 1980, Smith telah menghasilkan cara baru untuk pengeluaran MTBE. Ia adalah kombinasi dari reaktor dan kolum penyulingan dan penambah-baikan terhadap kaedah konvensional. Tujuan utama penyelidikan ini adalah untuk membangunkan model simulasi bagi kolum penyulingan tindak balas untuk pengeluaran MTBE menggunakan Aspen Plus sebagai landasan. Penyelidikan ini juga meliputi kajian terhadap kesan yang dapat mempengaruhi keadaan operasi sesuatu kolum. Kajian bermula dengan mencari model matematik yang sesuai untuk simulasi dan akan dimasukan ke dalam perisian simulasi yang ASPEN Plus. Analisis dan pemerhatian akan dilakukan setelah model simulasi lengkap dan beroperasi. Berdasarkan keputusan yang diperolehi, faktor utama yang dapat mempengaruhi tindak balas dalam penghasilan MTBE adalah kebanyakanya daripada keadaan Isobutilen. Manipulasi terhadap suhu pada aliran masuk untuk kedua-dua komponen tidak mempengaruhi keadaan Kolum penyulingan bertindakbalas. Komposisi Isobutilen dalam aliran kemasukan menyumbang kepada peningkantan terhadap penukaran methanol. Proses penukaran tindak balas peningkatan daripada 75.8% sehingga 94% ketika komposisi Isobutylene pada kemasukan perubahan dari 0.25 sehingga 0.57.

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a,b,c	Order of reaction of species A,B and C respectively
ΔH_A	Heat of adsorption of methanol, J/mol
ΔH_C	Heat of adsorption of MTBE, J/mol
ΔH_R	Exothermic reaction of component, Btu/lb-mole
C_B	Isobutylene concentration, mole/l
C_M	Methanol concentration, mole/l
r_b	Rate of reaction
K_1	Reaction rate constant for forward reaction
K_2	Reaction rate constant for backward reaction
A_1	Arrhenius frequency factor for forward reaction
A_2	Arrhenius frequency factor for backward reaction
E_1	Activation energy for forward reaction, J/mol
E_2	Activation energy for backward reaction, J/mol
R	Gas constant, 8.314 J/mol.K
T	Temperature, K
P	Pressure, psig

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND RESEARCH

According to statistics that has been provided from U.S Energy Information Administration in 2007 annual report, rapid increasing of demand for petroleum and gas production. World demand for oil is projected to increase 37% over 2006 levels by 2030. It is because the oil is widely used in the many of industries such as manufacturing, transportation, shipment, polymers and others.

Transportation consumes largest proportion of the energy and increase years by years. This growth has largely come from new demand for personal-use vehicles powered by internal combustion engines. Car and truck are predicted to cause the highest demand in the transportation approaching to 75%. In other to reduce the consumption of fuel as well as improvement of gas produced during combustion, MTBE has been used as an additive in the fuel.

It is used in gasoline blending as an octane enhancer to improve hydrocarbon combustion efficiency. MTBE is produced by reaction of methanol and isobutylene in the present of catalyst. In the conventional process, separate system between reactor and separation units has been used. The technology features a two-stage reactor system of which the first reactor is operated in a recycle mode. With this method, a slight expansion of the catalyst bed is achieved which ensures very uniform concentration profiles within the reactor and can avoids hot spot formation. Undesired side reactions, such as the formation of dimethyl ether (DME) also can be minimized.

Now days, the new reactive distillation technology has been a major interest to replacing the conventional method. Reactive distillation is new invention of technology that combines the two major unit operations into one unit. It is the process whereby simultaneous chemical reaction and vapor-liquid phase separation take place in the presence of a catalyst. Reactive distillation allows the increasing in conversion far beyond expectation due to the continuous removal of reaction products from the reactive zone.

1.2 INTRODUCTION TO REACTIVE DISTILLATION

Distillation column is well known equipment that used in the chemical process for the separation system. Even after several of decades distillation still remains as major equipment in separation for processing. All around the world, maintenance, capital investment and operating cost that involves in the distillation column is the significant fraction in the chemical industries. So, improvement and revolution of the distillation operation is the greatest achievement in that can be beneficial economically.

Reactive distillation is one major step in the history of distillation to achieving these targets. Reactive distillation is processes that combine chemical reactions and physical separations into a single unit operation. These processes as a whole are not a new concept as the first patent dates back to the 1920. The initial publications dealt with homogeneous self- catalyzed reactions such as esterifications and hydrolysis and heterogeneous catalysis in reactive distillation is a more recent development in the reactive distillation. While the concept existed much earlier, the first real- world of the system implementation of reactive distillation took place in 1980s.

The relatively large amount of new interest in reactive distillation is due to the numerous advantages it has over typical distillation. It can enhanced reaction rates, increased conversion, enhanced reaction selectivity, heat integration benefits and reduced operating costs are several of the benefic in reactive distillation. All these factors contribute to the growing commercial importance of reactive distillation. However, since heat transfer, mass transfer, and reactions are all occurring simultaneously, the dynamics which can be exhibited by catalytic distillation columns can be considerably more complex than found in regular columns. These results in an increase in the complexity of process operations and the control structure installed to regulate the process.

Principle that used in the reactive distillation system is quite simple. A distillation column having a catalyst zone that placed in the column to carry out the desired reaction is a reactive distillation column. The catalyst that used in the process may be in the same phase as that of the reacting species or it can be in the solid phase. The feed for the process is fed either above or below the reactive zone depending upon the volatility of the components and to carry out the desired reaction. The reaction occurs mainly in the liquid phase, in the catalyst zone.

A simple example for the system that considering a reversible reaction can be used as an explanation. Consider a chemical reaction in the process is A + B↔C + D, where the boiling points of the components follow the order A, C, D and B.

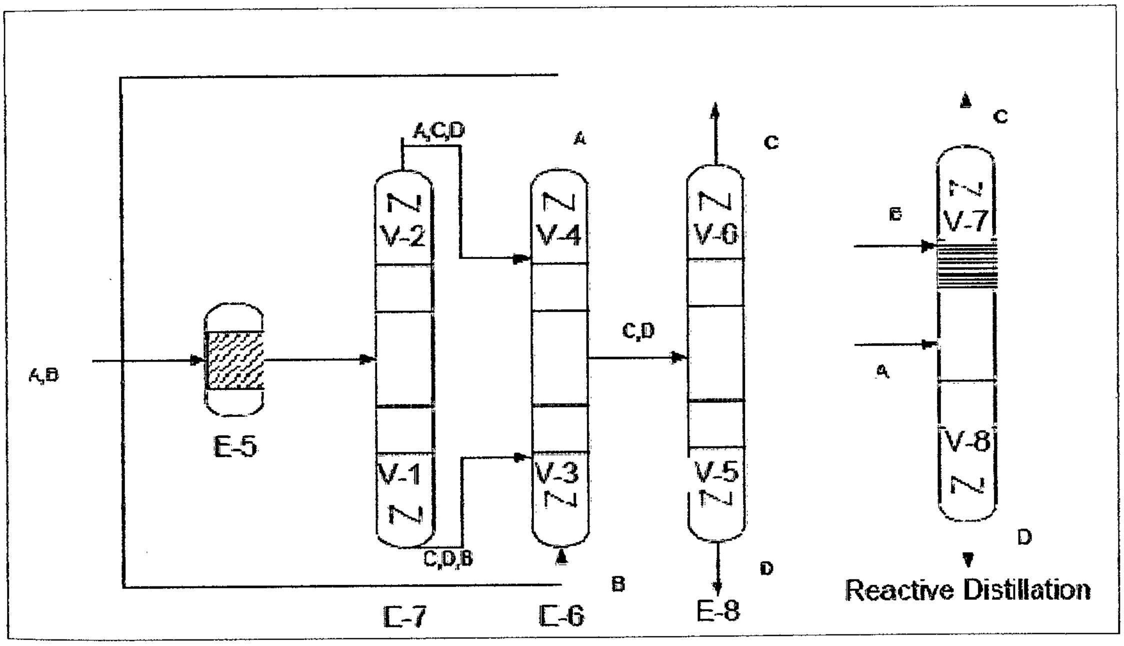

Figure 1.1: Comparison of conventional scheme and reactive distillation system.

The traditional flowsheet can be a series of distillation columns as shown in Figure 1.1 where the mixture of A and B is fed to the reactor, where the reaction takes place in the presence of a catalyst. The mixture of reactant and product is passed through a series of distillation columns and the unreacted components A and B are recycled back to the reactor. The alternative reactive distillation approach consists of a reactive section in the middle of the column. The task of the rectifying section is to recover reactant B from the product stream C. In the stripping section the reactant A is stripped from the product stream D. The relative volatility between the components has been used more effectively in the later case.

1.3 PROBLEM STATEMENT

Gasoline and diesel has been used worldwide as a main fuel source for transportation. Although recently, several of technology has been develop in order to reduce the utilization of the gasoline but demand of the source is still highest. However, the main source is reducing and combustion process of gasoline produce effect to the environment.

Several study that been done in order to improve combustion process of the gasoline. One of technique is blended with the MTBE to improve hydrocarbon efficiency. It has the desirable octane characteristics and is becoming increasingly important as stricter air pollution control measures are implemented.

Former production process of MTBE is by reaction of methanol and isobutylene in the reactor. It is followed by distillation process to separate the product. These conventional processes provide more usage of manpower, increasing in costing and energy consumption. Besides that, conventional process of the MTBE produces more several of waste from the reaction of the MTBE in the reactor.Reactive distillation is an alternative system that can reduce the problem and also can increase the production of MTBE. Reactive distillation is potentially process that can be used and process development, design and operation of system processes are highly complicated tasks.

1.4 OBJECTIVES

Several goals have been determined for this paper in order to achieve the purpose of the research title such as:-

1. To develop a simulation model of reactive distillation for production of Methyl Tertiary-Butyl Ether.
2. To study and evaluate the parameters (operation and design) to achieve highest conversion of product.
   a. Variables of inlet stages
   b. Variables of temperature inlet
   c. Variables of feed composition in the isobutylene stream

1.5 SCOPE OF STUDY

Main objectives of this research are to develop simulation model of reactive distillation using Aspen Plus system. Basic of the project is to determine whether Aspen Plus is compatible for the modeling of reactive distillation. Several scope has been determine to achieve the target of research which is

1. Modeling and simulate the reactive distillation system by using Aspen Plus 12.
2. Apply the simulation and study the effect on the parameters that has been determined.
3. Try to validate the result of the simulation with the actual data in the experiment if it is possible.

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1.6 SIGNIFICANT OF STUDY

Reactive distillation is the latest technology that has been used as a replacement to conventional system. It is provide more advantages in term of time saving and reduce cost of production. It also reduces maintenance cost of the plant and provides insight of the process. In this research, reactive distillation is used as a substitution for current technology and mainly to reduce the reduce waste and energy consumption. By simulate the system in the latest software of modeling and designing, this paper will produce a good result and can be used as a future references.

CHAPTER 2

LITERATURE REVIEW

2.1 METHYL TERTIARY BUTYL ETHER (MTBE)

Methyl Tertiary Butyl Ether (MTBE) is a chemical compound that primarily used in gasoline blending as an octane enhancer to improve hydrocarbon combustion efficiency. $C_5H_{12}O$ as a molecular formula, MTBE is volatile, flammable and colorless liquid that is immiscible with water. It has a low vapor pressure and can be blended with other fuels without phase separation *(European Fuel Oxygenates Association)*. MTBE also been used several others application such as solvent, chemical reagent and anti-knocking agent.

MTBE can be produced by addition of methanol to isobutylene in the liquid phase over an acidic catalyst consisting of sulfonated macroporous ion exchange resins. Methanol taken from natural gas and isobutylene is derived from butane obtained from crude oil.

J.R Smith registered a patent to process MTBE for Chemical Research and Licensing Company in the 1980's *(J. H. Gregor et al.1992)*. As a first person registered, he used a reactive distillation system that containing catalytic packing. The pilot plant was 76 mm in diameter. It was used to predict the operation variables of a large commercial plant.

Due the potential of the improvement design and commercial application, reactive distillation gained interest of researchers and industries. Figures 2.1 (*ACS databases CAPLUS, CHEMCATS and CHEMLIST*) show the growing interest in reactive distillation in recent years.

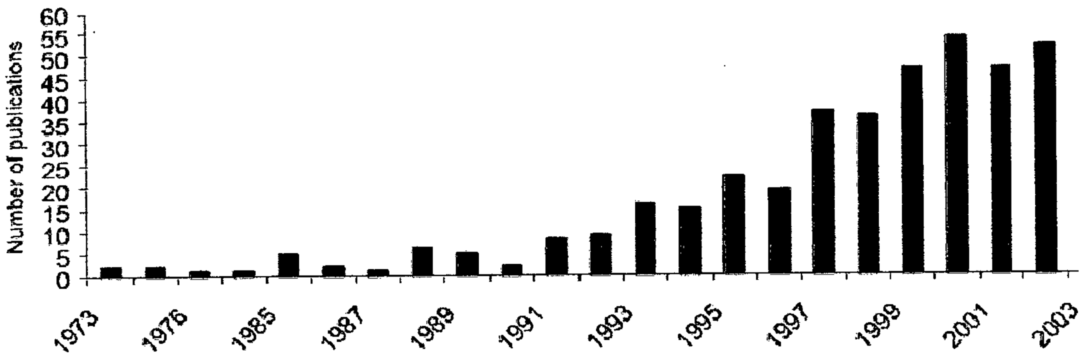

Figure 2.1: Trends of MTBE publication (1973-2003)

2.2 MTBE CHARACTERISTICS

MTBE belonging to oxygenates group. Oxygenates are hydrocarbons that contain one or more oxygen atoms. Component that also included in this group are alcohols, ethers and fuel ethanol. Oxygenates are added to vehicles fuels in order to make the burn more cleanly, thereby reduce producing of carbon monoxide. The physical properties for these components are shown in figure 2.2.

	Ethanol	MTBE	ETBE	TAME
Chemical formula	CH_3CH_2OH	$CH_3OC(CH_3)_3$	$CH_3CH_2OC(CH_3)_3$	$(CH)_3CCH_2OCH_3$
Oxygen content, % by weight	34.73	18.15	15.66	15.66
Octane, (R+M)/2	115	110	111	105
Blending vapor pressure, RVP	18	8	4	1.5

Source: National Petroleum Council, *U.S. Petroleum Refining: Meeting Requirements for Cleaner Fuels and Refineries* (Washington, DC, August 1993) Appendix L.

Figure 2.2: Typical properties of MTBE

MTBE is an excellent gasoline blending component because it contains of high octane numbers and has low volatility. It has blending properties similar to gasoline but do not exhibit undesirable properties such as azeoptrope formation, water pick-up, or phase separation. Table 2.1 shows the summarization of strength and weaknesses of the MTBE.

Table 2.1: MTBE competitive strengths and weaknesses

Strengths	Weaknesses
• High octane • Low volatility • Blending characteristics similar to gasoline • Widely accepted in marketplace by consumers and refiners • Reduces carbon monoxide and exhaust hydrocarbon emissions	• Availability of economical isobutylene feedstock's is limited • Possible methanol supply constraints Health hazard

2.3 CHEMISTRY OF MTBE

Methyl tertiary-butyl ether (MTBE) can be formed by the addition of methyl alcohol to the highly reactive double bond in isobutylene. Chemical reaction of the process as shown in the following equation

$$\underset{\text{Methanol}}{CH_3\text{-}OH} + \underset{\text{Isobutylene}}{(CH_3)_2C{=}CH_2} \leftrightarrow \underset{\text{MTBE}}{(CH_3)_3C\text{-}O\text{-}CH_3}$$

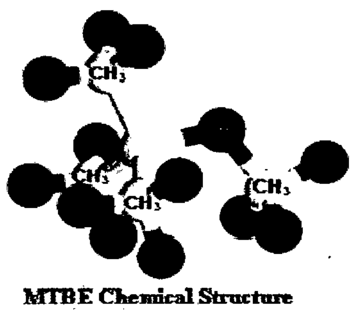

Figure 2.3: Structure of MTBE compound

Common MTBE *synthesis occurs in the liquid phase at temperature between* 40°C-100°C and 100-150 psig as an exothermic reaction with (ΔHR= -16,060 Btu/lb-mole). Reaction occurs in presence of a small amount of acidic cation exchange resin catalyst the reaction proceeds quantitatively. But, there are few reactions in industrial chemistry that demonstrate such high selectivity.

In the industries, MTBE is the intermediate process of the system. Isobutylene actually come from the previous process and not fully pure. Usually it will mix with the several chemical compounds in the butane group such as 1-butene, isobutene, propylene and several others. MTBE synthesis also produces n-butane as a side produce of the reaction.

2.3 DEMAND OF MTBE

Based on the CHEM SYSTEM (ACS Databases), demand of MTBE is increasing from year to year. MTBE is expected to grow at 4.0% annually from 1994 to 2010. In the 2000-2010 period, however, growth will slow to 1.7 % annually from 8.1 % from 1994-2000. All the data are shown on the figure 2.4.

	1990	1998	1999	2000	2001	2002	2003	2004	2005	2006	2010	Growth Rates, % per year 1990-2000	2000-2005	2005-2010
United States	4,000	12,500	13,600	13,200	12,300	10,900	8,600	5,700	2,900	-	-	12.7	(26.1)	-
Canada	25	320	320	320	320	320	256	205	102	-	-	29.0	(20.4)	-
Latin America	40	1,472	1,340	1,390	1,451	1,514	1,561	1,609	1,659	1,711	1,780	42.6	3.6	1.4
Japan	-	345	350	360	368	375	383	392	400	-	-	-	2.1	-
Other Asia	301	2,139	2,365	2,515	2,630	2,728	2,938	3,121	3,228	3,050	3,269	23.6	5.1	0.3
Mideast/Africa	70	270	323	440	793	1,028	1,153	1,199	1,215	1,232	1,306	20.2	22.5	1.5
W. Europe	2,350	2,691	2,907	3,255	3,705	3,881	4,057	4,463	4,909	4,933	5,033	3.3	8.6	0.5
E. Europe/FSU	164	594	609	624	658	694	732	772	807	843	1,006	14.3	5.3	4.5
TOTAL	6,950	20,332	21,814	22,105	22,227	21,440	19,680	17,461	15,221	11,770	12,394	12.3	(7.2)	(4.0)

Figure 2.4: Global MTBE demand *(thousand tons per year). Adapted from CHEM SYSTEM*

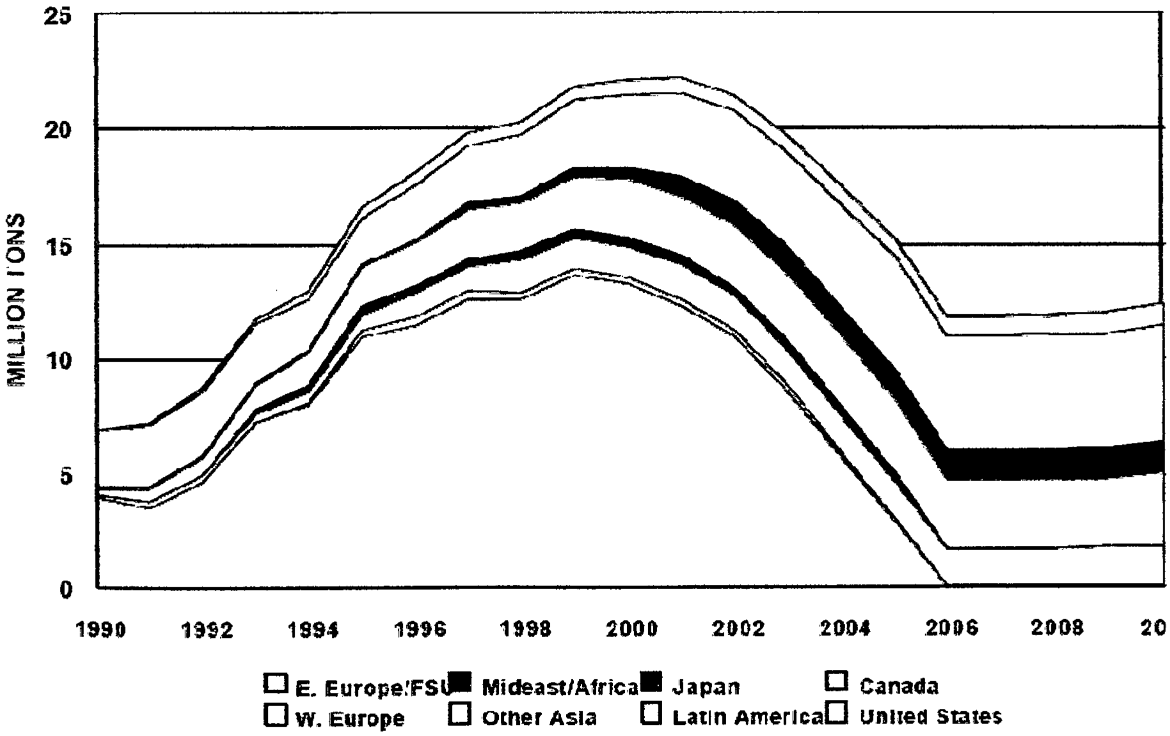

Figure 2.5: MTBE global demand distribution

2.4 CONCEPT OF REACTIVE DISTILLATION PROCESS

Reactive distillation is a process where simultaneous chemical reaction and vapor-liquid phase separation take place in the presence of a heterogeneous catalyst. It is a new technology that has been develop and modified to optimize the production of the product. It not only based on one unit but also allows for the great conversion.

By simultaneous of the both reaction and separation process in the system, reactive distillation offers certain advantages that cannot be matches with others systems. Several advantages that has been identified such as

1. It is reduce the capital cost of the production and give side benefits to the company.
2. An equilibrium reaction can be driven to completion by separation of the product from reacting mixtures.
3. Improve product selectivity
4. Improve the material that used in the process by reducing the percentage of the by produce in the reaction stages.
5. Reducing the heat boiler duty because of the saving energy that occurred by exothermic reaction of vaporization.
6. Saving energy due to the use of reaction heat for separation process (Baur et al., 2000).

2.6 PREVIOUS STUDY ON THE MTBE SIMULATION

Reactive distillation is an important technology which has been developed substantially since it was first patented for MTBE synthesis (*Smith, 1980*). Prior to 1980, reactive distillation had been used for esterification (particularly for methyl and ethyl acetate) but was under utilization in other areas. It was commercialized for MTBE synthesis in 1982 (*Smith and Huddleston, 1982*) and MTBE production is now its most important area of application. Reactive distillation has emerged as a highly promising process and bringing several advantages and improvement in the processes. In general,