THE SIMULTANEOUS PRODUCTION OF TERT-AMYL ALCOHOL AND TERT-AMYL-ETHYL ETHER IN A REACTIVE DISTILLATION COLUMN

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I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

Prof. Dr. Timur Doğu
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ABSTRACT

SIMULTANEOUS PRODUCTION OF TERT-AMYL ALCOHOL AND TERT-AMYL-ETHYL-ETHER IN A REACTIVE DISTILLATION COLUMN

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Due to the water pollution problems created by MTBE, significant research was focused on the production of alternative oxygenates, such as tert-amyl-ethyl-ether (TAEE), tert-amyl-methyl-ether (TAME) and higher alcohols as octane enhancing gasoline blending components. Tert-amyl alcohol (TAA) may also be considered as an attractive alternate to MTBE. These oxygenates are expected to improve the burning characteristics of gasoline and reduce exhaust emissions of CO and hydrocarbons. They may be produced by the reaction of C_5 reactive olefins (isoamylenes), which are already present in FCC light gasoline, with ethanol, methanol or water. Reactive distillation processes have attracted significant attention in recent years, for the production of similar ethers (such as MTBE and TAME) to enhance the conversion in such equilibrium limited reactions.

In the present study, simultaneous production of TAEE and TAA was investigated in a reactive distillation column using isoamylenes and ethanol-water mixture as reactants. Use of low purity ethanol (containing some water) in the production of such oxygenates might also offer a major advantage in terms of reactant cost. The batch reactive distillation column used in this work had 8 perforated plates and two of those plates were selected as the reaction zone. Amberlyst-15 catalyst packages (10g/plate) were placed over these two plates. Water/ethanol mole ratio in the liquid feed was 0.134, while mole fraction of isoamylene was changed between 0.03 and 0.18. Experiments were repeated in a temperature range between 70°-110°C. In this system, C_5 reactive olefins were converted to TAEE and TAA by two competing parallel reactions, by reacting with ethanol and water, respectively. Very high conversions of C_5 reactive olefins (over 93%) were achieved especially at high temperatures and low olefin concentrations. Selectivity of TAA with respect to TAEE was significantly increased of high temperature. It was shown that, water molecules were more strongly adsorbed on the $-SO_3H$ sites of Amberlyst-15 than alcohols (forming a hydrogen bonded network) leading to poisoning of the catalyst for TAEE production.

Keywords: Octane Enhancer, Isoamylene, TAEE, Reactive Distillation Column

ÖZ

TERSİYER AMİL ALKOL VE TERSİYER AMİL ETİL ETERİN REAKTİF DAMITMA KOLONUNDA EŞZAMANLI ÜRETİMİ

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MTBE'in neden olduğu çevresel problemler nedeniyle alternative oktan yükseltici bileşikler konusundaki araştırmalar tersiyer-amil-etil-eter (TAEE), tersiyer-amil-metil-eter (TAME) ve yüksek alkollerin üretimine yönelmiştir. Tersiyer-amil alkol (TAA), MTBE yerine kullanılabilecek iyi bir seçenek olarak görülmektedir. Yakıtın yanma özelliklerini arttıran, karbon monoksit ve yanmamış hidrokarbon emisyonunu azaltan bu eterler etanol ve methanolün FCC benzini içerinde bulunan C_5 reaktif olefinleri ile reaksiyonu sonucu üretilebilirler. Son yıllarda, "Reaktif Damıtma İşlemi" MTBE, TAME gibi dönüşümleri denge ile sınırlanan maddelerin üretiminde kullanılmaya başlanmış ve büyük ilgi görmüştür.

Bu çalışmamızda, reaktif damıtma kolonunda izoamilen, etanol ve su kullanılarak eşzamanlı TAEE ve TAA üretimi çalışılmıştır. Oksijenli bileşiklerin üretiminde düşük saflıkta etil alkol (içeriğinde su bulunan) kullanımının hammadde maliyetini düşürücü üstünlüğü vardır.

Çalışmamızda kullanılan kesikli damıtma kolonunda 8 adet delikli tepsi bulunmaktadır ve bu tepsilerden iki tanesi reaktif bölge olarak seçilmiştir. Hazırlanan Amberlyst-15 katalizör paketleri (10gr/tepsi), seçilen bu tepsilerin üzerine yerleştirilmiştir. Besleme karışımı içerisindeki su/etil alkol mol oranı 0.135'de sabit tutulurken, izoamilen mol oranı 0.03 ila 0.18 arasında değiştirilmiştir. Deneyler, reaksiyon bölgesi sıcaklığı 70°-110°C aralığında değiştirilerek yapılmıştır. Bu sistemde, C_5 reaktif olefinlerinin etil alkol ve su ile paralel 2 tepkimesi TAEE ve TAA oluşumunu sağlamıştır. Yüksek sıcaklık ve düşük olefin konsantrasyonlarında yüksek değerlerde C_5 reaktif olefinlerinin (93% üzerinde) dönüşümü sağlanmıştır. TAA'nın, TAEE'ye gore seçiciliği sıcaklıktaki artış ile büyük oranda artmıştır. Ayrıca, su moleküllerinin Amberlit 15 taneciklerinin $-SO_3H$ aktif noktalarına daha kuvvetli adsorblandığı (hidrojen bağı kurarak) ve bu durumun TAEE üretiminde katalizörü olumsuz yönde etkilediği gösterilmiştir.

Anahtar kelimeler: Oktan Yükseltici, İzoamilen, TAEE, Reaktif Damıtma Kolonu

To My Family,

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NOMENCLATURE

a_i	Activity of species i
K_j	Equilibrium Constant for reaction j
x_i	Mole fraction of species i in the mixture
X_{TAEE}	Conversion of olefin to TAEE
X_{TAA}	Conversion of olefin to TAA
S_{TAEE}	Selectivity of TAEE to both products
S_{TAA}	Selectivity of TAEE to both products
A_{ij}	The NRTL model energy parameter for ij binary pair
k_{ij}	The Wong Sandler Model binary interaction parameter

Greek Letters

γ_i	Activity coefficients of species i
υ_i	Stoichiometric coefficients of species i in reaction

Abbreviations:

2M2B	2 methyl 2 butene
2M1B	2 methyl 1 butene
MTBE	Methyl tert butyl ether
ETBE	Ethyl tert butyl ether
TAME	Tert amyl methyl ether
TAEE	Tert amyl ethyl ether
TAA	Tert amyl alcohol
FCC	Fluid Catalytic Cracking

CHAPTER 1

INTRODUCTION

Fuel oxygenates improve hydrocarbon burning efficiency of gasoline and reduce carbon monoxide emissions. They also help reduction in atmospheric ozone resulting from gasoline evaporative emissions due to their lower volatility.

The oxygenates which are commonly used in the blending of gasoline are Methyl tert-butyl ether (MTBE), Ethyl tert-butyl ether (ETBE), Tert-amyl methyl ether (TAME) and Tert-amyl ethyl ether (TAEE). MTBE is the most popular oxygenates but it creates water pollution problems and is thought to be carsinogenic. ETBE is a good alternative to MTBE since it is produced by the reaction of olefin and ethanol. Producing oxygenates from Fluid Catalytic Cracking olefins have several advantages. It allows higher levels of oxygenate production, so lowering the proportion of olefins in the gasoline pool and maximizing the use of FCC olefins. TAME and TAEE are produced by C_5 reactive olefins, which is present in FCC at a 13-weight percentage. Tert amyl alcohol (TAA) has been used as an alternative reactant to isoamylene so that the synthesized TAEE is completely obtained from renewable sources. Also, it may be used as an octane supplies, itself, in the gasoline.

The etherification reaction carrying out isoamylene and alcohol, and the hydration reaction between the isoamylene and water, are thermodynamically equilibrium limited. So, the synthesis process must include the separation of product from the reaction medium to increase the conversion and the overcome the equilibrium limitation. The combination of reaction and separation inside a single unit is generally called as Reactive Separations. Reactive Distillation process is one of the best known examples of a combined reaction and separation.

In this study, the simultaneous production of TAEE and TAA was investigated in a reactive distillation column. The elimination of equilibrium limitation was achieved by continuous removal of products from the reaction medium and high conversion values were obtained. The effects of temperature, reactant composition, reactive plate location on the overall olefin conversion and selectivities of TAEE and TAA are also investigated. Beside, the influence of isomerization reaction of isoamylenes, 2-metyh-2-butene and 2-methyl-1-butene, on the system was studied. Finally, a theoretical study on vapor liquid equilibrium of different binary pairs was carried out.

CHAPTER 2

OXYGENATES

As environmental concerns grow in the world, several alternatives have been studied for the contents of the gasoline. Impact of gasoline chemical and physical properties on human health, air quality and the environment, is the issue of greatest relevance for the definition of proper quality standards, which could really affect the end result of environmental legislations. Among the other issues concerned, the levels set for Reid Vapor Pressure (RVP), light olefins and oxygenates will be of the greatest interest for the refineries.

2.1 Historical Development of Fuel Oxygenates

Ancillotti and Fattore (1998) reviewed the information on historical market expansion of the oxygenates which were used as gasoline additives. Here, important steps through the development of fuel oxygenates discussed by these authors are presented.

At the end of the 1950's, petroleum refinery seemed to have reached a satisfactory technological level representing a good energy/economy balance. However, great increase in energy consumption and deterioration of the environment led to the recognition during the 1960's that energy production and automotive transportation were major causes of air-quality deterioration. By the

1970's it became clear that petroleum refining had to meet a new goal: energy, economy, and environment together.

The most publicized environmental measure adopted in the 1970's was the progressive phasing-out of lead additives in motor fuels and the introduction of severe emissions limits for 1975 that could be met only by the application of catalytic converters for the oxidation of CO and HC in automobile exhaust.

By 1978, NO_x emissions had to be reduced drastically. This requirement brought about the development of the three-way catalytic converter, which allowed simultaneous reduction of CO, HC and NO_x.

The complete removal of lead additives from gasoline was necessary for the technical operability of catalytic converters, because the catalysts were intolerant to lead. An important technical consequence of the reduction of lead concentration in gasoline was a notable drop in gasoline octane number, which could not be tolerated by millions of automobiles designed for high-octane-number fuel. The immediate solution for the problem was to raise octane number with increasing concentration of butanes and aromatics in gasoline. However, aromatics and especially benzene were known as carsinogenic species. Recent environmental regulations require total aromatics and benzene to be less than 15% vol and 1% (vol), respectively (Schipper et al., 1990). A second and more innovative solution was the use of a new class of high-octane oxygenated components, called as oxygenates.

According to the ASTM D 4814 'Standard Specification for Automotive Spark-Ignition Engine Fuel' an oxygenate is defined as *an oxygen containing, ashless organic compound, such as an alcohol or ether, which can be used as a fuel supplement.*

Knowledge of the good antiknock properties of some oxygenated compounds dates back to the 1930s, when improvements in aircraft performance resulted in demand for fuels of increasingly higher antiknock performance.

It was proved that some branched methyl ethers, like methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE) had very interesting octane behaviour.

The lead-phase-down of the early 1970's renewed the interest in oxygenates. Light alcohols such as methanol and ethanol, already existing on the market as chemical intermediates, and the first term of alkyl *tert*-alkyl ethers, namely the MTBE were considered. The first industrial plants producing industrial quantities of MTBE were put on stream by ANIC in Italy in 1973 and by Chemische Werke Huels in Germany in 1976.

Oxygenates began to be added to gasoline and to play an increasingly important role in gasoline formulation, as octane booster replacing alkyl lead, from 1973.

The oxygenate market was dominated by MTBE, due to its octane blending value, relatively low volatility, complete miscibility with gasoline, low susceptibility to phase separation in the storage and relatively low cost of methanol as compared to ethanol.

Specification for reformulated gasoline was presented by Schipper et a. (1990) and is given in Table 2.1.

Table 2.1 Specifications for Reformulated Gasoline (Schipper et al., 1990)

Benzene concentration of 1.0 vol% maximum
Minimum oxygen content of 2.0 wt %
Aromatic concentration of 25 vol% maximum
No heavy metals, specifically lead and manganese
Detergent additives for deposit prevention

A new more global approach was introduced by the Amendments of the Clean Air Act, issued in 1990 (1990 CAAA). Specifications for gasoline and diesel fuel were enforced by CAAA and two new fuels were mandated:

- Oxygenated gasoline during the winter months in areas that do not comply with CO emission standard and reformulated gasoline (RFG) all year round in areas that do not comply with ozone emission standard.

- Reformulated gasoline differs from conventional fuels at least three features: lower volatility, presence of an oxygenate and lower aromatics.

Other quality considerations, such as toxic or air toxic content (eg. Lead, benzene, etc) also come into play for a variety of other effects.

Both 'oxygenated gasoline' and RFG require certain oxygen content. The CAAA gave to oxygenate the new role of clean air additives, advancing that of octane supplier.

Despite the controversial future of oxygenates as "clean air additive", they are expected to maintain and extend the role of "octane supplier" to replace butanes and aromatics.

2.2 Properties and Production of Oxygenates

Fuel oxygenates improve hydrocarbon burning efficiency of gasoline and reduce carbon monoxide (CO) emissions. They also help reduce atmospheric ozone resulting from gasoline evaporative emissions due to their lower volatility and atmospherics characteristics in comparison with hydrocarbon constituents of the refinery gasoline they replace. Because oxygenates clean burning characteristics, they are expected to play a significant role in most of the countries in the world, where clean burning light octane fuels are needed.

The oxygenates which are commonly used in the blending of gasoline are alcohols, mainly methanol and ethanol, and tertiary ethers, such as Methyl-tert-butyl-ether (MTBE), Ethyl-tert-butyl-ether (ETBE), Tert-amyl-methyl-ether (TAME) and Tert-amyl-ethyl-ether (TAEE). Some properties of alcohols, isobutylenes and corresponding ethers are presented in Table 2.2.

Table 2.2 Properties of some hydrocarbons and oxygenates (Ancillotti *et al.*, 1998)

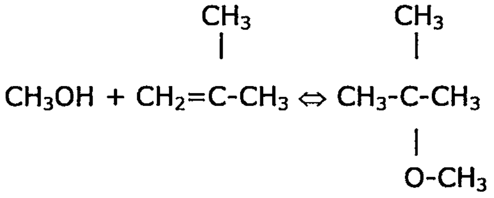
Compound	Octane Number (R+M)/2	Atmospheric reactivity	Oxygen (wt%)	Boiling Point (°C)	Blending RVP (psi)
Isobutylene		55		-3	66
2M2B	91 pure 158 blend	85		38	15
2M1B	92 pure	70		31	19
Methanol	116 blend	1	49.9	65	60
Ethanol	113 blend	3.4	34.7	78	18
MTBE	109 blend	2.6	18.2	55	9
ETBE	110 blend	8.1	15.7	72	3-5
TAME	104 blend	7.9	15.7	86	1-2
TAEE	105 blend		13.8	101	0-2

Among the oxygenates for reformulated gasoline, tertiary ethers are the preferred compounds to alcohols, because of their lower Reid vapor pressure (RVP; vapor pressure of component at 37.7°C), lower vaporization latent heats, and also they avoid phase separation in the presence of water, which accounts for their full compatibility with the petroleum refining and distribution systems.

2.2.1 MTBE (Methyl Tert Butyl Ether)

A significant step to improve the gasoline quality is the removal of lead by adding an octane enhancer such as methyl *tert*-butyl ether (MTBE). Another advantage of using oxygenates as gasoline additives to reduce emissions of CO and unburned hydrocarbons from motor vehicles. Schipper et al. (1990) indicated that blending of 15-vol % MTBE in gasoline decreased exhaust hydrocarbons by 5-7% and the presence of MTBE in gasoline reduced CO emissions.

MTBE is produced by the reaction methanol with isobutene. This is a reversible exothermic reaction, which might take place in gas or liquid phase, depending on the system pressure. In liquid phase, the reaction proceeds selectively and with high conversion if the equilibrium is attained at conveniently low temperatures (40-60°C). The reaction is:



$$CH_3OH + CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}CH_3 \Leftrightarrow CH_3{-}\underset{\underset{\displaystyle O{-}CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}{-}CH_3$$

Some side reactions, however can accompany the formation of MTBE, such as isobutene dimerization to 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene and methanol dehydration to dimethyl ether (DME). Traces of water in the reactants lead to formation of TBA due to the competitive addition of water to isobutene. This reaction proceeds to equilibrium conversion. However, because of the low amount of water in the reactants, TBA does not, generally, reach a concentration level above 0.5-1% in MTBE.

The thermodynamics of the reaction was first studied by Colombo et al. (1983). Also, Rehfinger et al. (1990), Izquierdo et al. (1994) and Zhang and Datta (1995) proposed different correlations for the equilibrium constant, K vs. temperature for MTBE synthesis reaction in the liquid phase. A substantial agreement between the Rehfinger and Hoffmann and Zhang and Datta data can be noted especially in the temperature range of 40°-90°C. Equilibrium constants calculated through the Colombo expression meet quite well those of Rehfinger and Hoffmann at low temperatures. However it become, progressively more favorable as the temperature increases.

Considering the nature of the reaction, the selection of catalyst for this synthesis was oriented to acid substrates. All the industrial plants built till today have adopted acidic cation exchange resins as catalysts. Less attention was given to inorganic acids that seem not offering, as a whole, convincing performances to substitute the resins in industrial applications. Related to ion exchange resin catalysts used for this reaction, a fundamental work was reported in the early work of Ancillotti et al. (1978).

The increasing demand of MTBE has for a long time been conditioned by the isobutene availability. Industrial quantities of isobutene were coming from C_4 streams of catalytic cracking processes for gasoline production and of ethylene manufacture. The availability of methanol is another key element in MTBE manufacture, but, unlike isobutene, methanol is extensively produced by number of firms from inexpensive natural gas other carbon sources.

As indicated by Ahmed (2001), in 1998, MTBE's total worldwide production was 6.6 billion gallons, with the US consuming the most, about 4.3 billion gallons annually and is considered as one of the top 50 chemicals in production (WHO, 1998). MTBE can be found in the environment during all phases of the petroleum fuel cycle (e.g. auto emissions, evaporative losses from gasoline stations and vehicles, storage tank releases, pipeline leaks and accidental spills, and refinery stock releases). Ahmed (2001) reviewed that, when MTBE was released into air, the greater part will exist in the atmosphere, with small amounts entering soil and water, with chemical degradation being the major removal source from air. When released into water, a significant amount of MTBE remains dissolved in surface water, with some partitioning into air and a much smaller amount into soil; the key removal process being volatilization (WHO, 1998). Because its high solubility, once released, it moves through the soil and into ground water more rapidly than other chemicals present in gasoline. Once in ground water, it is slow to biodegrade and is more persistent than other gasoline-related compounds (EPA, 1999). Thus, the potential exposure for humans to MTBE is considerable. These exposures generally occur through inhalation. Inhalation from fumes while fueling automobiles was reported as the principal route for human exposure (Dourson and Felter, 1997).

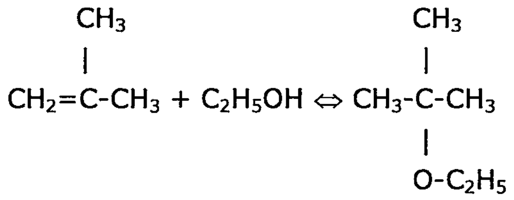
2.2.2 ETBE (Ethyl Tert Butyl Ether)

The principal oxygenates used today are methyl *tert*-butyl ether (MTBE) and ethanol to eliminate the leaded octane enhancers such as tetramethyl lead and tetraethyl lead. MTBE, thus, has a dual environmental advantage.

In Europe, MTBE is mainly used as an octane enhancer in high-octane gasoline it is called as "Super plus" and to achieve the specified oxygen content requirements, 5–15% MTBE in gasoline is required (Dekant et al., 2001). Due to the high concentrations of these ethers in gasoline, human exposure to these compounds is likely during production, gasoline blending, and refueling and by evaporation (Stern et al., 1997 and Vainiotalo et al, 1999). MTBE has also been found to leak from storage tanks and is a widely found water contaminant (Brown, 1997). Thus, the potential exposure for humans to MTBE is considerable However, recent studies have indicated that MTBE is claimed to be carsinogenic. MTBE is an animal carcinogen, but its human carcinogenic potential remains unclear. EPA based on animal studies which looked primarily at inhalation effects, concluded that MTBE poses a potential for carcinogenicity to humans at high doses. Some studies suggested that carcinogenicity of MTBE might be due to its two main metabolites, formaldehyde or tributanol. Concern over ground and surface water contamination caused by persistent MTBE has lead the Environmental Protection Agency (EPA) to proposed reducing or eliminating its use as a gasoline additive. The major potential alternatives to MTBE are other forms of ethers such as ethyl *tert*-butyl ether (ETBE) or *tert*-amyl methyl ether (TAME) (Ahmed, 2001).

ETBE has a slightly higher octane number and lower blending Reid vapour pressure (RVP). Also, it is produced from renewable ethanol. Moreover, there has been no evidence that ETBE is carsinogenic. In a computer-automated structure evaluation (CASE) study, where ETBE structure was compared with the structure of known determinants of carcinogenicity in rodents, ETBE was predicted to be neither a genotoxicant nor a carcinogen (Rosenkranz and Klopman, 1991). Thus, ETBE is a potential alternative to MTBE in spite of its higher cost at present. Recent advances in ethanol production from biomass may decrease the price of ethanol and the cost of ethanol-based ethers may become comparable to the cost of MTBE in the near future.

The formation of ETBE from ethanol and isobutene is an acid catalyzed, reversible, moderately exothermic reaction. The reaction can be represented as:



$$CH_2{=}\overset{\displaystyle CH_3 \atop |}{C}{-}CH_3 + C_2H_5OH \Leftrightarrow CH_3{-}\underset{| \atop \displaystyle O{-}C_2H_5}{\overset{\displaystyle CH_3 \atop |}{C}}{-}CH_3$$

The reaction is equilibrium limited in the industrially significant ranges of temperatures so that the equilibrium conversion from a stoichiometric mixture of reactant at 70 °C is only 84.7 (Sneesby et al., 1997). At higher temperatures, which are needed to increase the reaction rate, even lower equilibrium conversions were expected.

As for MTBE, the preferred catalysts appear to be the macroreticular ion exchange resins. Tau and Davis (1989) investigated the synthesis of ETBE in liquid and vapour phase on acid resins (A15, A35, fluorocarbonsulphuric acid polymer, FCSA, and phenylphosphoric acid, PPA, on active carbon) and on zeolites (ZSM-5 and S115 of Union Carbide). In the vapour phase Amberlyst 15 was found to be the most active catalyst. In the liquid phase, FCSA and ZSM-5 showed performances near to those of A-15 but at much higher temperatures. This prevents to attain equilibrium conversion at the more favorable lower temperatures. The selectivity is very high, but some byproducts such as diisobutene and diethyl ether may appear if the temperature is high enough and ethanol/isobutene molar ratio is far from the stoichiometric ratio. Side products become more important at longer residence times of reactants in the reactor. It is worth noting that the water impurity accompanying ethanol can be higher than with methanol, therefore the competitive formation of TBA is a more important side reaction in ETBE synthesis.

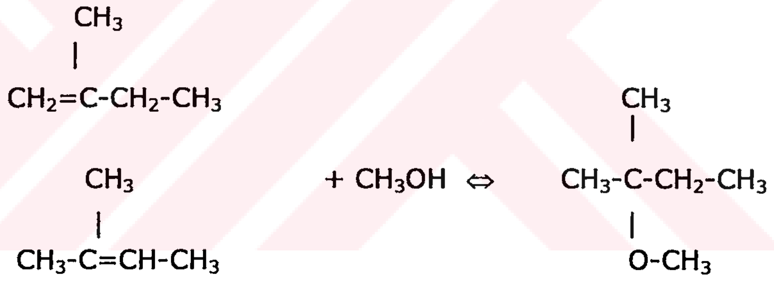
Izquierdo et al. (1994) and Jensen and Datta (1995) have investigated thermodynamic equilibrium of the liquid phase ETBE synthesis.

2.2.3 TAME (Tert Amyl Methyl Ether)

TAME received serious consideration as an oxygenate in the early 1990s, in spite of its slightly lower octane content than other ethers, as it compares favorably for vapor pressure, boiling point, energy density and water mixability (Caprino, 1998).

TAME is obtained by reacting methanol with one of the two-branched C_5 olefins (2-methyl-1-butene, 2M1B, and 2-methyl-2-butene, 2M2B). The third C_5 branched olefin, 3-methyl-butene-1, is completely inert toward the reaction with methanol.

Some amount of tert-amyl alcohol can be present in the reaction product if water is an impurity of the reactants. The reaction can be represented as:



$$\begin{array}{c} \mathrm{CH_2{=}\overset{\overset{CH_3}{|}}{C}{-}CH_2{-}CH_3} \\ \\ \mathrm{CH_3{-}\overset{\overset{CH_3}{|}}{C}{=}CH{-}CH_3} \end{array} + \mathrm{CH_3OH} \Leftrightarrow \mathrm{CH_3{-}\underset{\underset{O-CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CH_2{-}CH_3}$$

Like MTBE and ETBE, TAME synthesis is an acid catalyzed reversible reaction where three equilibrium reactions proceed simultaneously. The catalyst is a macroreticular ion exchange resin as in MTBE and ETBE synthesis.

Krause and Hammarström (1987) investigated the reaction giving the limits of the thermodynamic equilibrium at various temperatures and pressures. Rihko et al. (1994) experimentally measured the reaction equilibrium in the liquid phase. In the study of Solà et al. (1997) it was given that under standard operation conditions, working pressure of 700-900kPA, temperature range of 313-373 K, isoamylene equilibrium conversion was about 70%.

During TAME synthesis, isomerization reaction between 2M2B and 2M1B takes place in addition to reaction of olefins with methanol. The initial rate of double bond isomerization is faster than methanol addition, so two isoamylenes equilibrate before TAME equilibrium is achieved and the initial etherification rate for the two isomers proved to be different, 2M1B being 10 times more reactive (Ancillotti et al., 1998).

Differently from MTBE and in spite of the good octane quality, TAME is not a true 'octane supplier' because it is normally produced from two high-octane olefins present in the gasoline pool, coming from the front end of catalytic cracking gasoline. The net TAME octane contribution corresponds therefore to the difference between the octane contribution of TAME produced and the loss of the octane contribution of reacted isoamylenes.

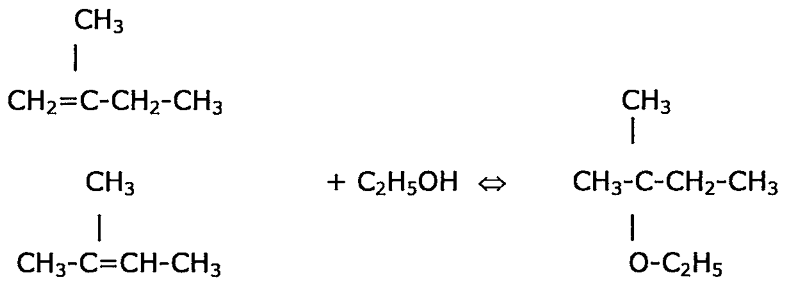
Notwithstanding its minor octane contribution, TAME is important as a 'clean air additive' contributing to meet three important requirements of reformulation: introduction of oxygen, reduction of volatility and removal of highly volatile and photochemically reactive olefins.

The TAME potential capacity is strictly related to the reactive isoamylene present in the light gasoline cracking plants. Availability that will be to be some extent influenced by the evolution of catalytic cracking system. An additional minor contribution to TAME capacity can arise from C_5 coming from naphtha steam cracking for ethylene manufacture, after a selective hydrogenation to remove dienes.

Compared with MTBE, ETBE is less economical to produce, and TAME is more toxic (Ahmed, 2001).

2.2.4 TAEE (Tert Amyl Ethyl Ether)

Tertiary amyl ethyl ether, which is catalytically synthesized from isoamylenes 2M1B and 2M2B and ethanol, has been identified as a suitable additive to gasoline in order to reduce pollution and to enhance octane ratings.



$$\begin{array}{c} \mathrm{CH_3} \\ | \\ \mathrm{CH_2{=}C{-}CH_2{-}CH_3} \\ \\ \mathrm{CH_3} \\ | \\ \mathrm{CH_3{-}C{=}CH{-}CH_3} \end{array} + \mathrm{C_2H_5OH} \Leftrightarrow \begin{array}{c} \mathrm{CH_3} \\ | \\ \mathrm{CH_3{-}C{-}CH_2{-}CH_3} \\ | \\ \mathrm{O{-}C_2H_5} \end{array}$$

Kinetic studies on the production of TAEE are very few. Major kinetic studies on TAEE synthesis have been using isoamylene (IA) from fuel cracking streams, and EtOH as reactants were carried out by Rihko and Krause (1993), Rihko, Linnekoski, & Krause (1994), Kitchaiya & Datta (1995), Linnekoski, Krause & Rihko (1997), Linnekoski, Krause & Struckmann (1998), Oktar et al. (1999).

Rihko and Krause (1993) obtained conversion data for etherification and isomerization of isoamylenes using plug flow and batch reactors and showed that etherification conversions declined above 60°C due to the equilibrium limitations.

Kitchaiya and Datta (1995) have studied this reaction in a wide range of compositions and temperatures. They reported a thermodynamic analysis of the liquid phase synthesis of TAEE and of the accompanying mutual isomerisation of the two olefins. The etherification reactivity of isoamylenes with ethanol in liquid phase has been studied by Rihko and Krause (1993), the liquid phase equilibrium by Rihko et al. (1994) and Kitchaiya and Datta (1995) and the kinetics by Linnekoski et al. (1996).

Oktar et al. (1999) investigated the reactivities of 2-methyl-1-butene (2M1B) and 2-methyl-2-butene (2M2B) in the etherification reaction with ethanol catalysed by a strongly acidic macroreticular resin catalyst in a temperature range of 333-360 K using liquid phase differential flow reactor. They showed that 2M1B was more reactive than 2M2B and its activation energy was also lower in the etherification reaction.

A particular advantage of TAEE is that ethanol, the other reagent, can be produced by fermentation from renewable resources, such as molasses, sugarcane, sugar, corn and potatoes. Although ethanol is higher in price than methanol, using a less pure ethanol that is an azeotropic or sub-azeotropic mixture of ethanol and water could diminish the difference.

TAEE presents lower blending Reid vapour pressure (less than 5.3 kPa) and lower solubility in water than in other oxygenates. Despite the positive convenience for hot places and underground water contamination, TAEE is not yet on the market (Ancillotti & Fattore, 1998).

Ethyl ethers show slightly better blending octane properties than methyl ethers and lower blend RVP that favors the blending with more low cost butanes. The alternative use of methyl or ethyl ethers will mainly depend on availability and price of the two alcohols.

Producing oxygenates from all potential FCC tertiary olefins is one of the most economic methods for reducing olefins and Reid vapor pressure (Rvp) in motor gasoline. This route allows higher levels of oxygenate production, thereby lowering RVP and the proportion of olefins in the gasoline pool and maximizing the use of FCC olefins. Higher ethers (TAME and TAEE) can be used to meet the amended blend Reid vapor pressure (bRVP) levels, and the limits on the olefin content of reformulated gasoline. TAME and TAEE have lower bRVP values than the isoamylenes from which they are produced. Production of TAME and TAEE from isoamylenes thus reduces the olefin content of the light FCC (Fluid catalyst cracking) gasoline.

The FCC unit can be identified as a major issue, because almost all light olefins and a large proportion of aromatics come from here. The typical composition of FCC light gasoline is given in Table 2.3.

Table 2.3 The typical composition of FCC light gasoline (Ignatus et al., 1995)

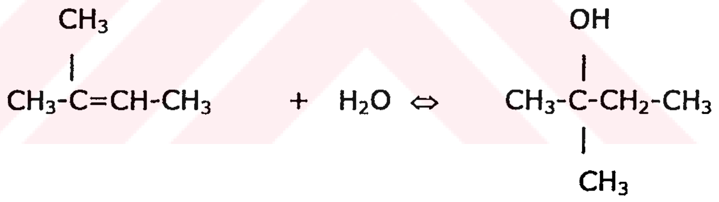
Component	Fraction, wt %
C4 or lighter	2.1
C5 reactive	13.0
C5 inerts	31.3
C6 reactive	11.7
C6 inerts	25.7
Dienes	1.0
Benzene	1.5
C7 reactives	3.0
C7 inerts + heavier	10.7

By using all the components, produced by an FCC efficiently, many gasoline problems can be solved. But, little attention has been given to the fact that FCC light gasoline contains much more reactive olefins that can be converted to ethers. This way, more octanes are produced and less octanes from reformate are required. Therefore, olefins and aromatics content of the gasoline pool can be reduced. The trend in FCC development allows much deeper conversion to light olefins and lower amounts of aromatics-rich FCC heavy gasoline. By producing more oxygenates like MTBE, TAME and heavier ethers, a refinery can be sufficient in blending reformulated gasoline and oxygenates need to be purchased. The olefin content in the FCC light gasoline stream represents roughly 90% of the gasoline pool olefins. By converting the reactive light olefins into ethers, the FCC gasoline RVP decreases by 0.9 psi (6 kPa). The olefin content is reduced by about 23% (Ignatius et al., 1995).

2.2.5 TAA (Tert-Amyl Alcohol)

tert-amyl alcohol (TAA) is one of the major products of fusel oil, issued from biomass fermentation. It has been used as an alternative reactant to IA so that the synthesized TAEE is completely obtained from renewable resources (Aiouache and Goto, 2003).

The hydration of 2-methyl-2-butene to produce tert-amyl alcohol can be represented as:



$$CH_3\text{-}\overset{\overset{CH_3}{|}}{C}=CH\text{-}CH_3 \quad + \quad H_2O \Leftrightarrow \quad CH_3\text{-}\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}\text{-}CH_2\text{-}CH_3$$

The reaction of isoamylene and water to produce TAA is very similar to the well-studied etherification reactions to produce MTBE, TAME, and ETBE. All of these reactions are carried out in the presence of strongly acidic macroporous resins, at a temperature range of 50-90°C and pressure range of 300-1500 kPa. The polar compound (water or alcohol) adsorbs preferentially in the resin, inhibiting favorable adsorption of the olefin. All reactions are proceeding by the formation of a stable tertiary carbenium ion and they are thermodynamically equilibrium limited, and are moderately exothermic (heats of reaction 25-40 kJ/mol) (González and Fair, 1997).

As indicated by Linnekoski et al. (1998) the hydration reactivity of isoamylenes was studied about this subject. The kinetics of simultaneous hydration and etherification of isoamylenes with sub-azeotropic mixture of ethanol and water and the equilibrium was studied by Jayadeokar and Sharma (1993) using a batch reactor.

Several kinetic and thermodynamic studies have been reported on the dehydration/hydration of TAA (Gonzalez & Fair, 1997). But, in our knowledge, there is not available data for the octane number of TAA in the literature.

Linnekoski et al. (1998) studied the simultaneous etherification and hydration of 2-methyl-2-butene and 2-methyl-1-butene in a continuous stirred tank reactor. They founded that addition of a small amount of water to the feed, caused a marked drop in the overall olefin conversion and in the etherification rate.

2.3 The Catalyst Used in Etherification Reactions

Ancillotti and Fattore (1998) reviewed the catalysts used for the etherification reactions. In this section, some important results are summarized.

Ancillotti et al. (1978) did a fundamental study about ion exchange resins as catalyst for the production of MTBE, firstly. A15 is a macroreticular sulfonic resin manufactured by Rohm and Haas. It is a sulphonated copolymer of styrene and divinylbenzene. Its surface area is 45 m^2/g and ion exchange capacity is 4.8 mequiv. of H^+ /g dry, as reported by Kunin et al. (1962). In the study of Oktar et al. (1999) detail information about the pore size distribution, surface area (59.2 m^2/g), porosity (ε_a= 0.32), average macropore diameter (2.28×10^{-8}m) and apparent density (ρ_p =0.99 g/cm^3) were reported.

The morphology and the active sites were mentioned in the work of Ancillotti and Fattore (1998). Differently from gel type resins, where the polymeric gel phase occupies, as a continuum, the macroreticular porous resins are structurally composed of small microgel particles to form clusters bonded at the interfaces. The geometry of microgel tends towards spherical symmetry and the diameter of the individual microgel can range from 0.01 to 15 μm (Dooley et al., 1985). In the study of Doğu et al. (2003), the average particle radius of the resin used was 0.037cm and they estimated the average micrograin diameter of the catalyst as 8.2×10^{-8}m from the SEM photographs. Also, in the same study, from the SEM photographs, the average micrograin diameter of $FeCl_3$ or NaCl treated catalyst particles was estimated as about 9.4×10^{-8} m, which corresponded to about 50% volume swelling of these microspheres. The porosity arises from the void spaces between and within the clusters. The void region is a continuous open-celled system with essentially all the pores are interconnected. The gel phase is also a continuum, so that a macroreticular porous polymeric particle is constructed of two phases; a continuous pore phase and a continuous gel phase. The surface area arises from the exposed surface of microgel glued together into clusters.

The pore system makes macroreticular resins suitable for anchoring catalytic sites, namely SO_3H groups, that can lie either on the surface of microspheres or inside the gel phase. Increasing the crosslinking density of the polymer, it is possible to raise the porosity and the surface area but at the same time a less penetrable and less effective gel phase is obtained. Porous macroreticular resins generally show an enhanced catalytic activity compared with nonporous gel polymers of the same level of crosslinking but an increase in porosity and in area surface of a functionalized macroreticular polymer does not univocally result in an increased catalytic activity. In fact, the most part of sulfonic groups in macroreticular resins are located inside the gel phase, more than 95% for A15, and such a situation remains also increasing the surface area unless very high surface areas are obtained.

It is clear that, when the most part of the catalytic sites are inside the microgel particles, the gel phase is the working one. So, till the working phase is the gel phase, an excessive surface area, obtained by increasing the crosslinking density, could reduce the catalytic effectiveness, due to a reduced penetrability of microgel particles.

It is worthy to note that macroreticular resins, when the gel phase is the working one, have advantage on gel type polymer due to the smaller dimensions and enhanced accessibility of the gel domine. If the gel phase has sufficient penetrability for the molecules involved in reaction, macroreticular resins with the gel phase working represent the best solution, since sulfonic groups in the gel portion are more active than those on the surface. This is due to the environment within the gel portion that gives rise to a higher Hammett acidity with respect to that found on the surface and to a more stabilized activated complex (Panneman et al., 1995).

Resins such as A15, having a large number of interior catalytic sites, would represent the best catalytic solution for MTBE synthesis, provided that the gel phase is easily penetrable by methanol and isobutene. Macroreticular ion exchange resins actually represents the chosen class of catalyst for MTBE synthesis. Other acidic materials were tried.

The first synthesis of MTBE and similar ethers was done using inorganic catalyst as mineral acids. Sulphuric acid (Evans and Edlund, 1936) was active but not selective, favoring the formation of dehydrated by-products, dimethyl ether, and oligomers of the olefin. Moreover, the use of soluble inorganic acids makes the separation and purification of ethers a rather complex operation.

Attention to complex silicates (like montmorillonites and bentonites), with defined structure and ion exchanged to introduce acidity and metal ions, was given by Adams et al. (1982). Catalytic activity and/or selectivity of these catalyst resulted always lower compared to macroreticular acid resins. Better results, yet still not at the same level of those given by resins, were reached when operating in certain reaction conditions; addition of water to the reacting feed, different solvent (1,4-dioxan). In conclusion, all these catalyst represent an interesting effort to introduce easily regenerable substrates but they are penalized by limited yields in comparison to resin based catalyst.

Synthetic zeolites were demonstrated to be good catalyst in different reactions requiring acidic properties. Chu and Kuhl (1987) investigated zeolites for MTBE synthesis in vapour phase conditions. Their work considered large (Y, mordenite, etc), medium (ZSM5 and 11) and small (ferrierites) pore zeolites. All zeolites tested were shown to be less active than resins and the optimum performances were given at higher temperature (80°-110°C instead of 60°-90°C).

Chu and Kuhl (1987) utilized the most promising zeolites selected (namely ZSM5 and ZSM11) in liquid phase reaction conditions and made a comparison with Amberlyst 15. The results are quite near to those of A15 and the authors claim higher thermal stability, regenerability by calcination, low sensitivity to the methanol/isobutene ratio and higher productivity.

The heteropoly acid (HPA) possesses strong acidity to be applicable to several acid-catalyzed reactions in the liquid phase at moderate temperatures.

HPA catalyzes methanol addition to isobutene much more effectively than the ordinary protonic acids. It was proposed that high catalyst efficiency of HPA is essentially due to those specific properties of heteropoly anion that can be characterized by very weak basicity and great softness, in addition to a large molecular size of polyhedral heteropoly anion (Izumi et al., 1983). Knifton and Edwards (1999) demonstrated 12-tungstophosphoric acid and 12-molybdophosphoric acid, on Group III and IV oxide supports, such as titania, HF-treated montmorillonite clays, as well as mineral acid-activated clays to be effective for methyl *tert*-butyl ether (MTBE) syntheses from methanol/*tert*-butanol (TBA) feed mixtures using a continuous, plug-flow, reactor system. Gas phase synthesis of methyl tert-butyl ether (MTBE) from methanol and isobutylene was studied with several heteropolyacids at different temperature (Shikata et al. 1995). Major problem of using HPA's in such etherification reactions is their solubility in alcohols.

CHAPTER 3

REACTIVE SEPARATIONS

Chemical manufacturing companies produce materials based on chemical reactions between selected feedstocks. In many cases the completion of the chemical reactions is limited by the equilibrium between the reactants and the products. The process must then include the separation of this equilibrium mixture and recycling of the reactants. Usually, reaction and separation stages are carried out in discrete equipment units, and thus equipment and energy costs are added up from these major steps (Noeres et al., 2003).

In recent decades, a combination of separation and reaction inside a single unit has become more and more popular. This combination has been recognized by the chemical process industries for having favorable economics of carrying out reaction simultaneously with separation for certain classes of reacting systems, and many new processes, called Reactive Separations, have been invented based on this technology (Doherty et al., 1992; Agar 1999, Kelkar 1999). Such processes bring several important advantages among which are, a shift of the reaction product composition beyond the equilibrium by an in-situ separation/removal, increase of reaction yield and selectivity, overcoming thermodynamic restrictions e.g. azeotropes, and considerable reduction in energy, water and solvent consumption.

The integration of reaction and separation takes place purely on the equipment level, without introducing any new functional interrelations between the operations involved-the reaction does not influence the separation, nor has the separation process any effect upon the reaction. The aimed result of such combination can be: smaller inventory, compacter plant layout and/or better energy management (Stankiewicz, 2003).

Important examples of reactive separation processes (RSP) are reactive distillation (RD), reactive absorption, reactive adsorption and membrane reactors.

3.1 Reactive Distillation

Reactive (catalytic) distillation is one of the better-known examples of a combined reaction and separation, and is used commercially (De Garmo, 1992).

In this case, the multifunctional reactor is a distillation column filled with catalytically active packing. In the column, reactants are converted to products with simultaneous separation of the products and recycle of unused reactants. In most cases, the reaction is catalysed homogeneously or preferably heterogeneously. The catalyst used for heterogeneous reactive distillation is usually incorporated into a fiberglass and wire mesh supporting structure, which also provides liquid redistribution and disengagement of vapor. Also, a reverse process to the one described above, that is, combination of reaction and condensation, has been studied (Ben Armor et al., 1999).

The RD process can be efficient both in size and cost of capital equipment as well as in energy used to achieve complete conversion of reactants. Since the reactor costs are often less than 10% of the capital investment the combination of a relatively cheap reactor with a distillation column offers great potential for overall savings. Among suitable RD processes are etherifications, nitrations, estefications, transesterifications, condensations and alcylations (Doherty et al., 1992).

In some cases, it can replace conventional reaction-distillation sequences or it can be used to complete existing plants in order to lower production cost or to improve the purity of the products.

3.2 Reactive Absorption

Reactive Absorption is probably the most widely applied type of a reactive separation process.

In RA, reactions occur simultaneously with the component transport and absorptive separation. These processes are predominantly used for the production of basic chemicals, e.g. sulphuric or nitric acids and the removal of components from gas and liquid streams. This can be either the clean up of process gas streams or the removal of toxic or harmful substances in flue gases and liquids. Absorbers or scrubbers where RA is performed are often considered as gas-liquid reactors (Noeres et al., 2003).

RA represents a process in which a selective solution of gaseous species by a liquid solvent phase is combined with chemical reactions. Noeres et al. (2003), indicated that, as compared with purely physical absorption, RA does not necessarily require elevated pressure and high solubility absorbed components: because of the chemical reaction, the equilibrium state can be shifted favourably resulting in enhanced solution capacity. Most of the RA processes involve reactions in the liquid phase only, in some of them both liquid and gas reactions occur.

Difficulties of RA applications may be caused by the reaction heat through exothermic reactions and by relatively difficult solvent regeneration. Most of the RA processes are steady-state operations, either homogeneously catalysed or auto-catalysed. Some important industrial applications olefin/paraffin separations; amine washing, gas drying (Safarik and Eldridge, 1998, Yu and Astarita, 1987).

3.3 Reactive Adsorption

Numerous research groups investigated integration of reaction and adsorption, for instance, in chromatographic reactors (Bjorklund et al 1995, Mazotti et al. 1996) and in periodic separating reactors, which are a combination of a pressure swing adsorber with a periodic flow-forced packed-bed reactor (Vaporciyan et al., 1989). The simulated moving-bed reactor integrates continuous countercurrent chromatographic separation with chemical reaction. Such a combination allows achieving higher conversions and better yield by separating products of an equilibrium reaction form each other.

Stankiewicz (2003) indicated that in contrast to non-reactive adsorption techniques, the industrial-scale applications of adsorptive reactors are still to be seen. Challenges involve materials development of catalysts/adsorbents and matching of process conditions (same temperatures) for both reaction and adsorption, so that high yields/selectivities can be achieved.

3.4 Membrane Reactors

The membrane can play various functions in the reactor system (Sirkar et al., 1999).

The scientific literature on catalytic membrane reactors is exceptionally rich and includes many interesting ideas, such as heat- and mass- integrated combination of hydrogenation and dehydrogenation processes in a single membrane unit. Yet, practically no large-scale industrial applications of catalytic membrane reactors have been reported so far. The primary reason for this is the relatively high price of membrane units, although other factors, such as low permeability, sealing problems as well as mechanical and thermal fragileness of the membranes also play an important role. Possible application areas of catalytic membrane reactors in the base-chemical sector, include: Dehydrogenations, e.g. ethane to ethane, ethylbenzene to styrene, methanol to formaldehyde; methane steam forming; water-gas shift reaction; selective oxidations, e.g. propane to acroleine, butane to maleic anhydride, ethylene to ethylene oxide, oxidative coupling of methane (Stankiewicz, 2003).

3.5 Other Reactive Separations

Reactive extraction processes involve simultaneous reaction and liquid-liquid phase separation. Reactive extraction can be efficiently utilized to obtain significant improvements in yields of desired products and selectivities to desired products in multi-reaction systems, thereby reducing recycle flows and waste formation. The combination of reaction with liquid-liquid extraction can also be used for separation of waste by-products that are hard to separate using conventional techniques (Minotti et al. 1998; Samant, 1999).

Numerous research groups have investigated reactive crystallization, or precipitation. Processes of industrial relevance include liquid-phase oxidation of *para*-xylene to terephthalic acid, the acidic hydrolysis of sodium salicylate to salicylic acid and the absorption of ammonia in aqueous sulfuric acid to form ammonium sulfate (Kelkar et al., 1999).

CHAPTER 4

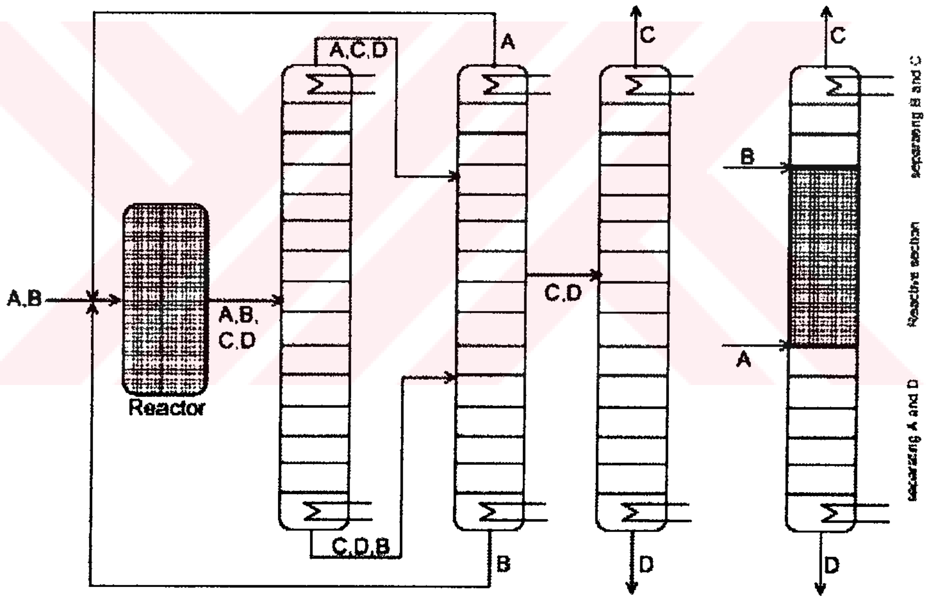
REACTIVE DISTILLATION

Currently, there is considerable academic and industrial interest in multifunctional reactors, involving in situ separation of products from the reactants (Krishna and Sie, 1994).

Reactive Distillation, the combination of chemical reaction and distillation in a single column, is one of the most important industrial applications of the multifunctional reactor concept. It has drawn considerable attention because of its advantages, especially for equilibrium-limited reactions.

4.1 The Importance of Reactive Distillation Process

Taylor and Krishna (2000) explained the importance of the reactive distillation column by a reversible reaction scheme: $A+B \Leftrightarrow C+D$ where the boiling points of the components followed the sequence A, C, D and B. In Figure 4.1 (Stichlmair and Frey, 1999) the traditional flow-sheet for this process consists of a reactor followed by a sequence of distillation columns and the reactive distillation column for the same process was given. In the traditional case, Figure 4.1 (a) the mixture of A and B was fed to the reactor, where the reaction took place in the presence of catalyst and reaches equilibrium. A distillation process was required to produce pure products C and D. The unreacted components, A and B, were recycled back to the reactor. If one or more azeotropes were formed in the mixture, the distillation could be much more complex than the one given in this scheme. The alternative reactive distillation configuration is shown in Figure 4.1 (b). In this scheme the RD column consists of a reactive section in the middle with non-reactive rectifying and stripping sections at the top and bottom, respectively. In the rectifying section, reactant B is recovered from the product stream C. In the stripping section, the reactant A is stripped from the product stream D. In the reactive section the products are separated in situ, driving the equilibrium to the right and preventing any undesired side reactions between the reactants A (or B) with the product C (or D). For a properly designed RD column, virtually 100% conversion can be achieved.



(a) Conventional process

(b) Reactive Distillation

Figure 4.1 Processing schemes for a reaction sequence A+B ⇔ C+D where C and D are both desired products. (a) Typical configuration of a conventional process (b) The reactive distillation configuration (Stichlmair and Frey, 1999)

4.2 Advantages of Reactive Distillation

Reactive distillation has many advantages over sequential processing, such as a fixed-bed-reactor followed by a fractionating column, in which the distillate or bottom of the reaction mixture is recycled to the reactor inlet. Noeres et al.(2003), Tunchlenski et al. (2001), Taylor and Krishna (2000), Higler et al.(1999) and Qi et al.(2002) published the advantages of reactive distillation processes. The most important advantage of using RD in the case of equilibrium-controlled reactions is the elimination of conversion limitations by removing products from the reaction zone, continuously. Apart from increased conversion the following benefits can also be obtained:

- An important benefit of RD technology is a reduction in capital investment, because two process steps can be carried out in the same device. Such integration leads to lower costs in pumps, piping and instrumentation.
- If RD is applied to exothermic reaction, the reaction heat can be used for vaporization of liquid. This leads to savings of energy costs by the reduction of reboiler duties.
- The maximum temperature in the reaction zone is limited to the boiling point of the reaction mixture, so that the danger of hot spot formation on the catalyst is reduced significantly. A simple and reliable temperature control can be achieved.
- Product selectivities can be improved due to fast removal reactants or products from the reaction zone. This lowers the probability of consecutive reactions, which may occur in the sequential operation mode.
- Selective reactions using a reactive entrainer in order to separate a closely boiling mixture (Qi et al., 2002).
- If the reaction zone in the RD-column is placed above the feed point, poisoning of the catalyst can be avoided. This leads to longer catalyst lifetime compared to conventional systems.

- Avoidance of azeotropes. RD is particularly advantageous when the reactor product is a mixture of species that can form several azeotropes with each other. RD conditions can allow the azeotropes to be "reacted away" in a single column.

It was reported that endothermic reactions are not suitable for the RD-technology because of vapor condensation. Although an endothermic reaction require more reboiler duty and therefore exhibits no large energy savings, there are no restrictions to the application of RD (Sakuth and Peters, 1995).

4.3 The Constraints and Difficulties in Reactive Distillation Application

Against the above-mentioned advantages of RD, there are several constraints and foreseen difficulties (Towler and Frey, 2000):

- Volatility constraints. The reagents and products must have suitable volatility to maintain high concentrations of reactants and low concentrations of products in the reaction zone.
- Residence time requirement. If the residence time for the reaction is long, a large column size and large tray hold-ups will be needed and it may be more economic to use a reactor-separator arrangement.
- Scale up to large flows. It is difficult to design RD processes for very large flow rates because of liquid distribution problems in packed RD columns.
- Process conditions mismatch. In some processes the optimum conditions of temperature and pressure for distillation may be far from optimal for reaction and vice versa.

4.4 Criteria Applying Reactive Distillation Process

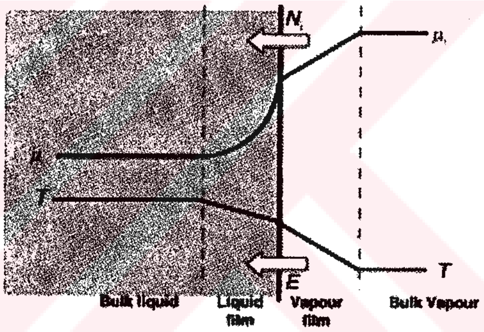
Applying RD-technology in industrial scale, three constraints have to be fulfilled (Tunchlenski et al., 2001):

- The use of RD technology is only possible, if the temperature window of the vapor-liquid equilibrium is equivalent to the reaction temperature. By changing the column operating pressure, this temperature window can be altered. However, the thermal stability of the catalyst can limit the upper operation temperature of the distillation column.
- Because of the necessity of wet catalyst pellets the chemical reaction has to take place entirely in the liquid phase.
- As it is very expensive to change the catalyst in a structured catalytic packing catalysts with a long lifetime are strongly required.

4.5 The Complexity of Reactive Distillation Process

The design and operation issues for RD systems are considerably more complex than those involving either conventional reactors or conventional distillation columns. The introduction of an in situ separation function within the reaction zone leads to complex interactions between vapor–liquid equilibrium, vapor–liquid mass transfer, intra-catalyst diffusion (for heterogeneously catalysed processes) and chemical kinetics (Taylor and Krishna, 2000). Figure 4.2 shows the various transfer processes in homogeneous and heterogeneous RD. In heterogeneous RD the problem is exacerbated by the fact that these transfer processes occur at length scales varying from 1 nm (pore diameter in gels, say) to say a few meters (column dimensions) (Figure 4.3). The time scales vary from 1 ms (diffusion within gels) to say a few hours (column dynamics). The phenomena at different scales interact with each other. Such interactions, along with the strong non-linearities introduced by the coupling between diffusion and chemical kinetics in counter-current contacting, have been shown to lead to the phenomenon of multiple steady-states and complex dynamics, which have been verified in experimental laboratory and pilot plant units (Bravo, Pyhalathi & Jaervelin, 1993; Mohl et al., 1999; Rapmund, Sundmacher & Hoffmann, 1998). Successful commercialisation of RD technology requires careful attention to the modelling aspects, including column dynamics, even at the conceptual design stage (Doherty & Buzad, 1992). The potential advantages of RD could be nullified by improper choice of feed stage, reflux, amount of catalyst, boilup rate, etc. Thus, it is possible to decrease conversion by increasing the amount of catalyst under certain circumstances (Higler, Taylor & Krishna, 1999b). Increased separation capability could decrease process performance (Sneesby, Tadé, Datta & Smith, 1998a).

(a) homogeneous liquid phase reaction



(b) heterogeneous catalysed reaction

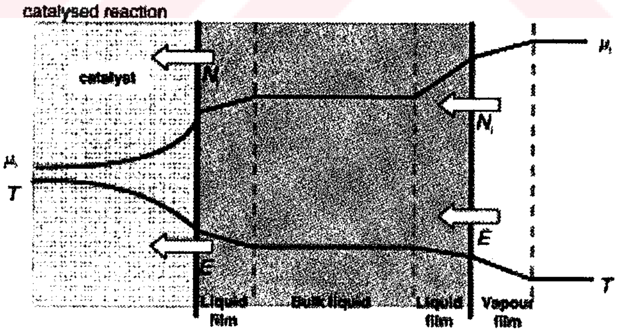


Figure 4.2 Transport processes in RD. (a) homogeneous liquid-phase reaction, and (b) heterogeneous catalysed reactions (Sundmacher 1995)

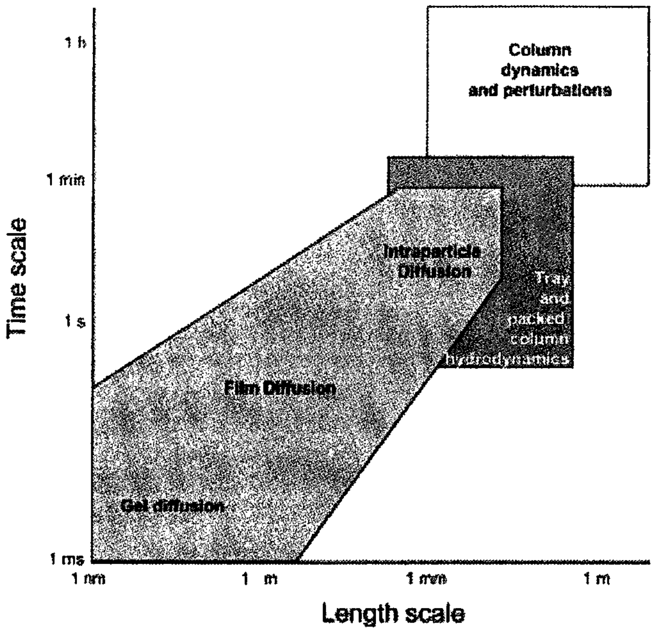


Figure 4.3 Length and time scales in Reactive Distillation (Sundmacher, 1995)

4.6 Practical Design Considerations

Towler and Frey (2000) have highlighted some of the practical issues in implementing a large-scale RD application. These are discussed below.

4.6.1 Installation, containment and removal of the catalyst

It is important to allow easy installation and removal of the RD equipment and catalyst. If the catalyst undergoes deactivation, the regeneration is most conveniently done ex situ and so there must be provision for easy removal and installation of catalyst particles. Reactive distillation is often passed over as a processing option because the catalyst life would require frequent shutdowns. An RD device that allowed on-stream removal of catalyst would answer this concern.

4.6.2 Efficient contacting of liquid with catalyst particles

Taylor and Krishna (2000) presented the conditions to be meet in order to ensure the hardware design as the following:

- Good liquid distribution and avoidance of channeling. Liquid distribution can be expected to have a more severe effect in RD than in conventional distillation (Podrebarac et al., 1998)
- Good radial dispersion of liquid through the catalyst bed. This is required in order to avoid reactor hot spots and runaways and allow even catalyst aging. The requirement of good radial mixing has an impact on the choice of the packing configuration and geometry.

4.6.3 Good vapor/liquid contacting in the reactive zone

If the reaction rate is fast and the reaction is equilibrium-limited then the required size of the reactive zone is strongly influenced by the effectiveness of the vapor–liquid contacting. Vapor–liquid contacting becomes less important for slower reactions. Commonly used devices for good vapor–liquid contacting are the same as for conventional distillation and include structured packing, random packing and distillation trays.

4.6.4 "Low" pressure drop through the catalytically packed reactive section

This problem arises because of the need to use small catalyst particles in the 1–3 mm range in order to avoid intra-particle diffusional limitations. Counter-current operation in catalyst beds packed with such small-sized particles has to be specially configured in order to avoid problems of excessive pressure drop and "flooding".

4.6.5 Sufficient liquid hold-up in the reactive section

The liquid hold-up, mean residence time, and liquid residence time distribution are all important in determining the conversion and selectivity of RD. This is in sharp contrast with conventional distillation where liquid hold-up and RTD are often irrelevant as the vapor–liquid mass transfer is usually "controlled" by the vapor side resistance. For trayed RD columns the preferred regime of operation would be the froth regime whereas for conventional distillation we usually adopt the spray regime.

4.6.6 Designing for catalyst deactivation

It is desirable to allow on-line catalyst removal and regeneration, such devices have not been commercialised as yet. Catalyst deactivation is therefore accounted for in the design stage by use of excess catalyst. Besides adding excess catalyst, the reaction severity can be increased by (a) increasing reflux, leading to increased residence time and (b) increasing reaction temperature (by increase of column pressure).

4.7 Homogeneous and Heterogeneous Reactive Distillation Processes

RD processes can be divided into homogeneous ones, either auto-catalysed or homogeneously catalysed, and heterogeneous processes, in which a solid catalyst catalyses the reaction. The latter, often referred as catalytic distillation (CD), permits an optimum configuration of the reaction and separation zones in a RD column whereas expensive recovery of liquid catalysts may be avoided. However, it should be mentioned that CD shows general drawbacks of heterogeneous catalysis like, e.g. limited catalyst lifetime due to deactivation usually caused by undesired reaction products and increased operating temperature.

Taylor and Krishna (2000), Baur and Krishna (2002) and Noeres et al. (2003) all summarized the design aspects of reactive distillation columns in their work. Here, some of the important issues for homogeneous and heterogeneous reactive distillation processes are presented from these studies. The chart prepared by Noeres et al. (2003) is a good summary of the internals for reactive distillation, which an important type of reactive separation processes, Figure 4.4.

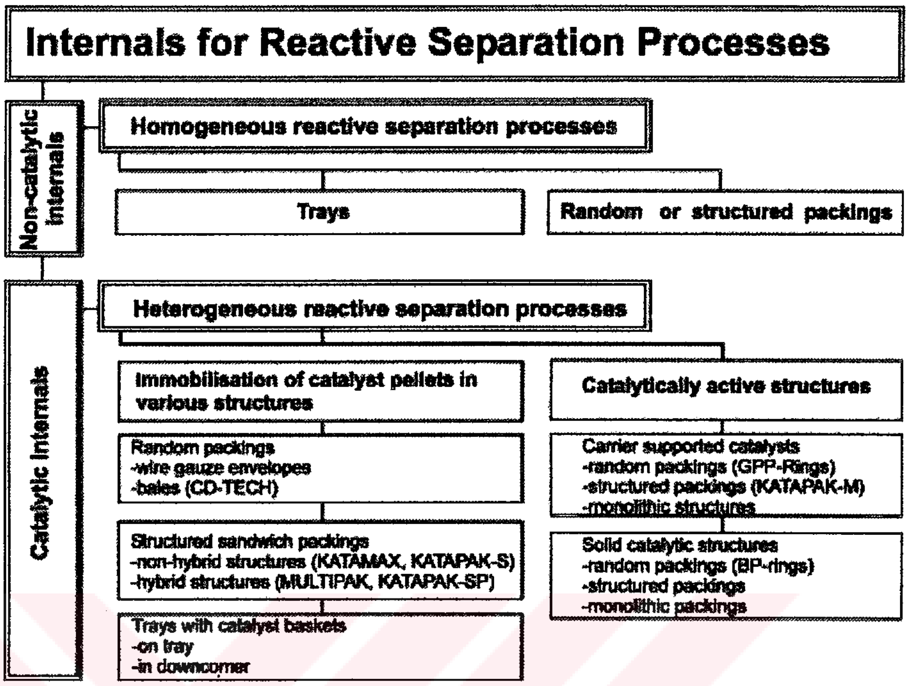


Figure 4.4 Internals for RSP (Noeres et al., 2003)

Taylor and Krishna, 2000, indicated that for homogeneous RD processes, counter-current vapor–liquid contacting, with sufficient degree of staging in the vapor and liquid-phases, could be achieved in a multi-tray column, in Figure 4.5, or a column with random or structured packings, in Figure 4.6. Tray columns were recommended for homogeneous reactive distillation columns because of the greater hold-up and the associated longer residence times in the work of Tuchlenski et al. (2001).

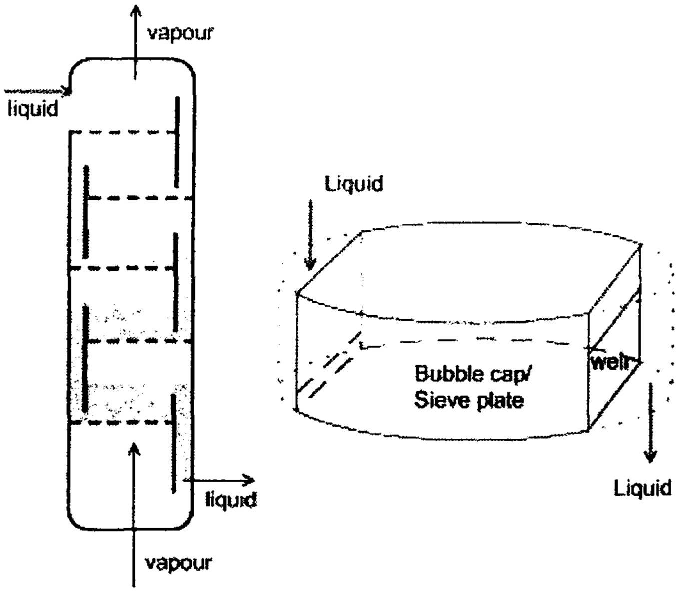


Figure 4.5 Counter-current vapor–liquid contacting in trayed columns
(Taylor and Krishna, 2000)

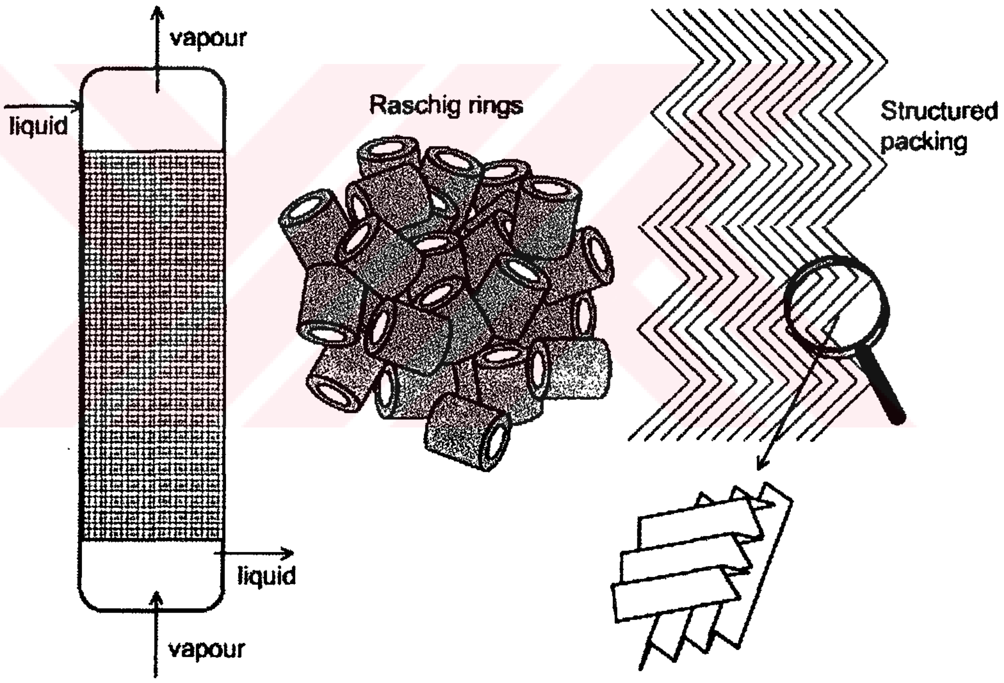


Figure 4.6 Counter-current vapor–liquid contacting in packed columns
(Taylor and Krishna, 2000)

4.7.1 Catalytically Packed RD columns

Taylor and Krishna (2000), Noeres et al. (2003), Baur and Krishna (2002) were also discussed hardware design for heterogeneously catalyses processes. The catalyst particle sizes used in heterogeneously catalysed RD processes are usually in the 1-3 mm range. Larger particle sizes lead to intra-particle diffusion limitations. To overcome the limitations of flooding the catalyst particles have to be enveloped within wire gauze envelopes. The catalyst pellets is immobilized by using these wire gauze mesh from objects of different shapes. These objects together with the catalyst itself form certain structures, which should meet the demands of optimum hydrodynamic behaviour under gas/vapour-liquid counter-current flow conditions. Noeres (2003) presented the requirements to use small solid catalyst particles under counter-current flow conditions as; uniform liquid flow in the catalyst bed without stagnant zones and liquid bypassing; wide gas/vapour and liquid loading ranges without floading; limited catalyst abrasion; possibility of variable catalyst amount and simple catalyst exchange.

Almost every conceivable shape of these catalyst envelopes has been patented; some basic shapes taken from Taylor and Krishna (2000). These were, porous spheres filled with catalyst inside them (Johnson, 1993) in Figure 4.7 (a); cylindrical shaped envelopes with catalyst inside them, (Johnson, 1993) Figure 4.7 (b); wire gauze envelopes with various shapes: spheres, tablets, doughnuts, etc. (Smith, 1984); Figure 4.7 (c).

Horizontally disposed wire-mesh "gutters", filled with catalyst (Van Hasselt, 1999); Figure 4.8(a); horizontally disposed wire-mesh tubes containing catalyst (Buchholz et al., 1995); Figure 4.8(b).

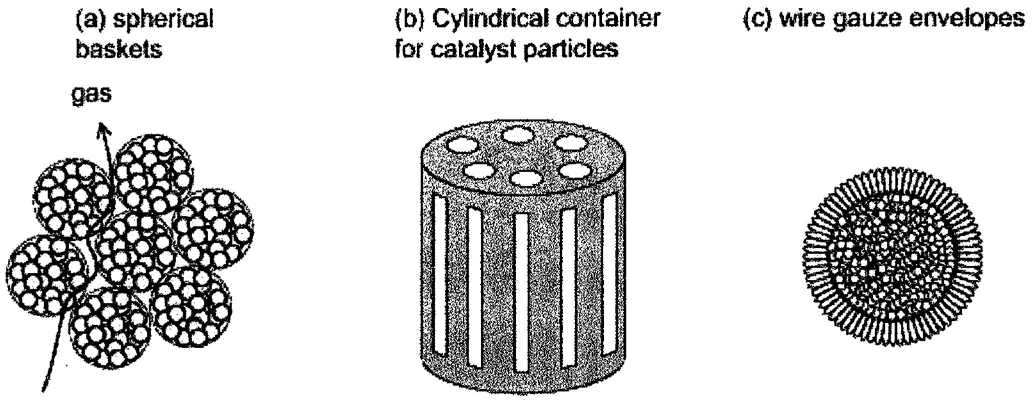


Figure 4.7 Various "tea-bag" configurations. Catalyst particles need to be enveloped in wire gauze packings and placed inside RD columns (Buchholz et al., 1993, Johnson, 1993, Smith, 1984)

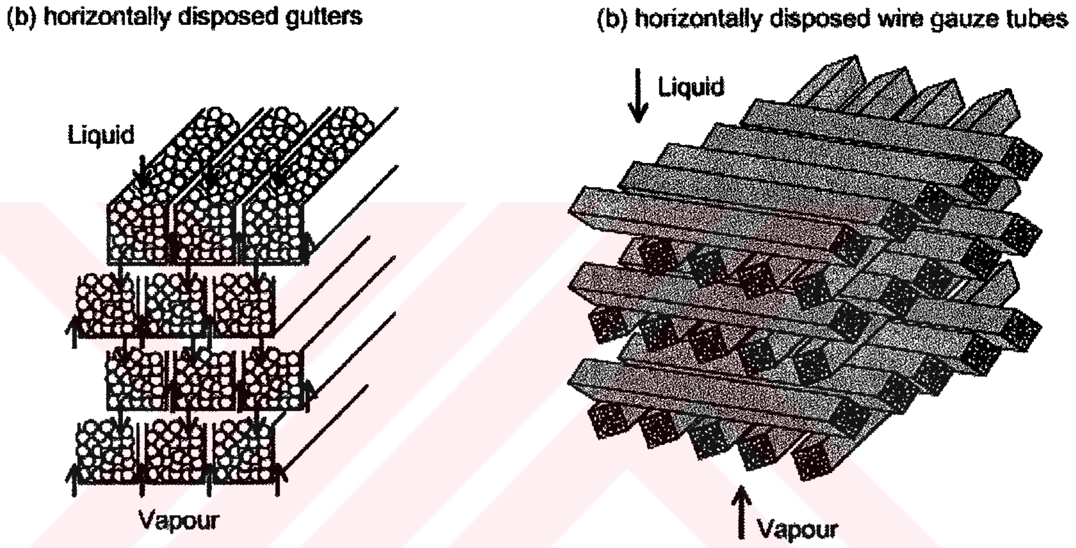


Figure 4.8 Horizontally disposed (a) wire gauze gutters and (b) wire gauze tubes containing catalyst (Van Hasselt, 1999, Buchholz et al., 1995)

Another commonly used structure in the industry to be mentioned by Taylor and Krishna (2000) and Baur and Krishna (2002) is catalyst particles enclosed in cloth wrapped in the form of bales (Johnson & Dallas, 1994; Smith, 1985). This is the configuration used by Chemical Research and Licensing in their RD technology for etherification, hydrogenation and alkylation of aromatic compounds. The catalyst is held together by fibreglass cloth. Pockets are sewn into a folded cloth and then solid catalyst is loaded into the pockets. The pockets are sewn shut after loading the catalyst and the resulting belt or "catalyst quilt" is rolled with alternating layers of steel mesh to form a cylinder of "catalyst bales" as shown in Figure 4.9. The steel mesh creates void volume to allow for vapor traffic and vapor/liquid contacting. Scores of these bales are installed in the reactive zone of a typical commercial RD column. Bales are piled on top of each other to give the required height necessary to achieve the desired extent of reaction. When the catalyst is spent the column is shut down and the bales are manually removed and replaced with bales containing fresh catalyst.

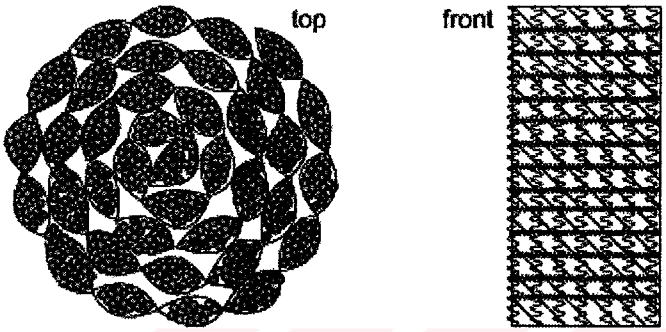


Figure 4.9 Catalyst bales licensed by Chemical Research and Licensing (Smith 1985)

Besides this type of random packings, structured sandwich-type packings were studied. In this case, catalyst pellets are immobilised between two sheets of corrugated wire gauze forming a sandwich, such as KATAMAX (Gelbein & Buchholz, 1991) (Figure 4.10). A parallel arrangement of these layers results into open and closed channels for the gas/vapour and liquid flow, respectively, which show hydrodynamic characteristics similar to those of traditional structured packings, e.g. reduced pressure drop and optimum flow conditions within a wide operating range. These catalyst "sandwiches" or "wafers" are bound together in cubes. The resulting cubes are transported to the distillation column and installed as a monolith inside the column to the required height. When the catalyst is spent, the column is shut down and the packing is manually removed and replaced with packing containing fresh catalyst.

The important advantage of the structured catalyst sandwich structures over the catalyst bales is with respect to radial distribution of liquid. Within the catalyst sandwiches, the liquid follows a criss-crossing flow path. The radial dispersion is about an order of magnitude higher than in conventional packed beds (Van Gulijk, 1998). Furthermore, frequent criss-crossing leads to a significant improvement in mass transfer within the sandwich structures (Higler et al., 1999a).

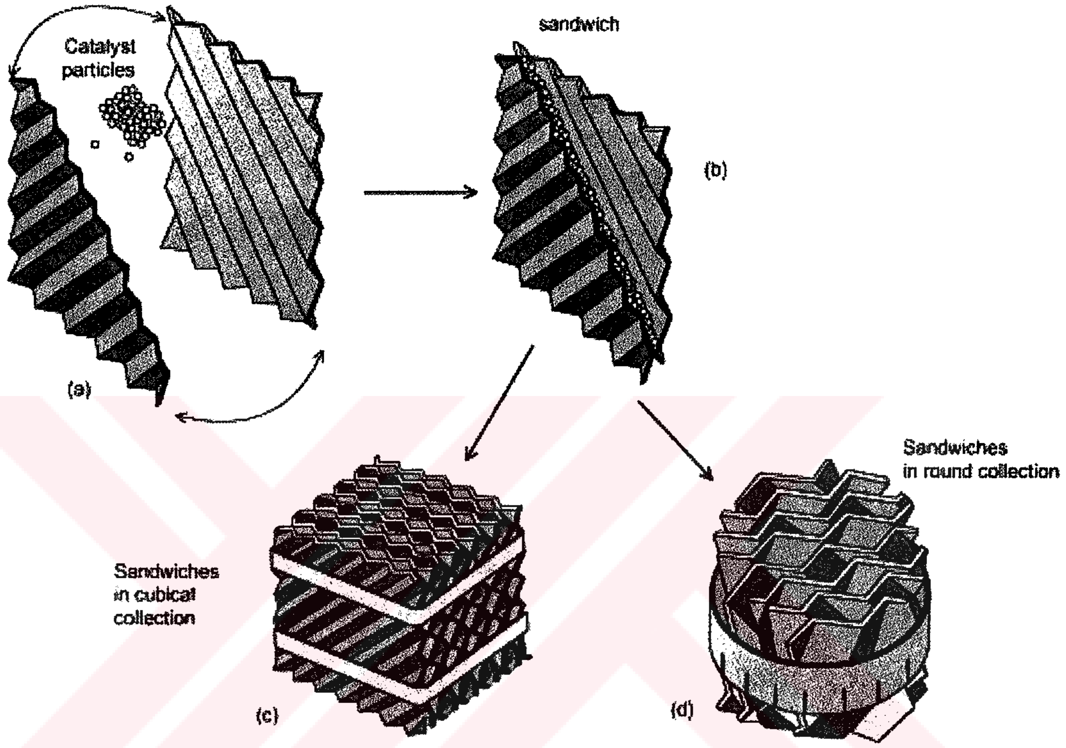


Figure 4.10 Structured catalyst-sandwiches. (a) Catalyst sandwiched between two corrugated wire gauze sheets. (b) The wire gauze sheets are joined together and sewn on all four sides. (c) The sandwich elements arranged into a cubical collection. (d) The sandwich elements arranged in a round collection (Taylor and Krishna, 2000)

Another alternative hardware choice for heterogeneous RD processes is to make the packing itself catalytically active, as indicated in the literature. These can be done in two ways either solid catalytic structures or carrier supported catalyst. The first possibility is the strategy adopted by Flato and Hoffmann (1992) and Sundmacher (1994) wherein the Raschig ring-shaped packings are made catalytically active; see Figure 4.11 (a). The catalyst rings can be prepared by block polymerisation in the annular space. Their activity is quite high, however, osmotic swelling processes can cause breakage by producing large mechanical stresses inside the resin. An alternative configuration is the glass-supported precipitated polymer prepared by precipitation of styrene-divinylbenzene copolymer, which is subsequently activated by chlorsulphonic acid.

The second possibility is carrier supported catalyst. Carrier supports can be coated with any kind of catalyst. For example, to coat structured packing with zeolite catalysts was used by Oudshoorn (1999) Figure 4.11 (b). The catalyst can also be "cast" into a monolith form and used for counter-current vapor–liquid contacting, Lebens (1999) has developed a monolith construction consisting of fluted tubes, Figure 4.11 (c).

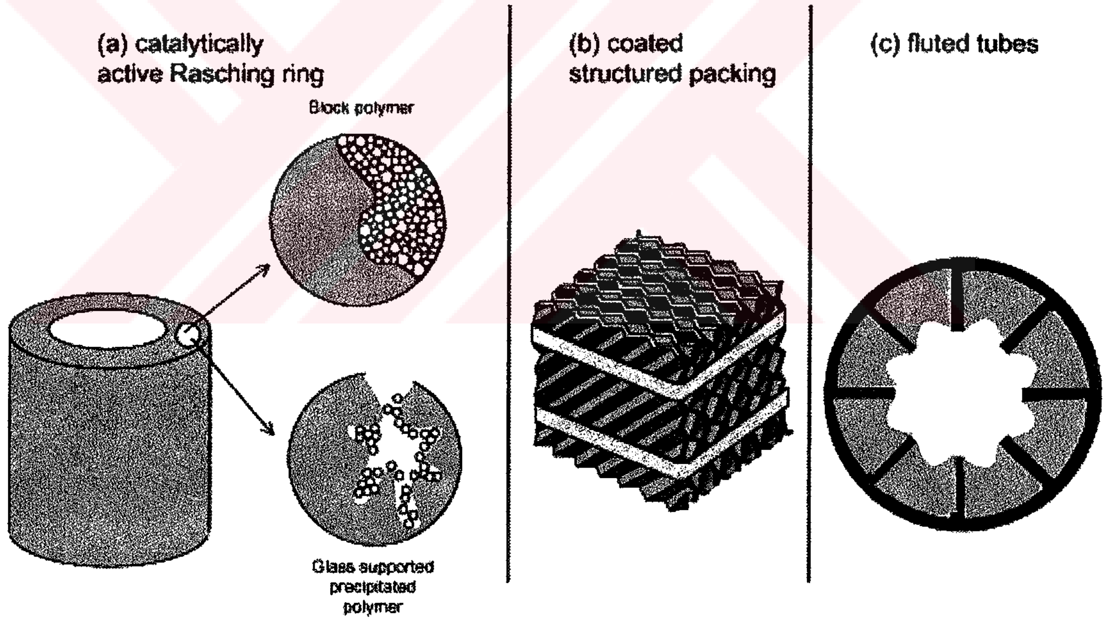


Figure 4.11 (a) Catalytically active Raschig ring (b) Structured packings coated with catalyst (c) Fluted catalyst monolith tubes (Sundmacher, 1995, Oudshoorn, 1999, Lebens, 1999)

Most commonly, the catalyst envelopes are packed inside the column. The catalyst envelopes can be placed in a tray RD column and many configurations have been proposed in the literature.

4.7.2 Trays or downcomers to hold catalyst

Wire gauze envelops filled with catalyst pellets can be placed on trays, either across the tray or in the downcomer section. Also, catalyst beads can be immobilised like in a fixed-bed reactor between two non-reactive distillation trays as well as in an external side stream reactor.

In the work of Jones (1985), vertically disposed catalyst containing envelopes were placed along the direction of the liquid flow path across a tray, Figure 4.12. These envelopes are almost completely immersed in the froth on the tray, ensuring good contact between liquid and catalyst. Furthermore, since the vapor and liquid-phase pass along the packed catalyst in the envelopes, and not through them, the pressure drop is not excessive.

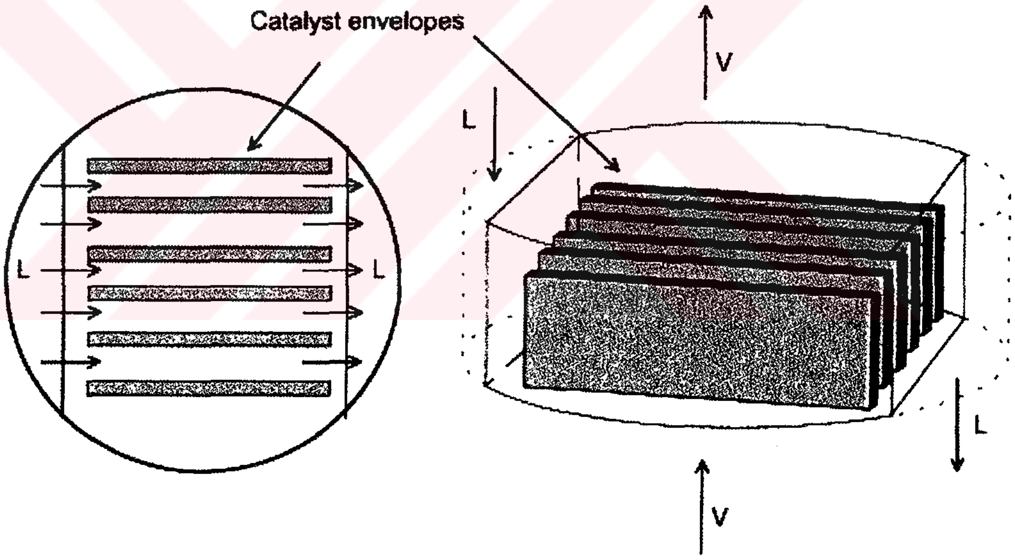


Figure 4.12 Catalyst envelopes placed along the liquid flow path (Jones, 1985)

Carland (1994) placed the catalyst envelopes within the downcomers as in the Figure 4.13 (a). The primary drawback with installing the catalyst within downcomers is the limited volume available for catalyst inventory. Each "stage" can be regarded as a reaction device (downcomer) followed by a separation section (froth on the tray). Whereas, Asselineau et al. (1994) placed catalyst envelops near the exit of the downcomer, Figure 4.13 (b). In this case, catalyst inventory is necessarily limited and the vapor does not pass through the catalyst envelopes.

Trays and packed catalyst sections can also be used on alternate stages (Nocca et al., 1989; Quang et al., 1989); see Figure 4.13 (c). The vapor flows through the packed section through a central chimney without contacting the catalyst. The liquid from the separation trays is distributed evenly into the packed reactive section below by a distribution device.

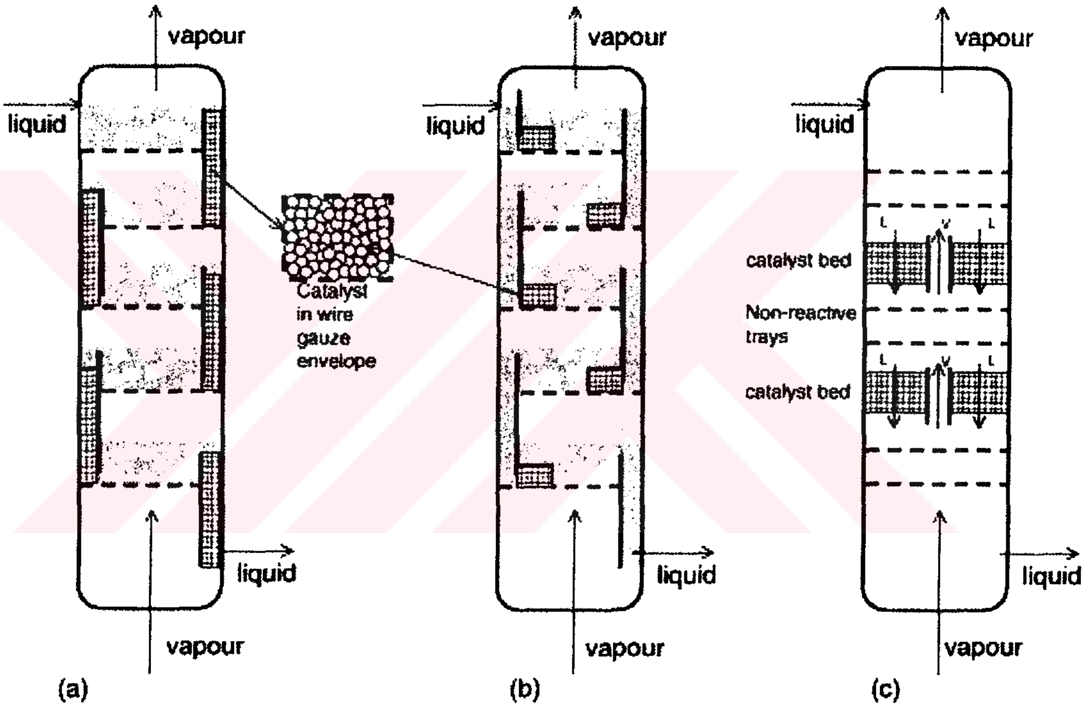


Figure 4.13 Counter-current vapor–liquid–catalyst contacting in trayed columns. (a) catalyst in envelopes inside downcomers (Carland, 1994) (b) tray contacting with catalyst placed in wire gauze envelopes near the liquid exit from the downcomers (Asselineau, Mikitenko, Viltard & Zuliani, 1994) and (C) alternating packed layers of catalyst and trays (Nocca et al., 1989)

Other designs have been proposed for tray columns with catalyst containing pockets or regions that are fluidised by the upflowing liquid, Jones (1992).

4.8 RD Applications to Etherification Reactions

The application of RD is quite attractive for the heterogeneously catalyzed production of fuel ethers, because their formation is affected by the chemical equilibrium.

The flow scheme of a common industrial process for the production of the fuel ethers, *tert*-amyl-methyl ether (TAME) or methyl-*tert*-butyl ether (MTBE), in comparison to a possible process in which a reactive distillation was involved, Sundmacher et al. (1999) is given in Figure 4.14 (a) & (b), respectively.

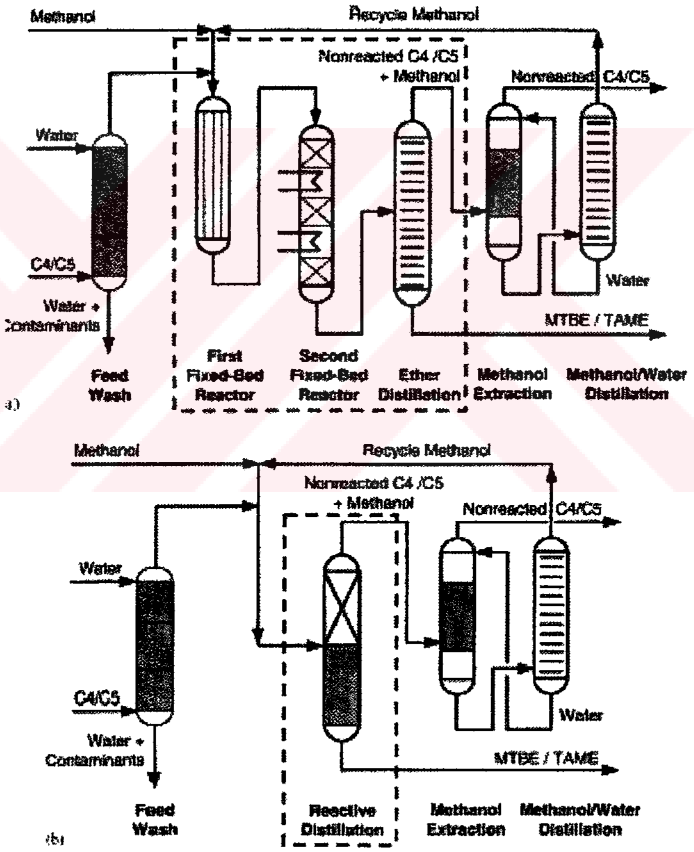


Figure 4.14 (a) Flow scheme of a conventional process fro the production of fuel ethers. (b) Flow scheme of a process including a reactive distillation column for the production of fuel ethers (Sundmacher, 1999)

In the first step of both processes, impurities were removed from the mixture of the reactive olefins and inert hydrocarbons in a feed wash. In the first fixed-bed reactor the main part of the overall conversion of reactive olefins was attained. This reactor was filled with an acid ion exchange resin as catalyst. For the further increase of the olefin conversion a second reactor was necessary in the common industrial process. In a fourth step the product TAME was isolated via distillation from hydrocarbons and methanol. This unreacted methanol was removed from unreacted and inert hydrocarbons via an extraction step and separated from water via distillation. Then, methanol could be recycled to the fixed-bed reactor. The process, which involved a reactive distillation, combines three process steps of the common process and, this achieves significant savings of energy and investment costs.

The development and start-up of a small-scale packed distillation column for the production of MTBE was discussed by Flato and Hoffmann (1992). The *iso*-butene conversion and MTBE selectivity as a function of methanol/*iso*-butene ratio in the feed and the effect of pressure on *iso*-butene conversion were investigated.

Nijhuis et al. (1993) simulated the MTBE synthesis in fixed-bed reactor and in a reactive distillation column. In a fixed-bed reactor, the isobutene conversion was limited by its thermodynamic equilibrium value and this equilibrium value decreased with increasing values of the reactor temperature. Also, in a countercurrently cooled reactor, hot spots might occur which resulted in a relatively low value of the isobutene conversion and in a decrease of the selectivity of the reaction. Therefore, MTBE reactors were operated with a recycle flow causing smooth temperature and reaction rate profiles. However, the obtainable isobutene conversion value in a recycle reactor was limited. These results of the Nijhuis et al. (1993) showed the benefits of the use of reactive distillation for the synthesis of MTBE.

Due to the interaction between chemical reaction and distillation, reactive distillation can exhibit highly non-linear behavior and multiple steady state (MSS) solutions are often possible. Instabilities and multiple steady states of reactive distillation processes can have different sources. Mohl et al. (2001) summarized the major sources for multiplicity/instability in reactive distillation processes as follows: the first type of multiplicity/instability can be caused by certain types of reactive vapor liquid equilibria for processes with fast reversible reactions, which are operated close to chemical equilibrium. Reactive residue curve maps can be used to analyze and to explain these multiplicities. Jacobs and Krishna (1993), Nijhuis et al. (1993), Hauan et al. (1995), Schrans et al. (1996) and Perez-Cisneros et al. (1996), studied MTBE production by reactive distillation which shows this type of multiplicities. In these studies, the column pressure was considered 11 atm, where the process was close to chemical equilibrium. Further, transport processes inside the porous catalyst were neglected in the first step. However, Mohl et al. (1997,1999) founded that the multiplicity regions in the space of the adjustable operating parameters are very small for the given column. Further, Higler et al. (2000), showed that that multiplicity region even seem to disappear entirely, when finite transport processes inside catalyst were taken into account.

The second type of multiplicity/instability can occur in the kinetic regime of the chemical reaction. In principle, kinetic instabilities are either related to self-inhibition by the reactants or to autocatalysis by the products (Matsuura & Kato, 1967). It was shown that this type of instability-in contrast to the so-called thermal instabilities-directly carried over to catalytic distillation processes. A typical example of this kind is the production of TAME, which was studied theoretically and experimentally by Mohl et al. (1999). In this case, self-inhibition was caused by the strong adsorption of the reactant methanol on the catalyst. It was found that these multiplicities existed under practically relevant operating conditions and that the multiplicity regions were much bigger than those for the MTBE case close to chemical equilibrium. Further, it was found transport processes inside the catalyst were negligible for the TAME process, because the microkinetic rate of reaction was one order of magnititude slower than in the MTBE cases and was therefore dominating for the operating conditions considered. Higler et al. (2000) confirmed this.

For identical column feed flows, reflux ratios, and catalyst weights, a multiplicity occurs in reactive distillation for production of MTBE. The occurrence of either case depends on the initial state of the column and that by changing operating conditions it is possible to jump from one state to the other. To investigate the multiplicity of steady-states in RD columns, RADFRAC that is part of the commercial program Aspen Plus, was used by Jacobs and Krishna (1993), Nijhuis et al. (1993) and Hauan, (1995).

The column configuration used by Jacobs and Krishna (1993) had two feed streams, a methanol feed and a mixed butenes feed (0.356 mol % iso-butene, 0.654 mol% n-butene). Varying the location of the stage to which methanol was fed resulted in a high or low conversion, 99% or 36% respectively. The same configuration was studied to analyze MTBE synthesis using nonequilibrium stage (NEQ) approach and equilibrium stage (EQ) approach by Higler et al. (1999). In the other study, Baur et al. (1999), observed steady-state multiplicity, when the methanol was fed to stages 10 or 11.

Jacobs et al. (1993) proposed that high conversion corresponded to residue curves starting near the n-butene-methanol azeotrope; low conversion corresponded to residue curves starting in pure isobutene. Hauan et al. (1995) presented the mechanistic explanation for the existence of the two conversion branches.

Nijhuis et al. (1993) used a column consisted of 17 equilibrium stage and reactive section was in the middle of the column to show the effect of amounts of catalyst in the column and the reflux ratio on the isobutene conversion. According to this study, it was proposed that at least two types of steady states might occur, a high isobutene conversion state with a relatively low temperature in the reactive zone; a low isobutene conversion state with a relatively high temperature in the reactive zone. At the high conversion state, the isobutene conversion increased with increasing amounts of catalyst until a limiting value reached and was independent of reflux ratio, providing reflux ratio higher than 4. In the case of low conversion state, conversion decreased increasing amounts of catalyst. However, increasing reflux ratio initially increased then decreased the isobutene conversion.

Generally, the etherification reactions of MTBE and TAME are carried out in the presence of inert components. As in the case of Jacobs and Krishna (1993), a binary mixture of isobutene (35.6 mol %) and 1-butene was used in the study of Nijhuis et al., (1993). This butene mixture was regarded as a simplification of FCC butene stream assuming that the C4's like trans-2-butene, cis-2-butene, and butanes do not significantly change in the physical and chemical behaviour of the isobutene and 1-butene mixture. This methanol, isobutene, 1-butene mixture can be regarded as a pseudobinary system. Schrans et al. (1996) and Chen et al. (2002) used n-butane rather than n-butene. Again, Mohl et al. (1999) used 1-butene to represent inert components result from upstream processing.

Schrans et al. (1996) carried out dynamic simulations, using SPEEDUP, of the MTBE synthesis process using essentially the Jacobs–Krishna column configuration. They showed that fixing the bottom flow rate or fixing the reboiler temperature lead to multiple steady states and the reactive distillation column was 'unstable' for certain disturbances of the feed. Also, it was proposed that, the isobutene conversion on the high conversion branch was not a monotonically increasing function of the reflux ratio. They showed that increase in the *iso*-butene feed by 4% leads to oscillatory behaviour. A further increase of *iso*-butene feed by 5% causes a jump from the high-conversion steady-state to the lower one. Hauan, Schrans and Lien (1997) also showed oscillatory behaviour and suggested that it is due to an internal recycle of MTBE in the reactive zone.

The experimental confirmation of multiple steady states in reactive distillation has been, also, provided by Bravo et al. (1993), Thiel et al. (1997), Mohl et al. (1997a), Rapmund et al. (1998) in their studies. For the TAME synthesis the experimental work of Bravo et al. (1993) indicates the existence of multiple steady states in a pilot plant catalytic distillation column. In theoretical studies, Mohl et al. (1997a) found multiple steady-states for operating conditions similar to those in Bravo et al. (1993).

Mohl et al. (1999) carried out a study on the MTBE and TAME production; the column had a single feed in the middle of the column, different from the Nijhuis et al. (1993). Also, the top the reflux ratio and at the bottom the heating rate (instead of the molar bottoms flow rate) were the input variables. They took the experimental temperature and concentration profile data for MTBE from Thiel et al., 1997, and those for TAME from Rapmund (1998). Mohl indicated that multiple steady states for the TAME processes are due to the kinetic instabilities.

Temperatures have been measured by means of thermocouples placed inside the column and as indicated by Baur et al. (2003) and it is not possible to specify whether the temperatures refer to the vapour or liquid phases. It is likely that the thermocouples record the higher of the two temperatures. Baur et al. (2003) developed the bifurcation diagram for the reactive distillation column using the reboiler load as continuation parameter and they conformed that at a reboiler load of 340W, there was a steady-state multiplicity. In their simulations, there was a finite difference between the vapour and liquid temperatures. This difference was due to the fact that the heat transfer between the gas and liquid phases in the laboratory column is not high. They noted that the vapour temperatures are closer to the experimentally determined values than the liquid temperatures. This was understandable in the view of the fact that the thermocouples probably sense the higher of the two temperatures. They also noted that the agreement in the temperature profiles between the experiments and simulations is not very good. The temperature rises are linked to changes in the composition profiles. The resulted values agree with the trends in the experimental values of Mohl et al. (1999).

Sundmacher (1999) selected operating parameters as reflux ratio, reboiler heat input and pressure on the process performance (conversion, yield, selectivity) for TAME and MTBE reaction. They performed experiment in stainless-steel laboratory columns with unstructured Rasching ring packings. These columns were operated at elevated pressures up to 1 MPA and temperature up to 200°C. The noncatalytic packing consists of the same porous glass rings without the ion-exchange polymer. In both columns the packing is distributed in an upper catalytic part and a lower noncatalytic part. The feed point of the premixed reactants and the inert components was in the middle between the two packings. They stated that due to the fact that the TAME-formation rate was more than ten times lower than the MTBE-formation rate, mass transfer resistances inside the catalysts bodies were negligible, land therefore a quasihomogeneous approach should be sufficient to describe the TAME-reactive distillation column. In this study, the bottom product contained no methanol and the composition of the distillate is dominated by the existence of the binary azeotrope between methanol and the C_5-components (the two reactive isoamylene isomers 2M1B and 2M2B and the inert solvent n-pentane are lumped together to one single C_5-fraction). The concentration of the desired product TAME in the bottom was not very high. This is caused by a relatively low reaction rate and a high reflux ratio, which forces considerable amounts of C_5-components to leave the column at the bottom. According to the TAME-reaction kinetics, higher etherification rates in the catalytic column section should be achievable at a higher content of isoamylene a lower content of methanol in the feed mixture. The formation of high boiling dimmers from isobutene and the accumulation in the liquid phase lead to a considerable increase of the temperatures in the bottom section of the MTBE-column.

Essentially, two different types of catalyst were employed for MTBE synthesis in catalytic distillation (Sundmacher, 1995). The first type consisted of ion-exchange resin spheres, which were filled into the pockets of some structured packing. These packings were either introduced into tray or packed columns. Typically, Amberlyst A 15 was used as ion exchange resin. The size of the catalyst particles was in the range of 0.3-1.2 mm. An alternative process with application to MTBE (Flato & Hoffmann, 1992; Sundmacher & Hoffmann, 1996; Higler et al., 1999) and TAME (Hoffmann et al., 1997) at the synthesis has been developed at the Institut für Chemische Reaktionstechnik (ICVT) at Technische Universität Clausthal. Here, the catalyst is introduced into the reactive distillation column in the form of a packed bed of catalytically active Raschig rings. The Raschig rings are either produced by block polymerization or precipitation polymerization on porous glass support (Kunz & Hoffmann, 1995). The main difference between these two polymers is the concentration of active sites. Both types are available as Raschig rings (hollow cylinder) with size 6×6 or 8×8 mm. In the remainder, focus is on Amberlyst A 15 and on Raschig rings produced by precipitation polymerization.

Both packed columns (random packed or structured) and tray columns were used in reactive distillation processes. Mohl et al. (2001), considered different system configurations such as one-tray, multi-tray, as well as packed reactive distillation columns. At the top of the one-tray column, Figure 4.15, the reflux ratio R is fixed. In practice, this is achieved by some suitable ratio control between the reflux and the distillate flow. At the bottom of the column, the ratio between the heating rate Q and the feed mass flow F_m is fixed. Again, this can be achieved by some suitable ratio control. In contrast to previous work (Jacobs & Krishna, 1993; Nijhuis et al., 1993; Hauan et al., 1995; Schrans et al., 1996; Perez-Cisneros et al., 1996) focus is on a column pressure of 7 bar, which is also used in industries. In a tray column with N_S trays, a total condenser being tray 1 and a total reboiler being tray N_S, reaction takes place in the upper half of the column, where the column trays are filled with catalyst. Instead, the lower half of the column is nonreactive. The feed is supplied on the lowest catalytically active column tray. Again, the reflux ratio R and the ratio of the heating rate Q and the feed mass flow rate F_m is fixed. In contrast to previous work (Mohl et al., 1999) the influence of intraparticle transport resistances in the catalyst phase was taken into account. Two different types of multiplicities have been identified. The first is induced by ignition and extinction of every single column tray. The second comes from isothermal multiplicity of the single catalyst pellet.

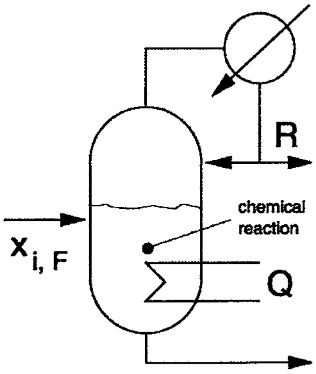


Figure 4.15 One-tray column with partial reboiler and total condenser (Mohl et al., 2001)

In tray columns the first mechanism is dominant. This can lead to a large number of different steady state solutions for a given set of operating conditions. If N is the number of steady states (typically an odd number). Then $(N+1)/2$ of these steady states are stable. This can lead to complex multi-stable dynamic behavior during column startup and set point or load changes. These phenomena were observed for vanishing as well as for finite intraparticle mass transfer resistance.

Instead for packed columns, a qualitative difference was found for finite and infinite intraparticle mass transfer resistance. For vanishing mass transfer resistance, the number of solutions is reduced to a few, typically three, as the discretization is getting finer and the volume of each cell tends to zero (Mohl et al., 2001). A different type of behavior was observed for finite intraparticle mass transfer resistance. In this case, it was found, that the number of steady state solutions increases as the discretization is getting finer. It is expected that this behavior is caused by isothermal multiplicity of the single catalyst pellet and is therefore similar to the well-known fixed-bed reactor. However, further research is required to verify this hypothesis.

In all cases, kinetic multiplicities can be avoided by an increase of the Damköhler number, i.e. increase of the number of catalytically active sites, or a decrease of the feed rate, respectively. Moreover, they will vanish if the column pressure is increased. In all cases the column gets closer to chemical equilibrium.

Also, Baur et al. (2001) selected two types of configuration for the reactive section. Firstly, ¼ in. random packed Rasching ring shaped catalyst and the second choice was that of sieve trays with catalyst envelopes maintained on the trays. The catalyst inventory in the reactive zone was the same for both configurations. In the base case tray configuration was chosen as 5-liquid pass as shown in Figure 4.16. They concluded that the tray and packed column configurations showed different bifurcation behaviors. When operating on the high conversion branch, the conversions obtained with the tray and packed column configurations were virtually the same. However, decreasing the number of liquid flow passes and thereby increasing the liquid load per weir height and liquid phase residence time could improve performance obtained in the tray column configuration. In that, as indicated by Van Baten et al. (2001), the liquid hold-up is usually much higher in sieve tray columns as compared to packed columns and this is advantage when carrying out relatively slow, catalysed, liquid phase reactions. A further advantage of a catalytic sieve tray construction is that the contacting on any tray is cross-current and for large diameter columns, there will be a high degree of staging in the liquid phase; this is advantageous from the point of view of selectivity and conversion. Of course, from an overall point of view, in a multi-stage catalytic sieve tray column the vapour–liquid contacting is *counter-current*. The catalytic sieve tray construction has been patented and is being used in industrial practice, there is no published information on the hydrodynamics of such contacting devices.

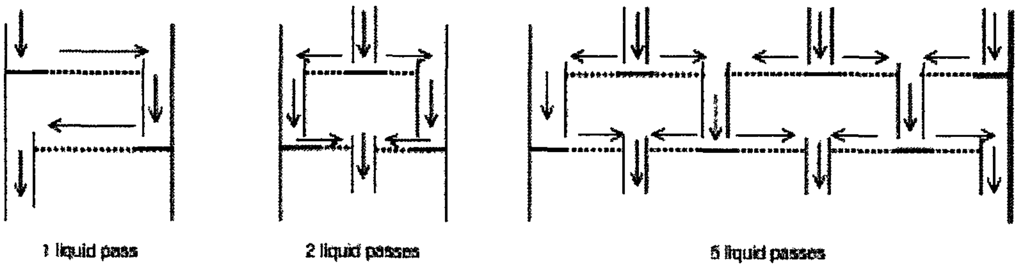


Figure 4.16 Tray configurations (Baur et al., 2001)

The flow scheme used by the Baur et al. (2002), consisted of a pre-reactor followed by an RD column is shown in Figure 4.17 which followed that of Subawalla and Fair (1999). The use of an isothermal pre-reactor is advantageous because high overall TAME production rates can be obtained when the IA conversion in the pre-reactor is in the range 55–65%. In this study it was assumed that a pre-reactor with an IA conversion of 62.7%, identical to that assumed by Subawalla and Fair (1999). Subawalla and Fair (1999), considered a feed stream to the pre-reactor to consist of four inert components: isopentane, *n*-pentane, 1-pentene and 2-pentene. In order to reduce the complexity of the system we decided to consider only a single inert component, isopentane. Although the boiling points of the inert components differ, by about 8 K at 4.5 bar pressure, the choice of a single inert component does not significantly alter the thermodynamic. The binary mixture of methanol and isopentane reveals a single minimum-boiling azeotrope (x_{MeOH}=0.269 at P=4.5 bar), just as found between methanol and the four C_5 inert components used in the Subawalla–Fair (1999) study.

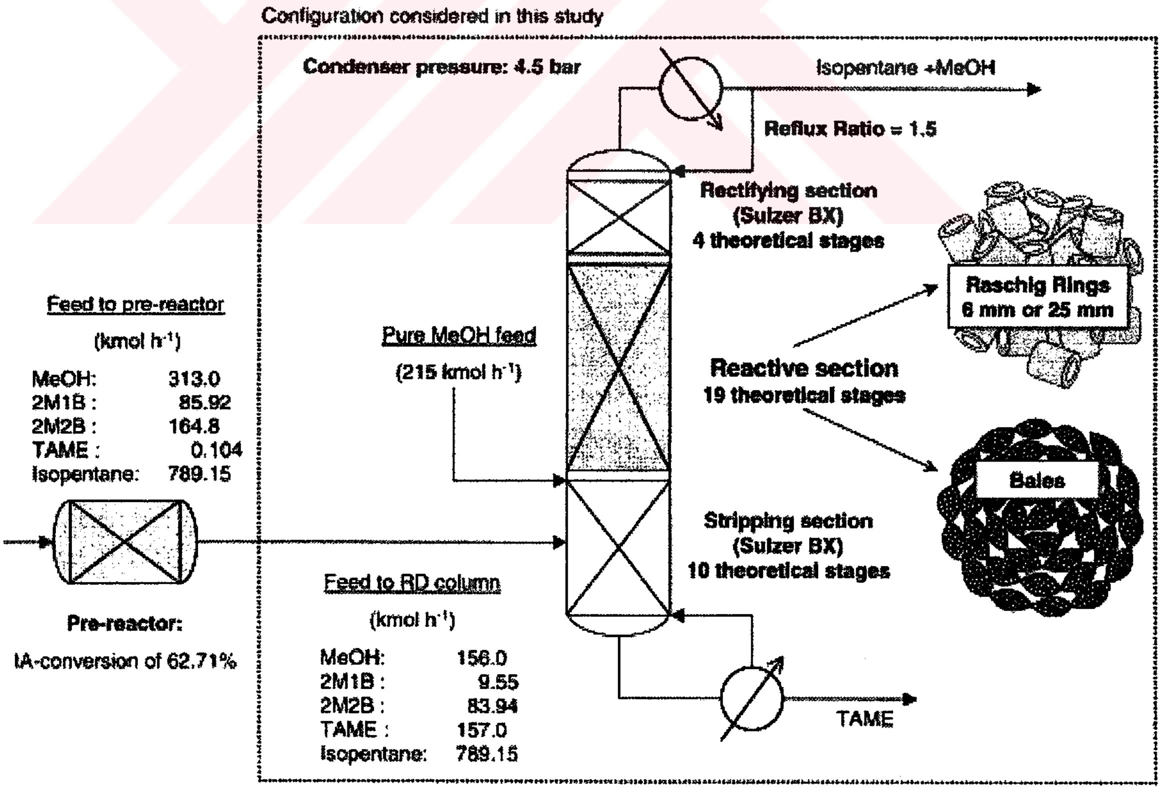


Figure 4.17 Column configuration including a pre-reactor (Subawalla and Fair, 1999)

The choice of the operating pressure is a trade-off between conversion and separation requirements. Increasing pressure causes increased reaction rates and a shift of chemical equilibrium due to higher boiling point temperatures in the reactive zone. On the other, increasing column pressure reduces the relative volatility. Increased pressure results in larger MeOH feed requirements whereas lower pressure requires higher demand of catalyst load in order to meet the desired specifications. Baur et al. (2002) investigated the influence of the operating pressure on conversion and separation requirements keeping both the catalyst load and MeOH feed flow constant. They founded that the local maxima when the reboiler load ranges from 17 to 19 MW at constant operating pressure. And they noted that the TAME impurity in the top product of the RD column increased sharply when the operating pressure increased beyond 4.5 bar. Low operating pressures resulted in lower boiling point temperatures in the reactive section and lower maximal attainable TAME purity in the bottoms flow rate. On the other hand, high operating pressure, say above 5 bar, would also significantly increase the TAME impurity in the distillate due to lower relative volatility and higher methanol requirements for the azeotropic mixture. Operating the column at a pressure between 4.3 and 5 bars, in the study of Baur et al. (2002) provided a potential setup that might satisfy all process specification.

Isla et al. (1996) pointed out the importance of the MeOH/total C4 feed ratio. If this ratio belongs to the C_4-rich side of the MeOH-total C_4 pseudobinary azeotrope, most of the methanol fed will flow upwards from the feed stage, trying to increase its concentration in the column upper stages. Under these feed conditions, MeOH dies out rapidly in the downward direction, reaching only a few stages below the feed position, and unreacted MeOH can be removed from the top of the distillation column despite the fact that it has the lowest pure-component vapor pressure among all components. Fractionation between MTBE against C_5 and C_4 hydrocarbons occurs along the stripping section, and a liquid stream of MTBE containing C_5 hydrocarbons can be withdrawn from the bottom. Increasing the reflux ratio can increase the iC_4 conversion to MTBE. This behaviour can be linked to the extent in which MTBE can be confined in the stripping section. Fractionation of MTBE against more volatile components in the stripping section improves by increasing reflux ratio, R, depleting the MTBE concentration zone with a minor modification of the iC_4/MeOH ratio and favoring the iC_4 conversion to MTBE. As R becomes larger than a certain value depending on the operating conditions, the iC_4 conversion can only be marginally improved by increasing the reflux ratio. The total catalyst load, the catalyst weight distribution among reactive stages, and positioning of the reactive stages in the rectifying section are design parameters with a great impact on the conversion. The iC_4 conversion to MTBE increases with the number of reactive stages at total catalyst load, due to the fact that the series of CSTR's each time approximates better the behavior of continuous plug flow reactor.

Besides MTBE and TAME production, ETBE synthesis was also carried out in a reactive distillation column in the literature. The column simulation of ETBE was performed by Sneesby et al. (1997 a, b), in a way similar to that for MTBE columns using both Pro/II and Speed-Up. The differences between the ETBE production and the MTBE production in a reactive distillation column were given in this study. While methanol was recovered with the distillate product from the MTBE reactive distillation column, ethanol was predominantly recovered with the bottom products, in the case of ETBE. Moreover, MTBE production was best around 60% isobutylene in the feed whereas ETBE production was more attractive with low isobutylene feed conditions. Also, they inferred the necessity of a high reflux rate for maximum conversion although satisfactory operation could be achieved with a low reflux rate and more stages.

Another dynamic simulation performed for a reactive distillation column with ETBE synthesis was the study of Jhon and Lee (2003). They performed adopting the startup policy with total reflux, which was used practically for the conventional distillation process in the industry. The RD performances for the total condenser, TC, and the partial condenser, PC, were compared with each other in this study. They presented the dependencies of the IB conversion and the ether purity on the reboiler duty for total condenser. They concluded that the optimal reboiler value was located in a very narrow region. Jhon and Lee (2003) presented that the ultimate composition profiles of TC and PC showed the considerable differences in the lower section of column (the stages 11–20), causing the temperature and liquid molar flow rates differences, from their results.

Most reports about the production of ETBE are focused on the method of liquid phase synthesis from (EtOH) and isobutylene (IB). However, the IB source is limited only to catalytic cracking or steam cracking fractions. It is also used in other chemical industries as a starting material, and cannot meet the increasing demand of *tert*-ethers. *tert*-butyl alcohol (TBA) which is a major by-product for the manufacture of propylene oxide from isobutane and propylene, can provide an alternative route for the synthesis of ETBE reacting with ethanol. Matouq et al. (1996), Quitain et al. (1999) and Yang et al. (2000), some of the researchers studied this reaction in the reactive distillation column.

Since the synthesis of ETBE from TBA and ethanol itself will produce water, the content of water in EtOH will become unimportant and it would reduce demand for the purity of EtOH.

The ion-exchange resin in the form of H^+ form has generally been used for the production of MTBE and ETBE. Unfortunately, there are two main drawbacks to employing this type of catalyst. Firstly, as indicated by Matouq and Goto (1993), Yin et al. (1995) and Yang et al. (2000), the dehydration of TBA to produce IB and water took place as a side reaction and reduced the selectivity to ETBE when the protonated cation-exchange resin Amberlyst 15 was used. Although IB reacted with EtOH by a general route to form ETBE, because the concentration of IB in the reactant solution were quite low under the reaction temperature, the reaction rate for the reaction was not so significant. Second, the presence of water has a strong inhibition effect on the catalytic activity (Cunill et al, 1993). Therefore, the ion exchange resin might not be suitable catalyst for synthesis of ETBE.

Matouq et al. (1996) compared different acid catalysts, $KHSO_4$, $NaHSO_4$, H_2SO_4 and Amberlyst 15 using low alcohol grade (mixture of 80 mol % water) in a batch reactive distillation. Potassium hydrogen sulfate ($KHSO_4$) showed the highest selectivity among the tested catalysts. The acid strength for $NaHSO_4$, H_2SO_4 and Amberlyst 15 might be too strong to produce ETBE, while $KHSO_4$ had a moderate acid strength. During the experiments, catalysts were added to the mixture of EtOH, TBA and H_2O, unlike Amberlyst 15. The Amberlyst pellets were placed in a closed pocket of cotton cloth due to the difficulty of holding the pellet on the sieve trays. Further this study showed that reactive distillation was a good choice to separate ETBE from the reacting mixture and a homogeneous catalyst.

In the study of Quitain et al. (1999), the ethanol concentration was aimed to be as low as that obtained from the fermentation of crob. For this reason experiments were carried out using 2.5 mol% ethanol in aqueous solution in a reactive distillation column. The column configuration was the same as that was used by Sneesby et al. (1997) in the synthesis of ETBE from IB and EtOH at operating pressure of 950 kPa. However, this system was operated at mild temperature and pressure. Under standard operating conditions (reflux ratio was 7.0), about 60 mol% ETBE could be obtained in the distillate and almost pure water in the residue and the conversion of TBA and the selectivity of ETBE were found to be 99.9 and 35.9%, respectively. They also investigated the effect of reflux ratio on the selectivity. It was founded that, at zero reflux, the selectivity was high at 48%, but the ETBE concentration was low, at 53 mol% so increasing reflux ratio decreases the selectivity of ETBE while conversion of TBA was still high. Also they suggested 2.5 mol% EtOH in the feed being suitable to produce ETBE since decreasing the feed mole fraction of EtOH to 2.5 % increases the conversion. Although it was known that the selectivity of ETBE could be improved by using catalyst other than Amberlyst 15, such as $KHSO_4$ or HPA catalyst, in this study these catalysts were not utilized, as pellets could not be formed. Quitain et al. (1999), also using the second reactive distillation to improve the overall selectivity of the ETBE to 99.9%.

Oudshoorn et al. (1999), proposed a novel structured catalyst packing as an alternative to existing catalytic distillation packings, containing bales or pockets of catalyst stacked in (a section of) the distillation column. The novel packing consists of common structured distillation packing, on which a binderless film of zeolite crystals is grown via *in-situ* hydrothermal synthesis. The combination of standard distillation packing structures and thin, binderless zeolitic catalyst films is expected to yield an active and selective system with good distillation characteristics. As a first step towards demonstrating this principle, structured packings coated with zeolites beta and mordenite were used to synthesize the `green' octane booster ETBE in a liquid phase batch system. The prepared structured catalyst packings showed activities and selectivities that are comparable to or higher than the activity of the conventional Amberlyst-15 ion-exchange resin catalyst. Even though the novel catalyst packing has a three times lower catalyst density compared to the currently used packings containing catalyst pockets, it is anticipated that this difference can be compensated for by the potential activity increase of the zeolitic coating, and the higher efficiency and selectivity of the coating. Furthermore, this concept can be applied to many other processes, especially since zeolitic catalysts can offer distinct advantages over more traditional heterogeneous catalysts.

Yang et al. (2000) also compared Amberlyst 15 with two kinds of Chinese catalysts, S-54, and D-72 in the form of H^+, for the ETBE synthesis from ethanol and tert-butyl alcohol in the liquid phase under atmospheric pressure. Among the catalysts, D-72 showed the highest activity, and S-54 showed the highest selectivity and the lowest inhibition coefficient of water.

Gonzalez and Fair (1997), studied preparation of tert-amyl alcohol in the reactive distillation. The hydration reaction of isoamylenes to produce 2-methyl-2-butanol (*tert*-amyl alcohol, or TAA) takes place in the liquid phase and in the presence of an acid catalyst. This reaction is strongly limited by chemical equilibrium to olefin conversions of less than 50%. The large difference in boiling point between isoamylene (38°C) and TAA (102°C) indicates an easy separation of the reaction products in a distillation column. Also, they stated that the liquid-phase synthesis of TAA seems to comply with these desirable characteristics of a reactive distillation application since the reaction is moderately exothermic, 26.5 kJ/mol, and the relative volatility between isoamylene and TAA is very high, 20-30. The temperature range at which the reaction takes place, 60-85°C, can be obtained in a distillation column that operates at pressures between 100 and 400 kPa. Acetone was used as a solvent to prevent the formation of aqueous and organic liquid phase; it was found that the acetone also enhanced the basic reaction rate significantly (about 15-fold).

CHAPTER 5

EXPERIMENTAL

In this study, simultaneous production of TAEE and TAA was investigated using isoamylenes, ethanol and water mixture, in a batch reactive distillation column where Amberlyst-15 was used as the catalyst.

5.1 Experimental Set-Up

The reactive distillation experiments were carried out in a batch reactive distillation column shown in Figure 5.1.

The column was made up of Stainless Steel. The preliminary experiments were carried out using a Pyrex-glass column, which allowed the operating pressure to be a maximum value of 1.5 bars. Exceeding this value was not safe for the operation. However, the operating pressure was an important criterion in the experiments and sometimes it was necessary to work with pressures higher than this limit. The boiling point of the mixture could be changed by pressure and the reboiler temperature could be adjusted in that way, therefore, the column material had to be suitable to be used at higher-pressure values, such as 6 bars. For this reason, a stainless steel column having the same dimensions as the glass column was manufactured and the glass column was replaced by the stainless steel column.

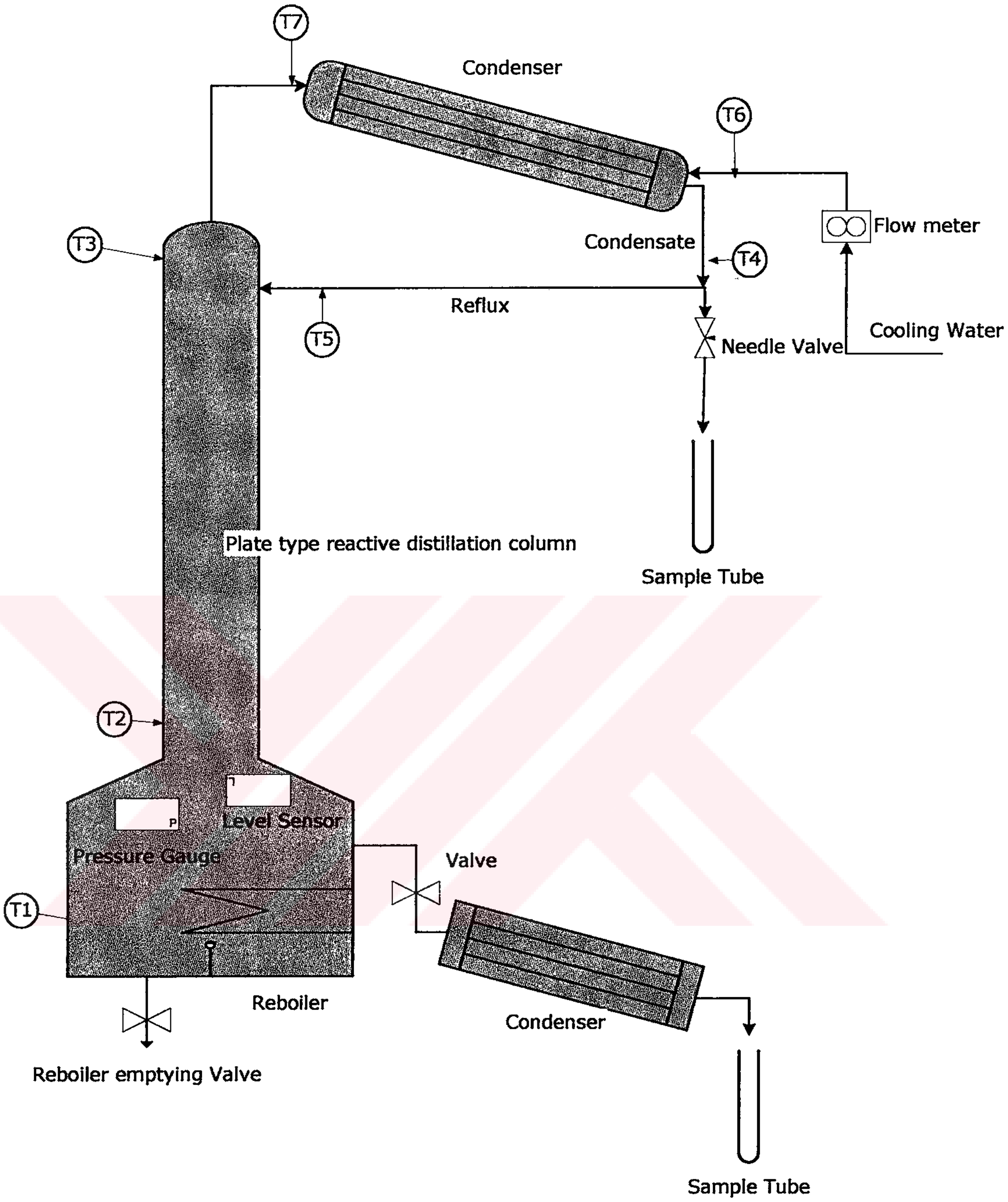


Figure 5.1 Experimental Reactive Distillation Set-Up

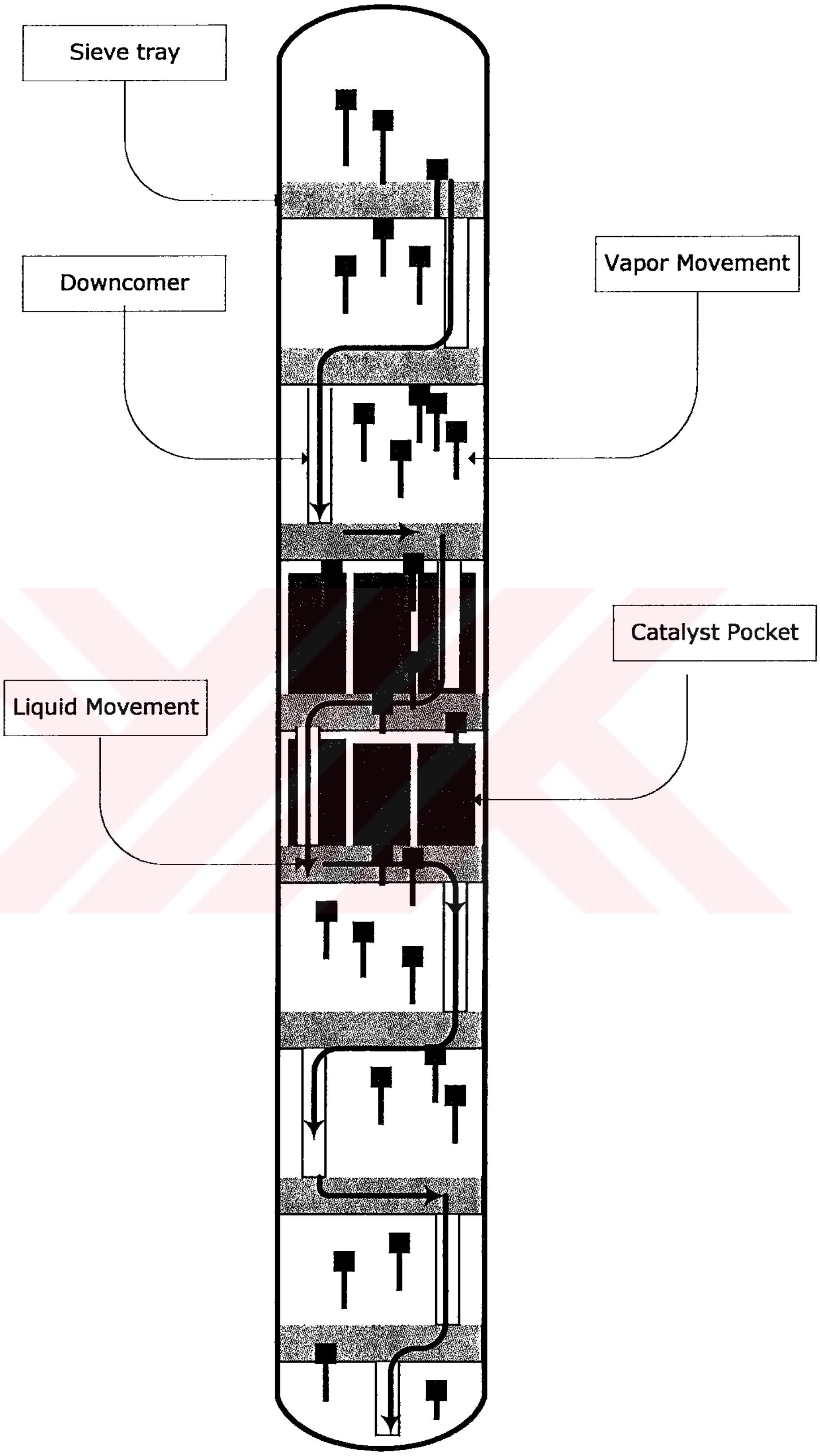


Figure 5.2 Column Configuration

The column, having an inner diameter of 5 cm and a height of 40 cm, had 8 perforated plates and the space between successive plates was 5 cm. Two of these plates were selected as the reaction zone as shown in Figure 5.2. In the preliminary experiments, the half of the space between the plates was filled with 10 g of catalyst. Wire sheets were placed on the base of each plate to prevent the sieve plates to be plugged during the process. Although the reboiler heater was controlled to give a gentle bubbling on the trays, catalyst particles were settled down on the base of the plate preventing the liquid flow. To solve this problem, catalyst pockets were used. Equal amounts of catalyst were weighed (1 gr) and put into wire gauze rectangular pockets, which was handmade in the size of 3-4.5 cm. The pockets were located perpendicular to the plate and parallel to each other so that maximum efficiency from the catalysts was obtained.

The feed tank, having a volume of 20L, was manufactured from corrosion resistant stainless steel and incorporated two electrically heated cartridge type heating elements. Power to the heaters might be continuously varied using a regulator and directly read from the wattmeter calibrated from 0-2kW. At the initial stage of the experimental period, it was set as 1.5 kW, but after the start of the boiling this value was decreased to control the temperature of the reboiler easily and to prevent the formation of flooding. A level sensor situated on the top of the feed tank protected the heating elements from overheating. The lower volume limit to be used during the experiment was 5.5 L and below this value, the controller shut down the system. In our experiments batch reactive distillation was used. The system allows continuous operation as well. The mixture of reactants were prepared in a different container and then poured into the reboiler before starting the process.

Temperatures were measured by 7 thermocouples located at different position on the apparatus. Two of them were at the top and the bottom of the column. Unfortunately, there were not any thermocouples placed along the column to measure temperatures of each plate. The inlet and outlet temperatures of the cooling water used in condenser; the temperatures of the reflux, the condensate and the reboiler were also measured by the other thermocouples.

In this system, different reflux ratio values could be manually set using two electronic timers, which proportion to the position of the reflux divider. For our experiments, the reflux ratio control was set to total reflux.

The samples were taken from the reflux and the reboiler. A needle valve was used in the reflux section in order to minimize vapor loss while taking sample so that decrease in the pressure of the column was avoided. Also, this valve allowed controlling the sample amount, easily, since the pressure inside the column was very high and this pressure resulted to spurt out liquid while taking samples.

Vapour from the top of the column passed through a water-cooled condenser. The volumetric flow rate of cooling water was monitored by a rotameter. After the reflux started, the inside pressure of the column could be adjusted by changing the volumetric flow rate of the cooling water. As the volumetric flow rate of cooling water increased, the heat transfer increased and more vapors condensed. This caused decrease in the column pressure. Another condenser was connected to the reboiler valve. Since the temperature of the reboiler was very high comparing to the room temperature, it was necessary to use this condenser to prevent evaporation of the components especially the more volatile ones in the liquid sample. The reboiler, the condenser, and the column was insulated to reduce any heat loses, especially in wintertime.

5.2 Chemicals and Catalyst

In the experiments, 2-Methyl-2-butene (purity > 95%) from Merck, ethanol (purity 96%) from Birpa and ethanol of analytical grade (purity, min 99.8 Vol %) from Sigma-Aldrich were used. For the chromatographic analysis TAME (> 97%) from Aldrich, TAA from Merck were used doing calibration. The properties and other details of the chemicals are listed in Appendix B.1.

The catalyst is a strongly acidic macroreticular ion-exchange resin, Amberlyst-15 from Sigma. Its properties are given in Table 5.1. Its pore size distribution is rather narrow but in polar medium, it is reported to swell appreciably. The active sites on the catalyst are the sulfonic groups (SO_3H) attached to the polystyrene chain. The particles are composed of macropores and inside macropores are the microspheres (Ihm, *et al.*, 1996). The average diameter of the macropores was reported as 2.28×10^{-8} m, which is four orders of magnitude smaller than the diameter of the catalyst particles (Oktar, *et al.*, 1999).

Table 5.1 Physical Properties of the Amberlyst-15 Catalyst (Oktar, *et al.*, 1999)

Average particle diameter (m)	7.4×10^{-4}
Macroporosity, ε_p	0.32
Apparent density (g/cm^3)	0.99
Average macropore diameter (m)	2.28×10^{-8}
Surface area (m^2/g)	
(nitrogen adsorption)	39.2[a]
(mercury porosimeter)	59.2[b]

[a] Corresponds to pores having diameter between 1.7×10^{-9} and 3×10^{-7}
[b] Corresponds to pores having diameters greater than 6.7×10^{-9}

Before starting the experiment, Amberlyst-15 particles were dried in a vacuum at 90°C overnight to remove moisture. Then, they were weighed with a sensitive balance to 1g. After preparing the wire pockets of equal size, they were filled with catalysts. These Amberlyst-15 catalyst packages (10g/plate) were placed over the two plates, which were selected as the reactive zone. After using for one set, pockets were replaced with the new ones easily.

5.3 Experimental Procedure

In our experiments, water-ethanol mole ratio in the liquid feed was 0.134, while mole fraction of isoamylene in the feed was changed between 0.03 and 0.18. Experiments were repeated in boiler temperatures ranged between 90°-125°C.

The experiments were carried out in three parts. In the first part, the effect of temperature on the overall conversion of olefin and the selectivities of TAEE and TAA was studied. The 4th and 5th stages were selected as the reactive zone and 20 g of Amberlyst-15 were used, totally. The feed composition was set 5 mol% 2M2B & Ethanol-Water (96 vol % pure).

In the second part of the experiments the influence of the feed composition on the overall conversion of olefin and the selectivities of TAEE and TAA was investigated, using the 7th and 8th stages as the reactive zone. The mole fraction of isoamylene in the feed was changed between 0.03 and 0.18 while water-ethanol mole ratio was 0.134. The reaction temperature was controlled at 90°C.

In the third part of the experiment, changing the reactive plates from 4 & 5 to 7 & 8, keeping the feed composition and reboiler temperature constant, the influence of reactive plate location on the overall conversion and selectivities on the product was studied.

In the final part, the water/ethanol mole ratio in the feed was changed from 0.135 to 0.0065 and the difference in overall conversion and selectivities was investigated.

In Table 5.2, all the experiments, carried out in this study, with their variables, operating conditions, parameters are summarized.

Table 5.2 Experiments carried out in this study

Exp#	$T_{reboiler}$	Estimated reaction zone temp	x_{2M2B}	x_{H2O}/x_{EtOH}	Plate Location	Catalyst Amount (g/plate)
1	90	70	5	0.1346	4 & 5	10
2	101	81	5	0.1346	4 & 5	10
3	111	91	5	0.1346	4 & 5	10
4	118	102	5	0.1346	4 & 5	10
5	125	110	5	0.1346	4 & 5	10
6	111	90	3	0.1346	7 & 8	10
7	114	89	5	0.1346	7 & 8	10
8	118	88	10	0.1346	7 & 8	10
9	118	90	18	0.1346	7 & 8	10
10	110	90	5	0.0065	4 & 5	10

5.4 Analytical Method

The samples taken from the reflux and the reboiler were injected to the Varian Aeograph Gas Chromatograph (GC) with a $5 \mu l$ Gas Chromatograph syringe. The GC had a Flame Ionization Detector (FID), and a column packed with 15 % FFAP on Chromosorb AW was used during GC analysis.

The column was operated using helium (He) as the carrier gas. At a constant carrier gas flow rate of 30 cc/min and at a constant column temperature of 100°C.

Before starting to analyze the samples, the column was conditioned for 3 hours with He gas. Dry air and hydrogen gases were fed to system for FID at a flow rate of 300cc/min and 30 cc/min, respectively. Injector and detector temperatures were also remained constant at 125 and 170°C, respectively.

With the data acquisition system connected to the chromatograph, the response peaks of the samples injected were analyzed with high precision. Before performing the experiments, for each component, chromatograph calibration factors (α) were evaluated which can be found in Appendix A.1. When the response peaks of experiments were obtained, using the calibration factors, the mole fraction or concentration of the components were found for each sample taken. By this way, the errors due to injection and the probable errors come from the detector were minimized.

In this study, the calibration factors for 2M2B, TAA and TAME were calculated to obtain quantitative results from the GC trace. The calibration factor of ethanol was taken as unity and the calibration factors of the other species were determined relative to ethanol.

The calibration factors of 2M2B, EtOH, TAEE and TAA found from the experiments was given in Table 5.3.

Table 5.3 Calibration Factors for reactants and products

Component	Calibration factor.α
2Methyl2butene. 2M2B	0.241
Ethanol, EtOH	1.000
Tert Amyl Alcohol. TAA	1.057
Tert Amyl methyl Ether. TAME	0.302

To find out these values, firstly 2M2B-EtOH, TAME-EtOH and TAA-EtOH mixtures were prepared within the composition range of experiments and these mixtures were injected to the column at different amounts and calibration factors of each condition were calculated. According to the results, it was concluded that the differences in concentration and injection amount did not affect the value of calibration factor of those species. The details of these calculations are given in Appendix A.1.

CHAPTER 6

RESULTS AND DISCUSSION

In this study, the simultaneous production of tert-amyl alcohol (TAA) and tert-amyl-ethyl-ether (TAEE) was carried out in a reactive distillation column. Considering both etherification and hydration reactions, olefin conversion and the selectivities of both products, TAEE and TAA, were investigated at different reboiler temperatures. In one of the experiments carried out to investigate the influence of water content on the process. Then, changing the olefin content of the feed, the second set of experiments was carried out. Finally, the location of the reactive plates was changed, and the overall conversion of olefin and product selectivities was investigated. In this system two parallel reactions were expected to take place,

$$2M2B + EtOH \Leftrightarrow TAEE$$

$$2M2B + H_2O \Leftrightarrow TAA$$

6.1 Effect of Temperature

6.1.1 Experimental Liquid Compositions in the Reboiler

In the first set of the experiments, catalytic zones were selected as 4th and 5th plates. In these experiments, the reboiler temperatures were changed between 90°C and 125°C, which corresponded to the initial system gauge pressures of 1.35-5 bars, respectively. The corresponding reaction zone temperatures were estimated as 70 and 110°C, assuming the temperature profile was linearly changing along the column. The verification of this assumption will be done by modeling the system. The feed composition of these experiments was around 5% (mole) 2M2B, 84% ethanol and 11%water. Among these reactants 2M2B has the highest volatility (boiling points of components are given in Appendix B.1).

The time dependence of concentration of 2M2B in the reboiler, at different temperatures, was given in Figure 6.1. It shows that, the increase in temperature accelerated consumption of olefin during the reaction. For reboiler temperatures higher than 100°C, there was no olefin left in the reaction medium for t>240 min. However, only half of the olefin in the feed mixture was reacted at 240 minutes in reboiler temperature of 90°C.

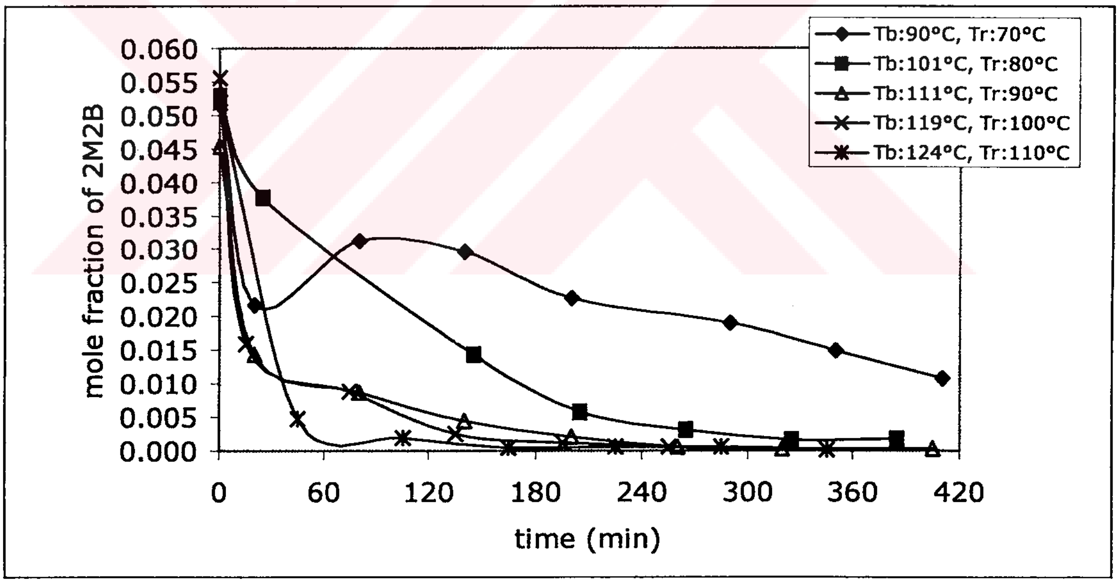


Figure 6.1 Concentration profile of 2M2B in the reboiler at different temperatures for 5 mol% 2M2B feed mixture (Exp No:1-5)

The time dependence concentration of ethanol in the reboiler, obtained at different temperatures, was given in Figure 6.2. In all these experiments ethanol was used in excess amount. Although the molar fraction of ethanol was changed during the experiments, the concentration range did not exceed the values between 0.83-0.88. From the Figure 6.2, it was observed that the mole fraction of ethanol increased with an increasing temperature. As it was seen in Figure 6.3, when temperature was increased, the formation of TAEE decreased especially at longer times. This also caused a decrease in the amount of ethanol consumed in the etherification reaction.

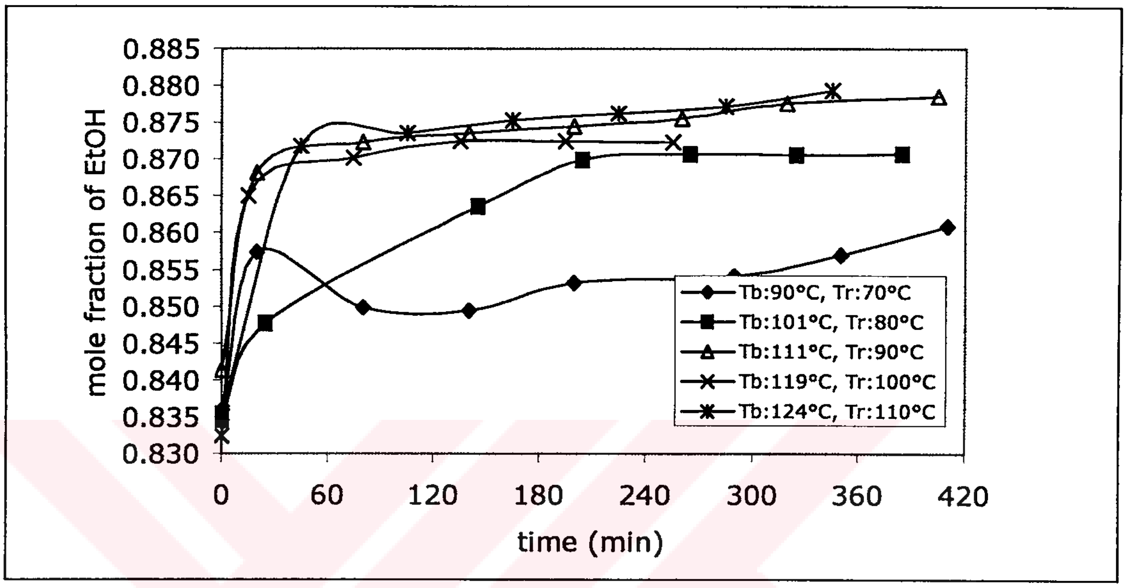


Figure 6.2 Concentration profile of EtOH in the reboiler at different temperatures for 5 mol% 2M2B feed mixture.

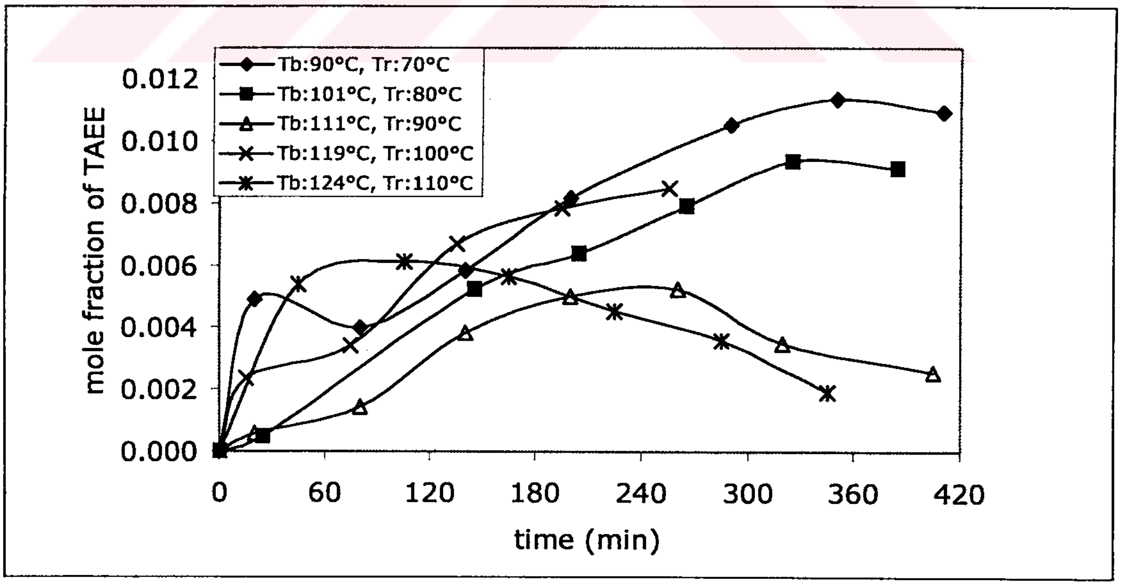


Figure 6.3 Concentration profile of TAEE in the reboiler at different temperatures for 5 mol% 2M2B feed mixture.

At higher temperatures, the decrease in TAEE formation could be explained considering the poisoning effect of water on the catalyst. The difference in adsorption of EtOH, TAA and H_2O on the Amberlyst 15 was seen in a discrete experiment. 1 grams of Amberlyst 15, after waiting in the vacuum at 100°C for 12 hours, was put into 10 mlt of distillate water, ethanol and TAA, separately. Before carrying out TGA, each sample was dried. The results of TGA showed that the water molecules more strongly adsorbed on the $-SO_3H$ sites of the Amberlyst-15 than alcohols. Independent TGA experiments carried out. The result was given in Figure 6.4, forming a hydrogen bonded network and caused a poisoning effect on the catalyst for TAEE production (Oktar et al., 1999).

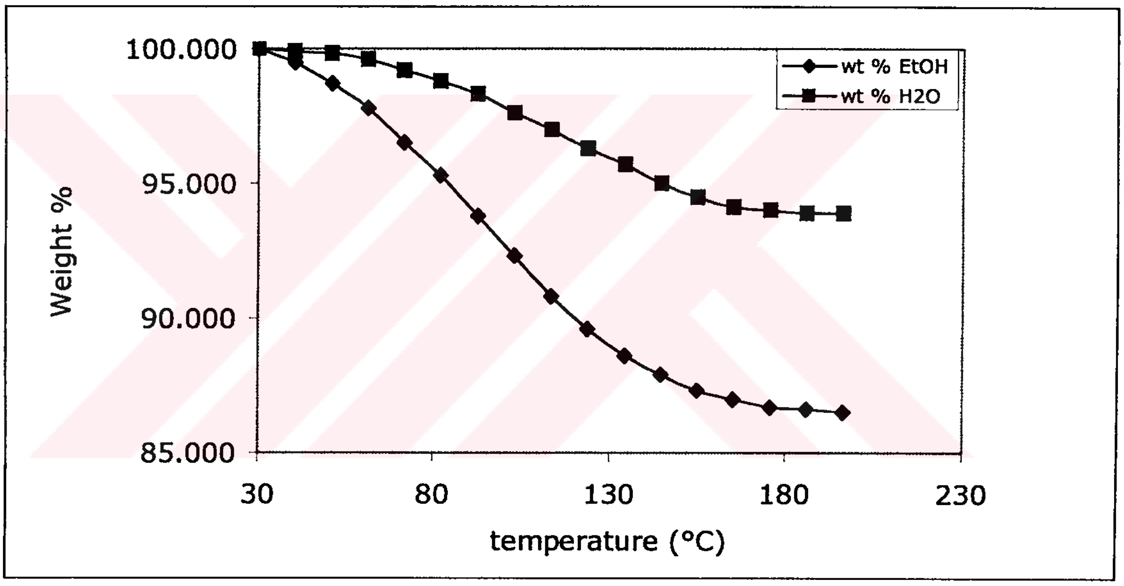


Figure 6.4 TGA results for Ethanol and Water

Figure 6.5 presented the concentration profile of the other product, TAA, in the reboiler at different reboiler temperatures. When Figures 6.3 and 6.5 were compared with each other, it was observed that the amount of TAA produced was approximately 3 times higher than that of TAEE. Generally, increase in temperature caused an increase in the formation of TAA. In Figure 6.6, the concentration profile of water present in the reboiler was given. Comparing this figure with Figure 6.5, it can be said that the amount of increase in TAA mole fraction was the same as the amount of decrease in the water mole fraction in the reboiler. Indeed, these two plots were symmetrical to each other, with respect to time scale.

There is one more important point to be mentioned here. FID (Flame Ionization Detector) was used to analyze samples taken from reboiler and reflux, but the mole fraction of water can not be obtained from these analyses. The mole fraction of water in the mixture was calculated by carrying out material balance and by considering reaction between the olefin and water. The procedure for calculation of water content in the mixture is given in Appendix D.1.

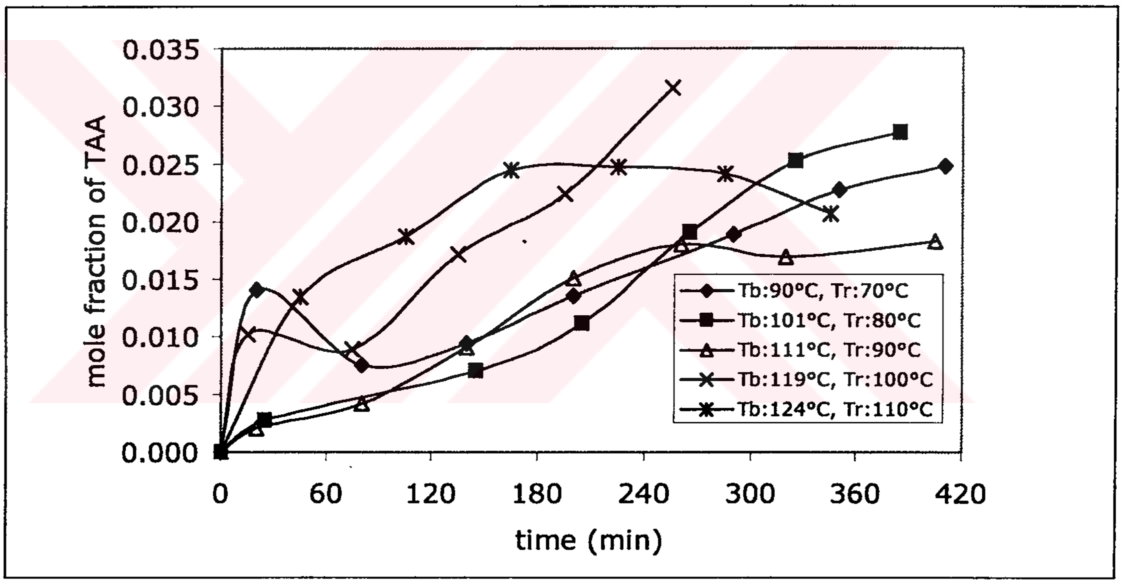


Figure 6.5 Concentration profile of TAA in the reboiler at different temperatures for 5 mol% 2M2B feed mixture (Exp No:1-5)

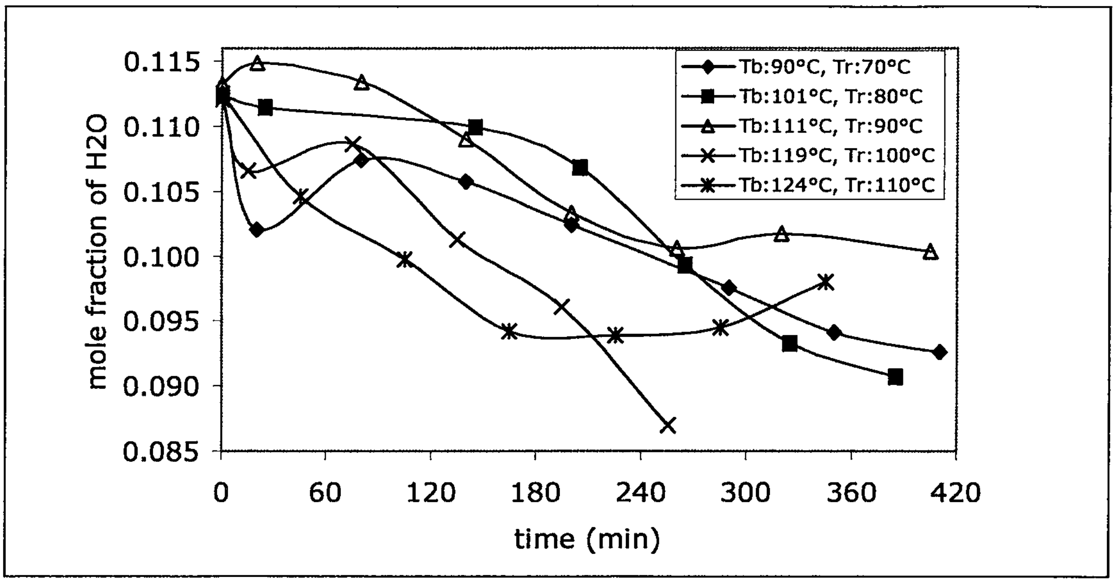


Figure 6.6 Concentration profile of H_2O in the reboiler at different temperatures for 5 mol% 2M2B feed mixture.(Exp No:1-5)

6.1.2 Estimated Vapor Compositions

For all these experiments, the vapor compositions of the components were calculated using the liquid mole fractions obtained from the experiments. In this calculation, the program WSMMAIN was used (Orbey and Sandler, 1998). This program calculated multicomponent VLE using the PRSV EOS and the Wong-Sandler mixing rule. Also, NRTL excess free-energy model was used with this mixing rule. A new input file for a multicomponent liquid mixture was created and this program could calculate the composition of the coexisting vapor phase for this mixture. Properties of components used in this program, i.e. critical temperatures, T_C, critical pressures, P_C, acentric factor,ω, and the κ_1 constants of the PRSV equation for each compound in the mixture were given in Appendix B.2. The program KOPT was used for the evaluation of the κ_1 constant of pure fluids in the PRSV equations. A sample input and output file of this program was given in Appendix E.1.

In addition to these properties, model parameters for each pair of components in the multicomponent mixture were supplied to run WSMMAIN. The

Wong-Sandler Model binary interaction parameters, k_{ij}, for each pair were calculated by using VDW program. This program was used to calculate binary VLE using the PRSV EOS and the van der Waals one-fluid mixing rules. Detail explanation of the program and a sample input and output files were given in Appendix E.2. The program was run for all the temperatures worked in this study, since k_{ij} values were temperature dependent. The average value of binary interaction parameters for each binary pairs are given in Table 6.1.

Table 6.1 Wong-Sandler Model Binary Interaction Parameters

Binary Pairs	K_{12}	K_{21}
2M2B-EtOH	0.1604	0.1029
2M2B-TAEE	-0.00859	0.0989
2M2B-TAA	0.1025	0.1001
2M2B-H2O	0.16445	-0.1241
EtOH-TAEE	-0.00296	0.1022
EtOH-TAA	-0.0658	0.0977
EtOH-H2O	-0.2509	0.1024
TAEE-TAA	-0.0409	0.1017
TAEE-H2O	0.1492	-0.3496
TAA-H2O	-0.0699	-0.1970

Indeed, in study of Orbey and Sandler (1995), for a binary that form highly nonideal mixtures, it could be set $k_{12}=0$.

In the required NRTL model, alpha parameter, α_{ij}, was set to 0.3, which was assigned by Orbey and Sandler for vapor –liquid equilibria.

Finally to run WSMMAIN, the required NRTL model energy parameters (Arce et al., 2001) for each pair of components, in cal/mol were calculated by Activity Coefficient Model, AC. The program AC can be used to correlate or predict VLE using activity coefficients model directly, without EOS and The "NON-

Random Two Liquid" (NRTL) was used. The NRTL Model Energy parameters of each pair was calculated for the temperature range studied in the experimental section and the results of two of them was given in Table 6.2 and the sample output file of the program was given in Appendix E.3.

Table 6.2 The NRTL Energy Parameter at different temperatures

Components	A_{ij} (cal/mol) 373 K	A_{ji} (cal/mol) 373 K	A_{ij} (cal/mol) 382 K	A_{ji} (cal/mol) 382 K
2M2B-EtOH	1287.4311	307.1868	1322.1564	285.4482
2M2B-TAEE	27.1861	75.5104	20.7667	77.4293
2M2B-TAA	800.3501	111.0254	791.5269	114.5656
2M2B-H2O	2838.5677	3157.3631	2977.7694	3310.8987
EtOH-TAEE	714.7750	118.8320	762.7739	80.2064
EtOH-TAA	-22.9780	73.3813	-23.4630	73.9318
EtOH-H2O	282.1008	646.4361	176.9039	831.0820
TAEE-TAA	427.0414	73.7560	419.0290	74.1848
TAEE-H2O	1578.1506	3496.9894	1542.8075	3021.2211
TAA-H2O	653.6026	1218.0232	682.0604	1219.4279

After finding all the necessary data, WSMMAIN was run to find out the coexisting vapor phase of the liquid mixture at the reboiler temperature. The calculation procedure was repeated for each sample taken from the reboiler during the experiments. In these calculations the temperature of the reboiler was considered to be a constant. As it was shown in Figure 6.7, the temperature profile of the column became steady after the samples were started to be collected. The sample output file of the program was presented in Appendix E.4.

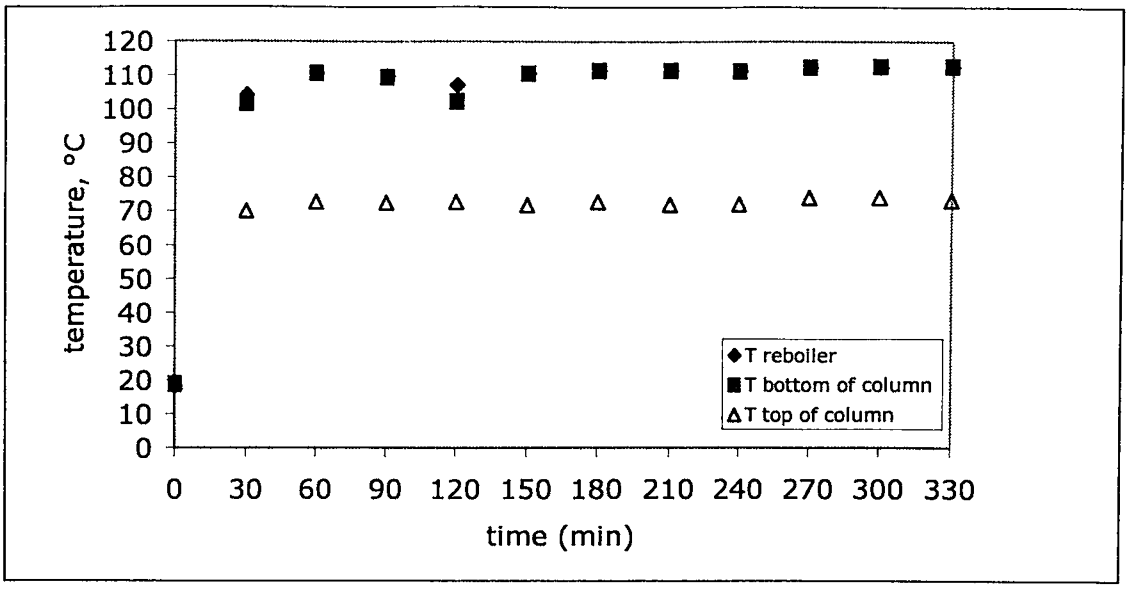


Figure 6.7 Temperature profile of reactive distillation column (Exp: 1)

The change in the vapor composition of olefin at different reboiler temperatures was given in Figure 6.8.

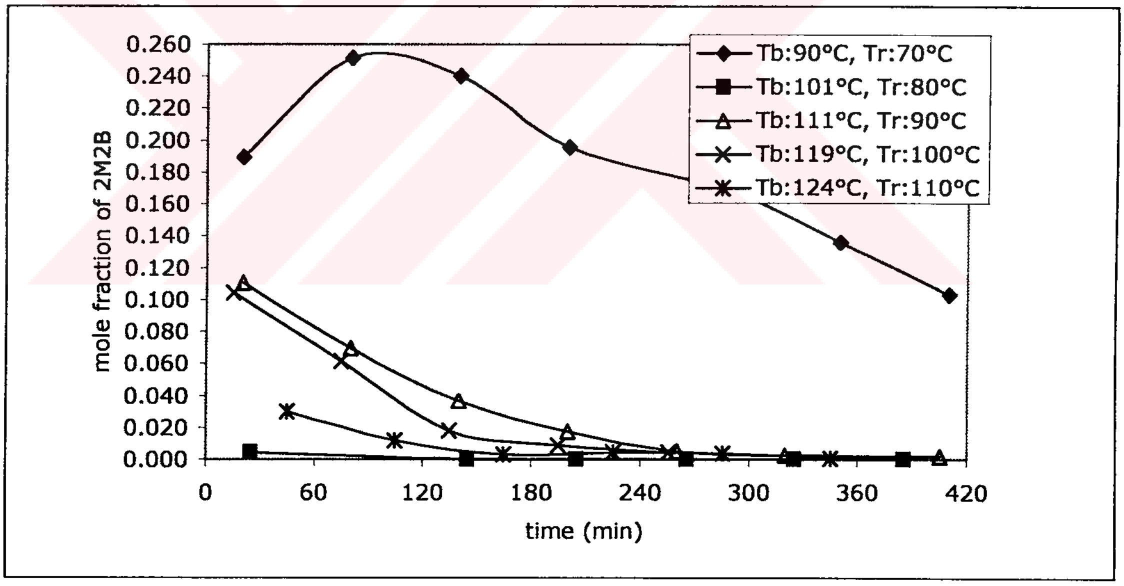


Figure 6.8 Concentration profile of 2M2B in the vapor phase at different temperatures for 5 mol% 2M2B feed mixture (Exp: 1-5)

It was expected that mole fraction of olefin in the reboiler to be low due to its higher volatility among the other components. This situation was followed so easily from Figure6.8. In Figures 6.9 and 6.10, the vapor composition of TAEE and TAA at different reboiler temperatures were presented, respectively.

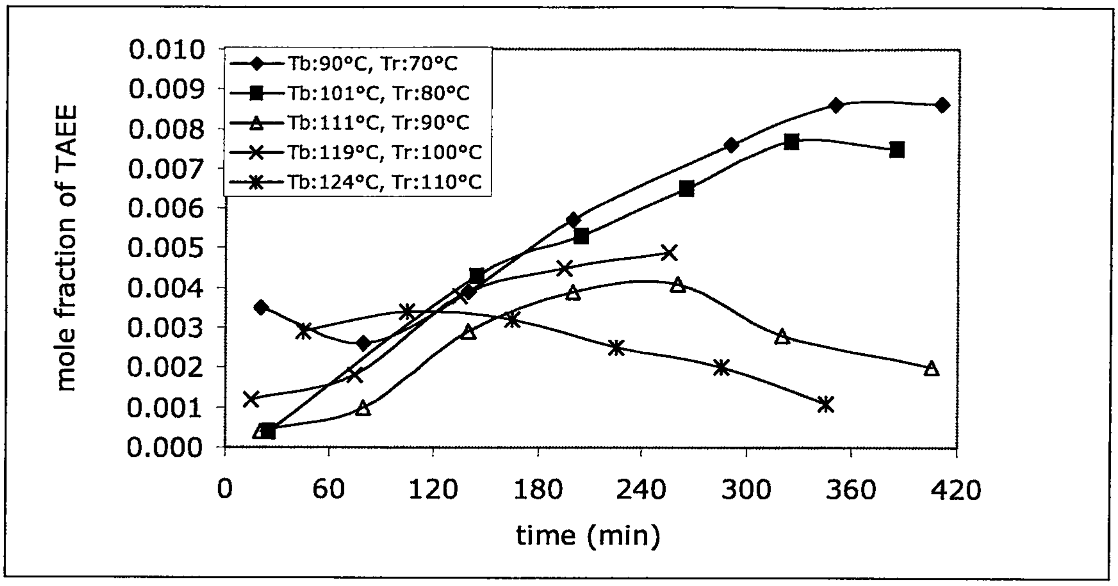


Figure 6.9 Concentration profile of TAEE in the vapor phase at different temperatures for 5 mol% 2M2B feed mixture (Exp: 1-5)

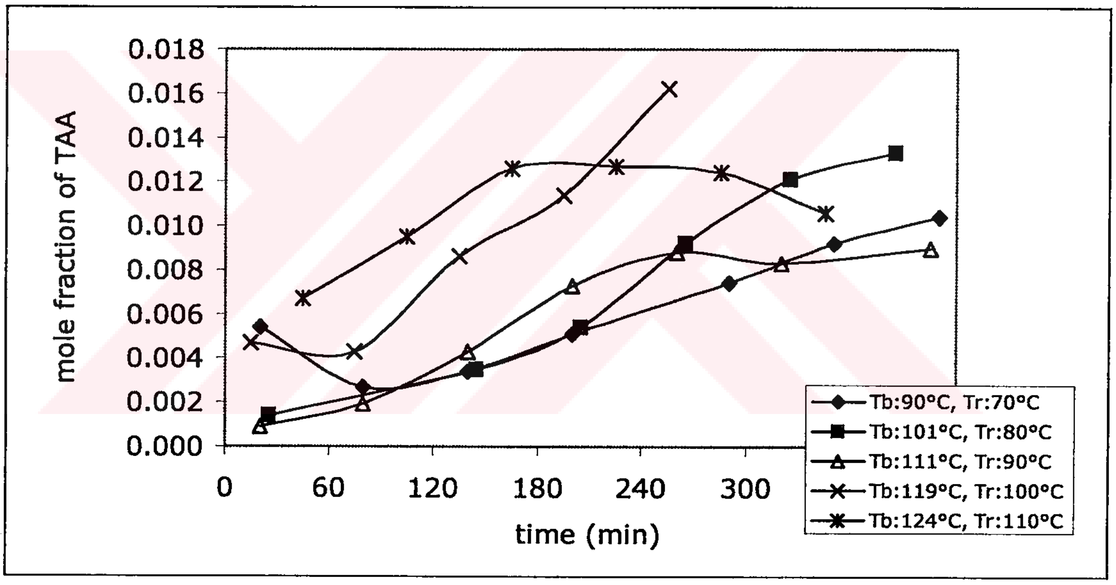


Figure 6.10 Concentration profile of TAA in the vapor phase at different temperatures for 5 mol% 2M2B feed mixture (1-5)

6.1.3 Conversion Values and Selectivities at Different Temperatures

The total conversion of 2M2B was calculated considering both reactions as it was defined by Equations 6.1, 6.2 and 6.3,

(Conversion of 2M2B to TAEE) $X_{TAEE} = \frac{x_C}{x_A + x_C + x_D}$ (6.1)

(Conversion of 2M2B to TAA) $X_{TAA} = \frac{x_D}{x_A + x_C + x_D}$ (6.2)

(Total conversion of 2M2B) $X_{total} = X_{TAEE} + X_{TAA}$ (6.3)

In these equations x_A, x_C and x_D correspond to instantaneous values of liquid phase mole fractions of 2M2B, TAEE and TAA respectively. Consequently the conversion values calculated from Equations 6.1, 6.2 and 6.3 correspond to instantaneous values of conversion evaluated from boiler compositions.

Figure 6.11 showed the variation of total conversion of 2M2B, at different temperatures during the reactive distillation process. This figure showed that by using reactive distillation column, high overall conversion values (at the reboiler) were found experimentally. Total conversion of 2M2B was found to increase with an increase in temperature.

The experimental results were compared with the calculated equilibrium conditions corresponding to each temperature. The equilibrium constant for reaction j can be expressed as,

$$K_j = \prod(a_i)^{\upsilon_i} = \prod(\gamma_i)^{\upsilon_i} \prod(x_i)^{\upsilon_i} \tag{6.4}$$

Here, a_i, γ_i, x_i and υ_i correspond to activity, activity coefficient, liquid mole fraction and stoichiometric coefficient of species i, respectively, in jth reaction.

Equation 6.4 was applied for both TAEE and TAA formation reactions and equilibrium conversions were solved by the simultaneous solution of these two equations. The activity coefficients, γ_i, have been calculated by the UNIFAC method. The equilibrium constant for isoamylene hydration was taken from

González and Fair (1997) and those for etherification and isomerization reactions were taken from Kitchaiya and Datta (1995). The details of equilibrium calculations was given in Appendix D.4.

Results of equilibrium calculations were collected in Table 6.3 and it was seen that the experimental overall conversion of 2M2B was much higher than the equilibrium conversion value corresponding to the boiler temperature. For instance, at 119°C, the overall equilibrium conversion was estimated to be around 0.416, which was less than half of the experimental value of 0.918. The experimental conversion data reported in Table 6.3 correspond to the boiler compositions reached at the end of each experiment (after the system was cooled down) carried out at different temperatures. These results showed that, instead of using a reactive distillation system, if the catalyst packages were put into the reboiler and the system were operated as a batch reactor maximum conversions would be less than half of the experimental findings of this work.

Another important point seen in the Figure 6.11 was that, at initial times, significant increase of conversion occurred with an increase in temperature. An instantaneous conversion value reaching to 0.996 was achieved at the reboiler at temperatures higher than 100 °C at longer times (t> 300 min). It was expected to reach such conversion values at much longer times for temperatures lower than 100°C.

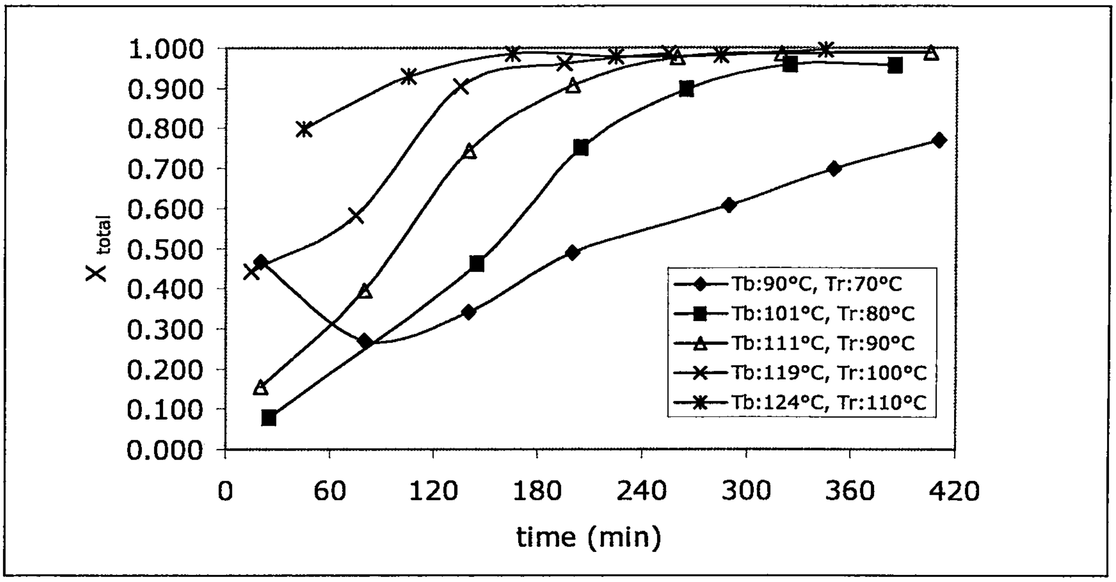


Figure 6.11 Variation of total conversion of 2M2B (the boiler composition) at different temperatures (Exp: 1-5)

Table 6.3 The Experimental and Equilibrium Conversion Values at Different Temperatures (Evaluated at the end of each experiment carried out at different temperatures)

$T_{reboiler}$ (°C)	X_{TAEE}	X_{TAA}	X_{Total}	$X_{TAEE,eqb}$	$X_{TAA,eqb}$
90	0.224	0.500	0.724	0.488	0.102
100	0.164	0.555	0.719	0.435	0.091
111	0.107	0.786	0.893	0.388	0.081
119	0.119	0.799	0.918	0.343	0.073
125	0.079	0.852	0.931	0.320	0.068

As temperature increases the equilibrium conversion values decreases. As seen from the Table 6.3, the olefin conversion to TAEE did not reach the equilibrium values. However, at each reboiler temperature, TAA conversion exceeds the equilibrium value.

Variation of instantaneous total conversion of 2M2B (as evaluated from the reboiler compositions) and the selectivities of TAEE and TAA were also plotted together, as a function of time at reboiler temperatures of 90, 101, 111, 119 and 124°C, in Figures 6.12, 6.13, 6.14, 6.15 and 6.16, respectively. In these plots, the selectivities of TAEE and TAA were estimated from Equations 6.5 and 6.6, respectively.

$$S_{TAEE} = \frac{X_{TAEE}}{X_{TAEE} + X_{TAA}} \tag{6.5}$$

$$S_{TAA} = \frac{X_{TAA}}{X_{TAEE} + X_{TAA}} \tag{6.6}$$

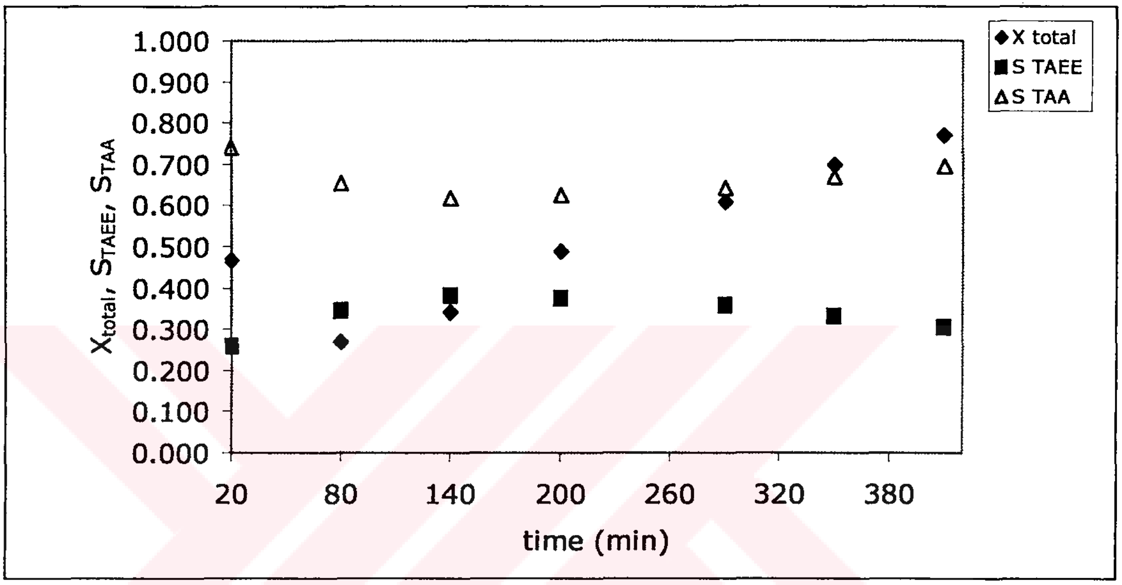


Figure 6.12 Total conversion of olefin, selectivity of TAEE and TAA at Tb: 90°C, Tr:70°C (Exp No:1)

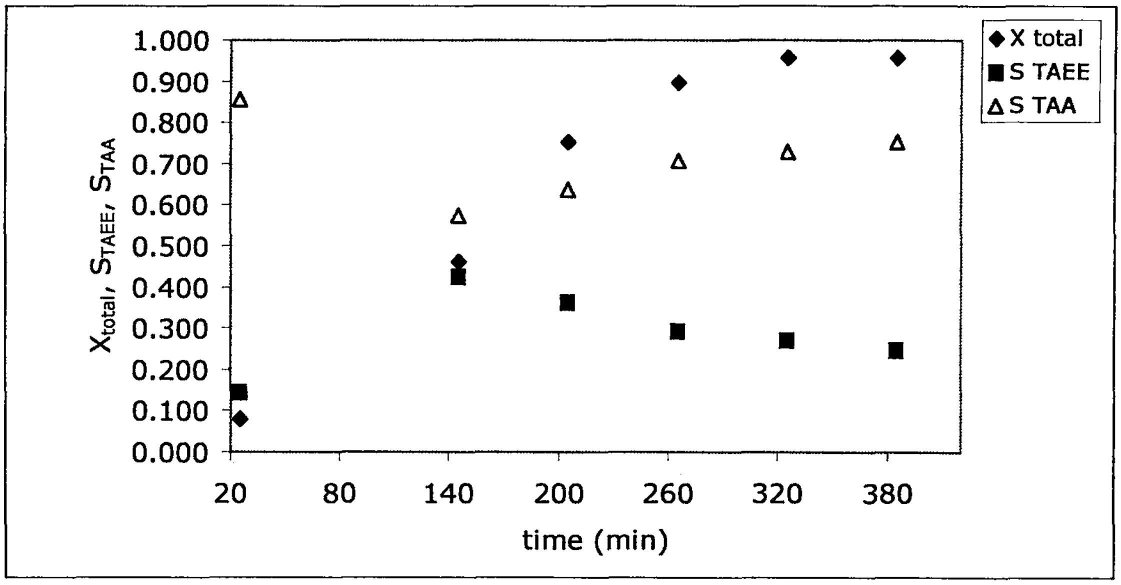


Figure 6.13 Total conversion of olefin, selectivity of TAEE and TAA at Tb: 101°C, Tr:80°C (Exp No:2)

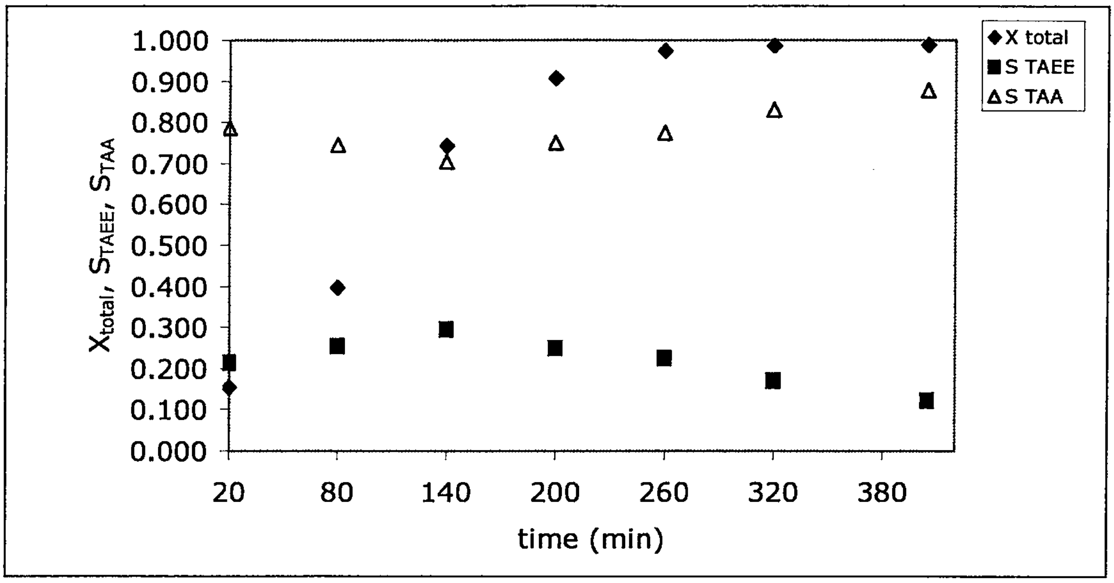


Figure 6.14 Total conversion of olefin, selectivity of TAEE and TAA at Tb: 111°C, Tr:90°C (Exp No:3)

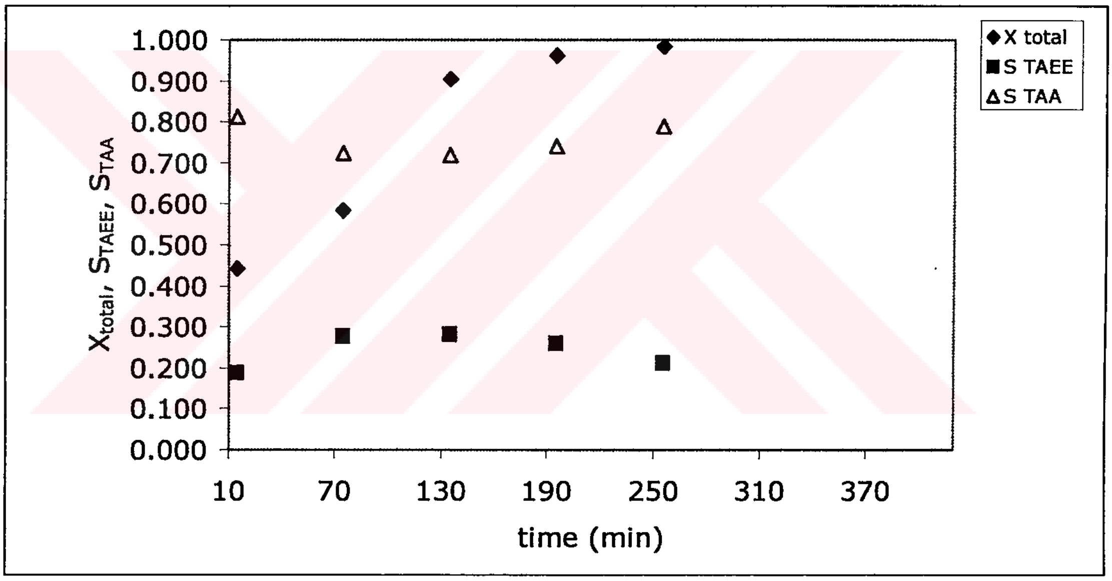


Figure 6.15 Total conversion of olefin, selectivity of TAEE and TAA at Tb: 119°C, Tr:100°C (Exp No:4)

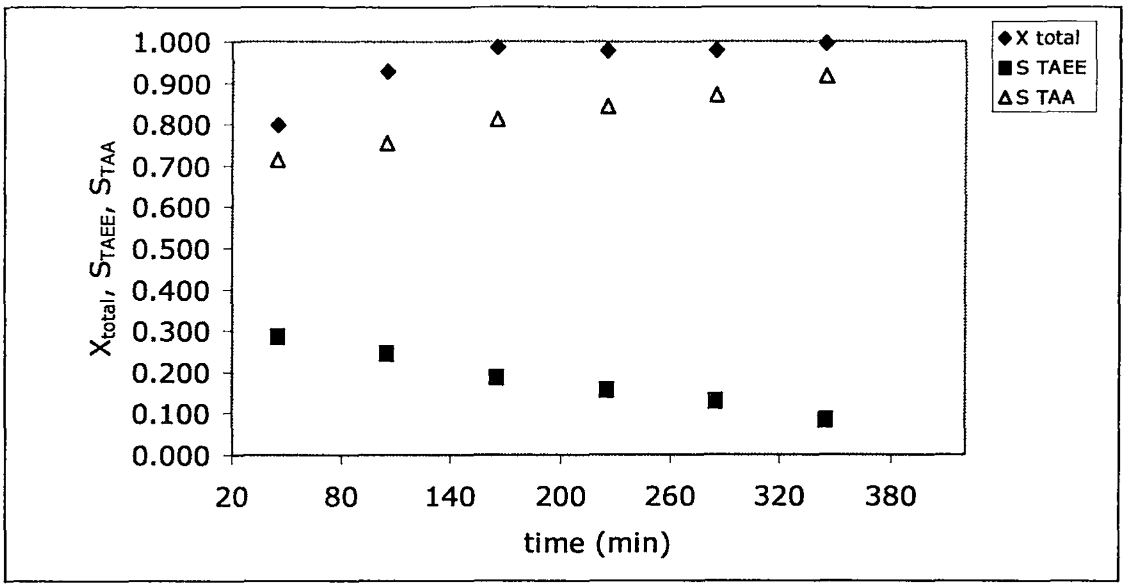


Figure 6.16 Total conversion of olefin, selectivity of TAEE and TAA at Tb: 124°C, Tr:110°C (Exp No:5)

The total conversion of olefin increased during the experiments (Figure 6.11). Increasing temperature favors the reaction to be completed at shorter time intervals. Also, another result to be discussed was that the selectivities of TAEE and TAA. These two selectivities showed opposite behaviour to each other. Selectivity values of TAEE passed through a maximum at all temperatures. However, TAA selectivities, passed through a minimum showing a significant increase at longer times. To see more clearly, variation of TAEE and TAA selectivities at different temperatures were given, in Figures 6.17 and 6.18, respectively. As the reaction temperature was increased, the maximum observed in TAEE selectivity shifted to earlier times. Comparison of selectivity values also showed that TAA selectivities were much higher than TAEE selectivities. TAA and TAEE were produced by competing parallel reactions of 2M2B and water with ethanol, respectively. It is well known that polar molecules, like water and alcohols, are much more strongly adsorbed on the acidic resin catalyst as compared to olefins. Considering a Langmuir Hinshelwood type reaction model, as justified in the literature (Dogu et al, 2001) higher selectivities of TAA may be explained by the higher adsorption equilibrium constant of water than adsorption equilibrium constant of EtOH on the catalyst. Maximum of the TAEE selectivity values shown in Figure 6.17 was explained by the significant decrease of 2M2B/water mole ratio in the vapor stream at longer times.

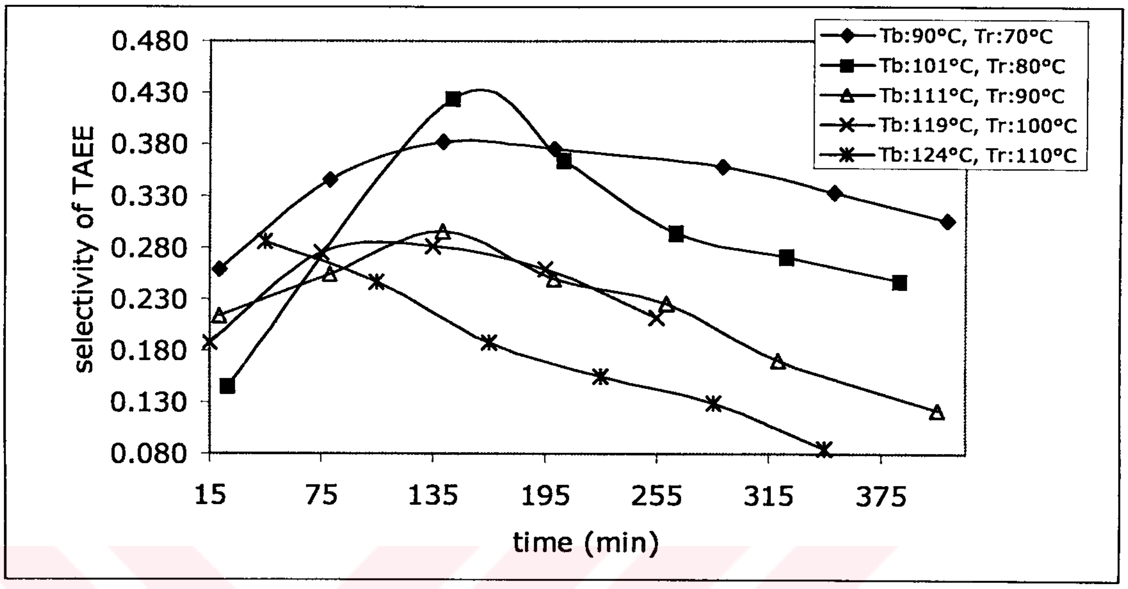


Figure 6.17 Variation of TAEE selectivities at different temperatures (Exp No: 1-5)

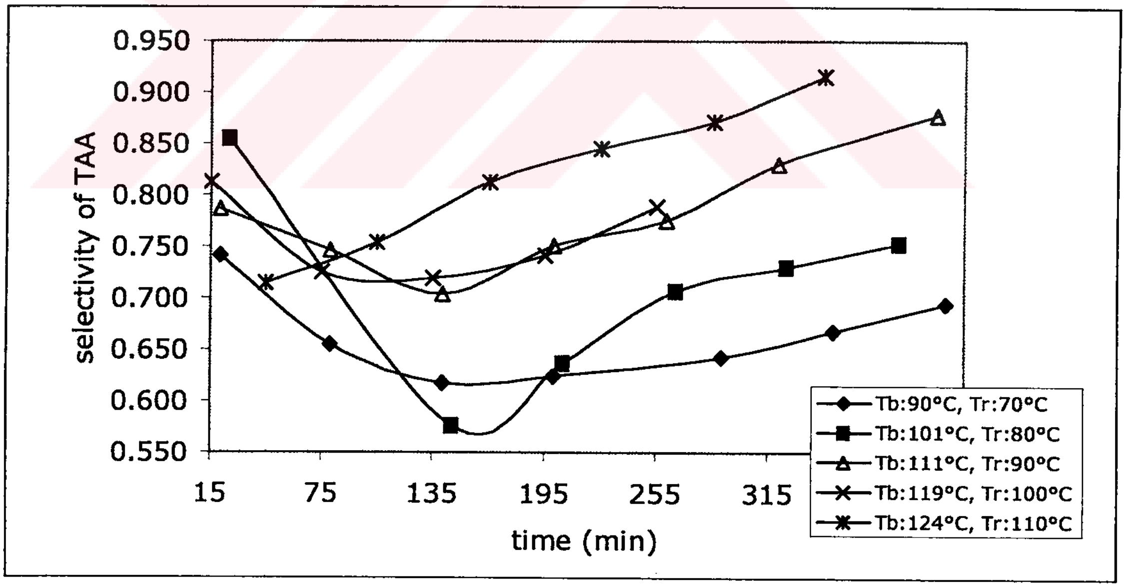


Figure 6.18 Variation of TAA selectivities at different temperatures (Exp No: 1-5)

Temperature dependence of overall conversion values obtained at longer times (t>300 min) was plotted in figure 6.19 and 6.20. The difference between these two graphs came from the source of data. At the end of each experiment, the system was left to cool so that vapor present in the column was condensed and to collected in the reboiler. Then, sample taken from this mixture was analyzed to calculate conversion and selectivities, as shown Figure 6.19. The other approach (Figure 6.20) was to use the instantaneous experimental values obtained at longer times (the final data point in each experiment). While the selectivity of TAA was the same approximately for two conditions, the overall conversion values and selectivities of TAEE were superior in the first case. So, it could be said that, if the system was operated continuously, higher conversion values could be achieved easily. Moreover, as it was given in Table 6.4, the selectivity ratio of TAA with respect to TAEE was significantly increased with an increase in temperature.

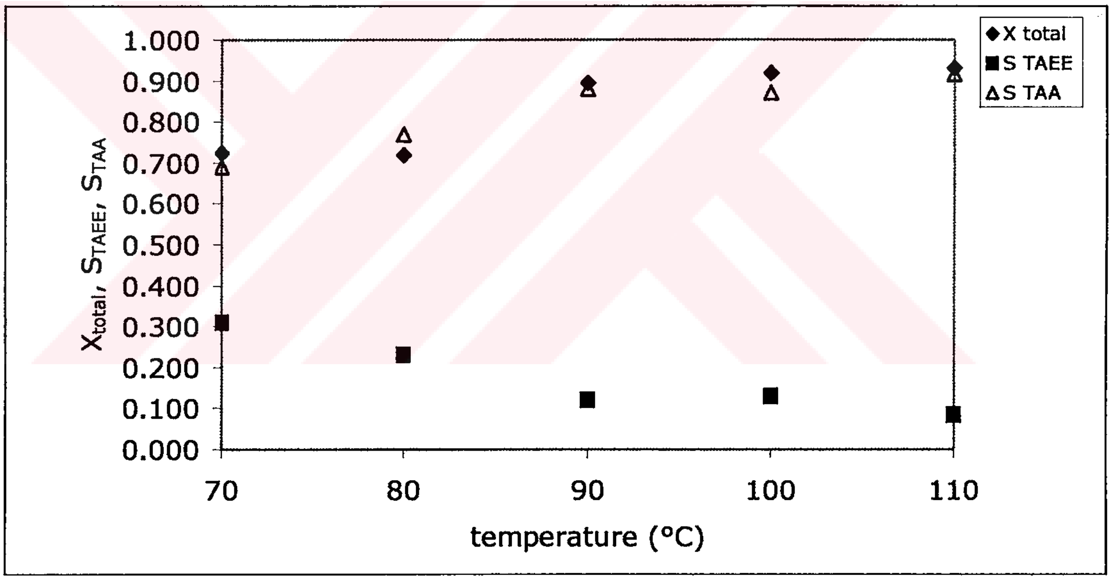


Figure 6.19 Total conversion of olefin and selectivities of TAEE and TAA for different reaction temperatures using the reboiler data (Exp No: 1-5)

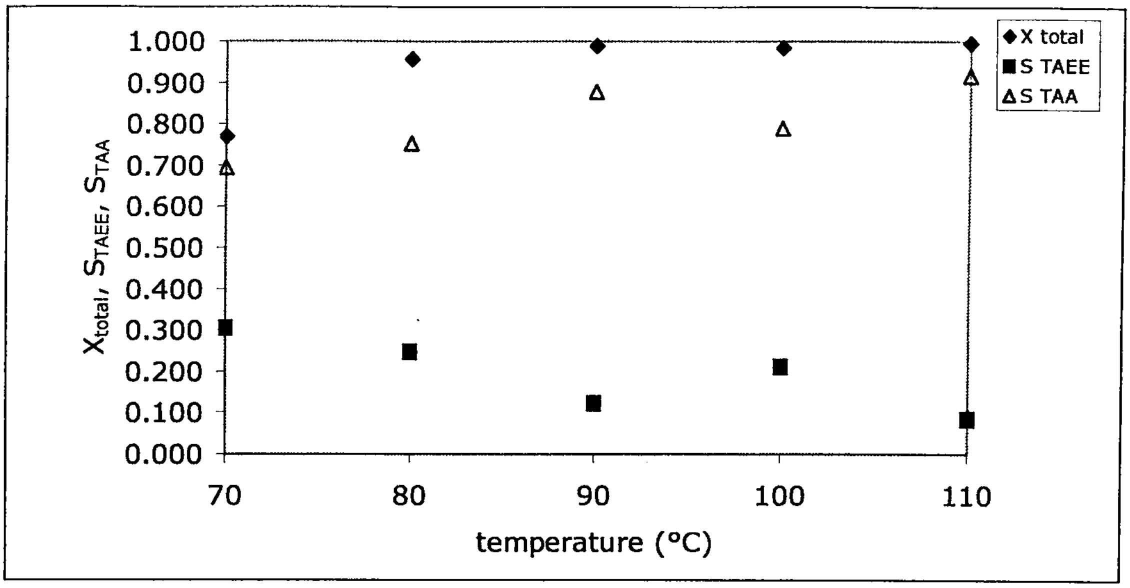


Figure 6.20 Total conversion of olefin and selectivities of TAEE and TAA for different reaction temperatures using the final experimental data (Exp No: 1-5)

Table 6.4 The Variation of Selectivity Ratio with Temperature (Evaluated at the end of each experiment carried out at different temperature)

$T_{reboiler}$ (°C)	S_{TAA}	S_{TAEE}	S_{TAA}/S_{TAEE}
90	0.690	0.310	2.226
101	0.770	0.230	3.348
111	0.880	0.120	7.333
119	0.870	0.130	6.721
124	0.915	0.085	10.805

6.2 Effect of Feed composition

The second set of the experiments were carried out at different feed compositions. In these experiments 2M2B amount was changed from 3% (mole) to 18% (mole) while in the mixture water to ethanol mole ratio was kept as 0.134. In these experiments catalyst zone was 7th and 8th plates and the reaction zone temperature was 90°C. Concentration profile of reactants and products were given in Figures 6.21, 6.22, 6.23, 6.24 and 6.25. For a feed mixture of 18 mol% 2M2B, the olefin concentration decreased to half of its initial value in first

60 minutes and became almost steady up to 300 minutes. However, the conversion of olefin was almost complete at lower molar ratio.

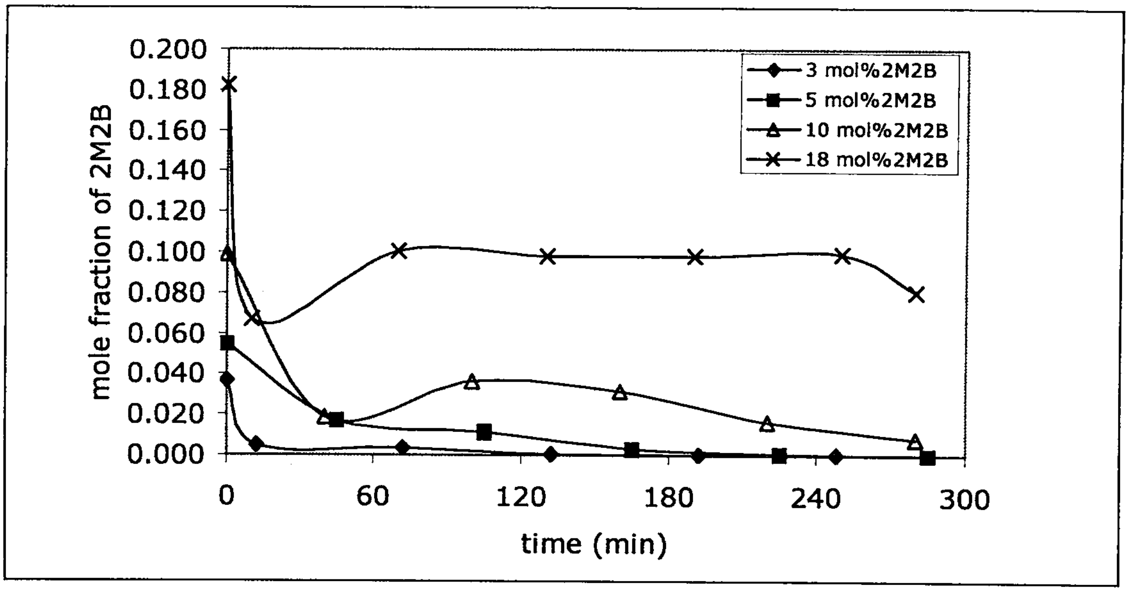


Figure 6.21 Concentration profile of 2M2B in the reboiler at different feed composition (Exp No:6-9)

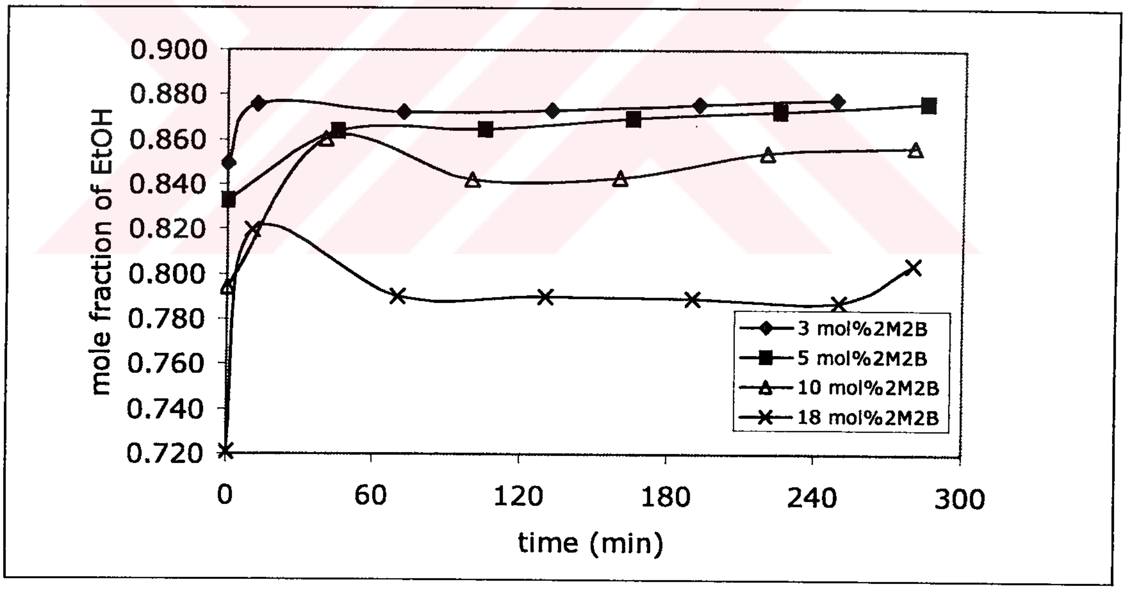


Figure 6.22 Concentration profile of EtOH in the reboiler at different feed composition (Exp No: 6-9)

The concentration of ethanol in the reboiler increased sharply at the beginning of the experimental period.

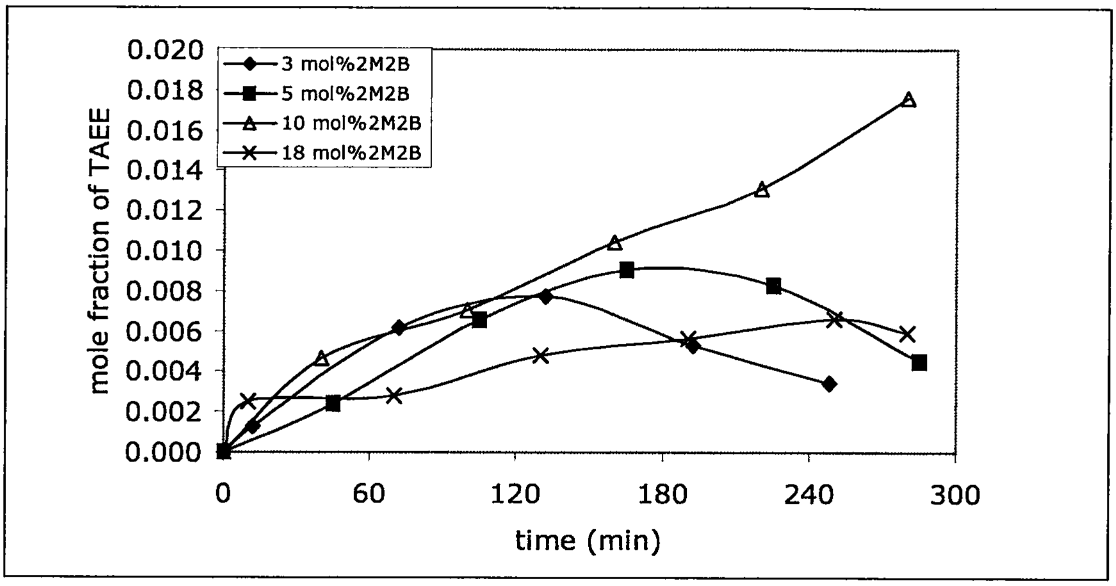


Figure 6.23 Concentration profile of TAEE in the reboiler at different feed composition (Exp No: 6-9)

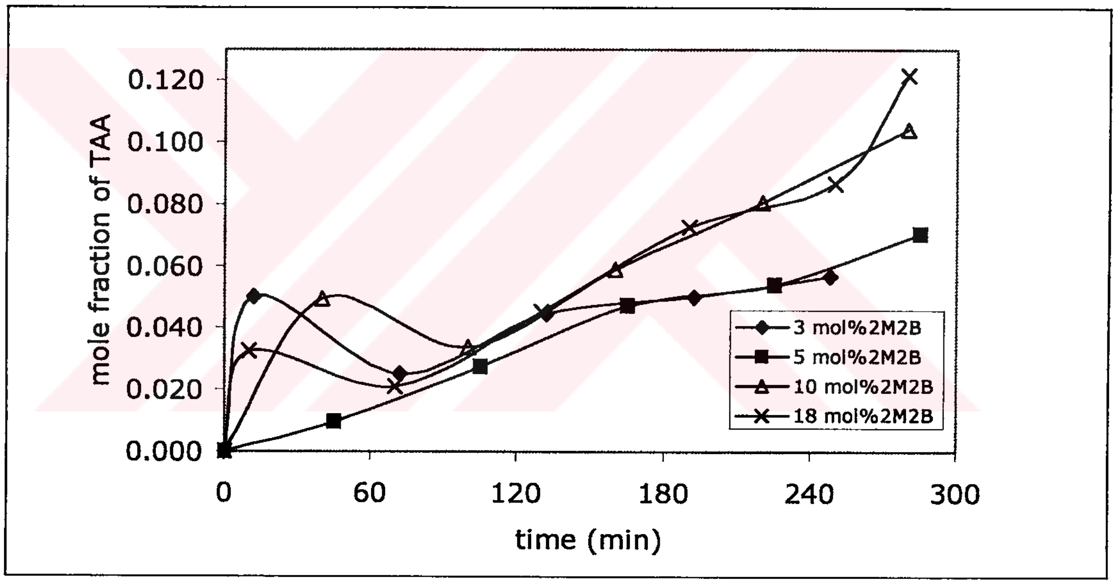


Figure 6.24 Concentration profile of TAA in the reboiler at different feed composition (Exp No: 6-9)

As it was seen in Figure 6.23 and 6.24, the formation of TAA was higher than the formation of TAEE.

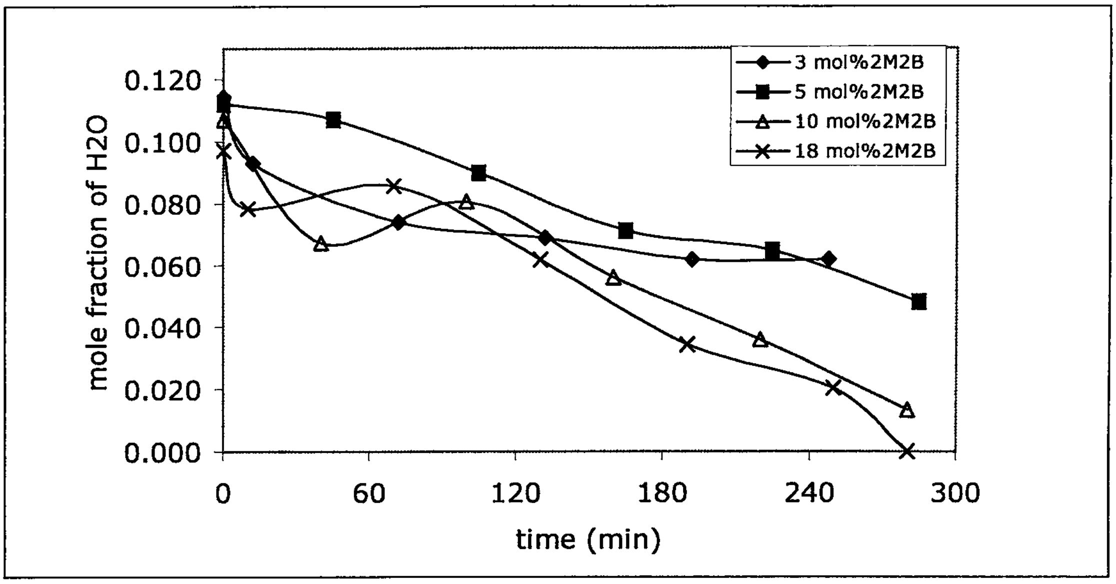


Figure 6.25 Concentration profile of H_2O in the reboiler at different feed composition (Exp No: 6-9)

Conversion values of 2M2B to TAEE, TAA and total conversion of 2M2B were again evaluated from Equations 6.1, 6.2 and 6.3, using the data reported in Figures 6.21, 6.22, 6.23, 6.24 and 6.25. A decrease of overall conversion of 2M2B was observed with an increase in concentration of 2M2B in the feed stream (Figure 6.26) indicating an apparent reaction rate order being less than one.

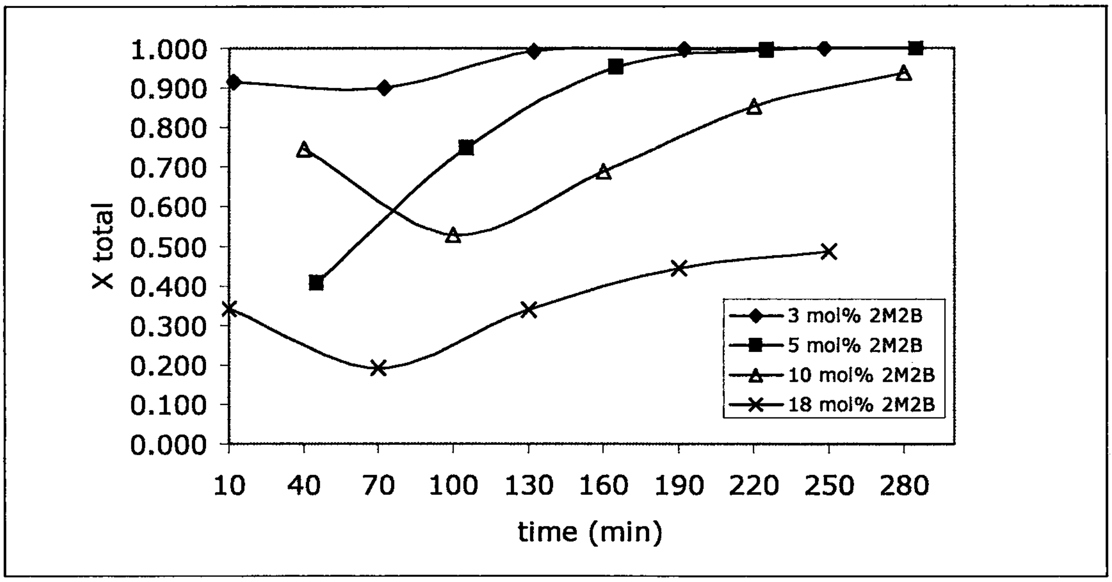


Figure 6.26 Variation of total conversion of 2M2B (the boiler composition) at different feed compositions (Exp No: 6-9)

In Table 6.5, experimental and the equilibrium conversion values are given. These results were calculated according to reboiler data. Increase of the olefin content caused decrease the overall conversion of olefin. Also, it is shown from this table, TAA conversion reaches to high values exceeding the equilibrium values.

Table 6.5 The Experimental and Equilibrium Conversion Values at Different Feed Compositions (Evaluated at the end of each experiment carried out at different feed composition)

2M2B mol %	Experimental Values			Equilibrium Values	
	X_{TAEE}	X_{TAA}	X_{Total}	$X_{TAEE,eqb}$	$X_{TAA,eqb}$
3	0.095	0.900	0.995	0.385	0.083
5	0.091	0.898	0.989	0.365	0.079
10	0.189	0.780	0.969	0.334	0.074
18	0.080	0.710	0.790	0.327	0.071

The total conversion and selectivities of TAEE and TAA at each feed compositions were given in Figures 6.27 , 6.28, 6.29 and 6.30.

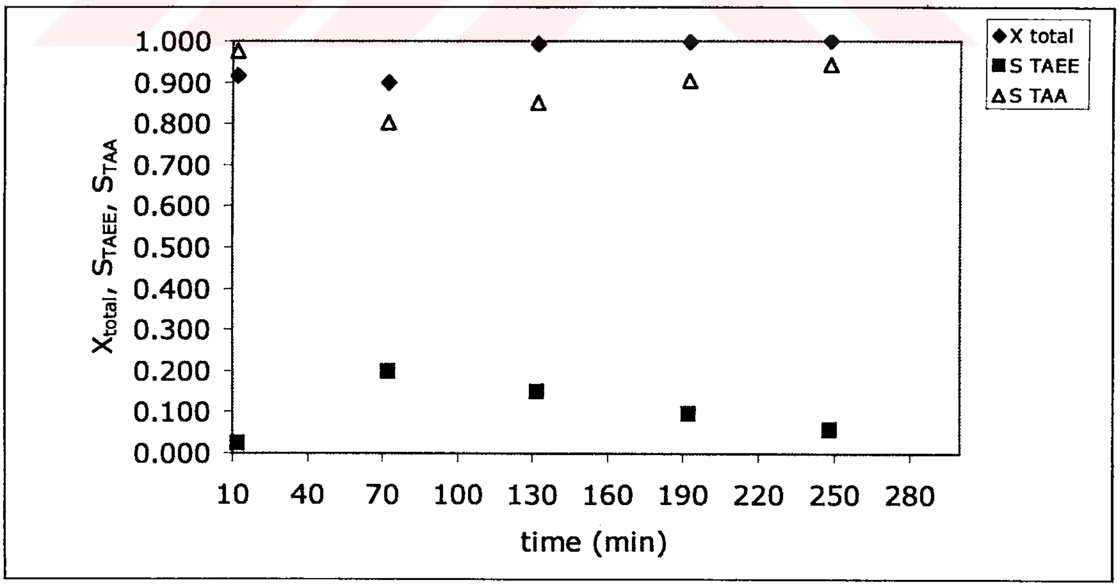


Figure 6.27 Total conversion of olefin, selectivity of TAEE and TAA at a feed composition of 3 mol% 2M2B (Exp No: 6)

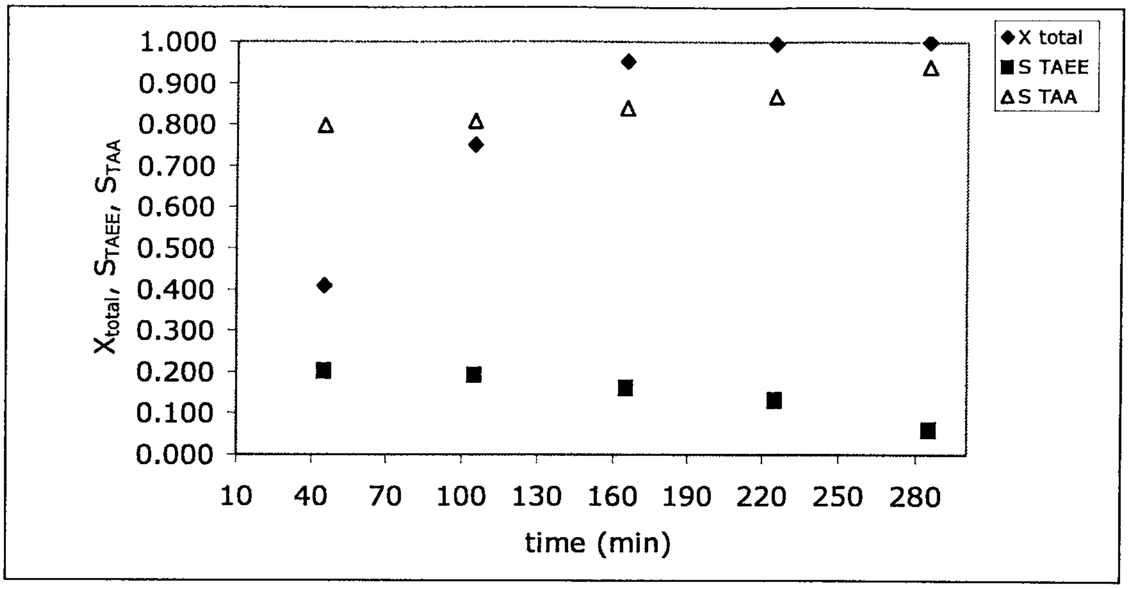


Figure 6.28 Total conversion of olefin, selectivity of TAEE and TAA at a feed composition of 5 mol% 2M2B (Exp No: 7)

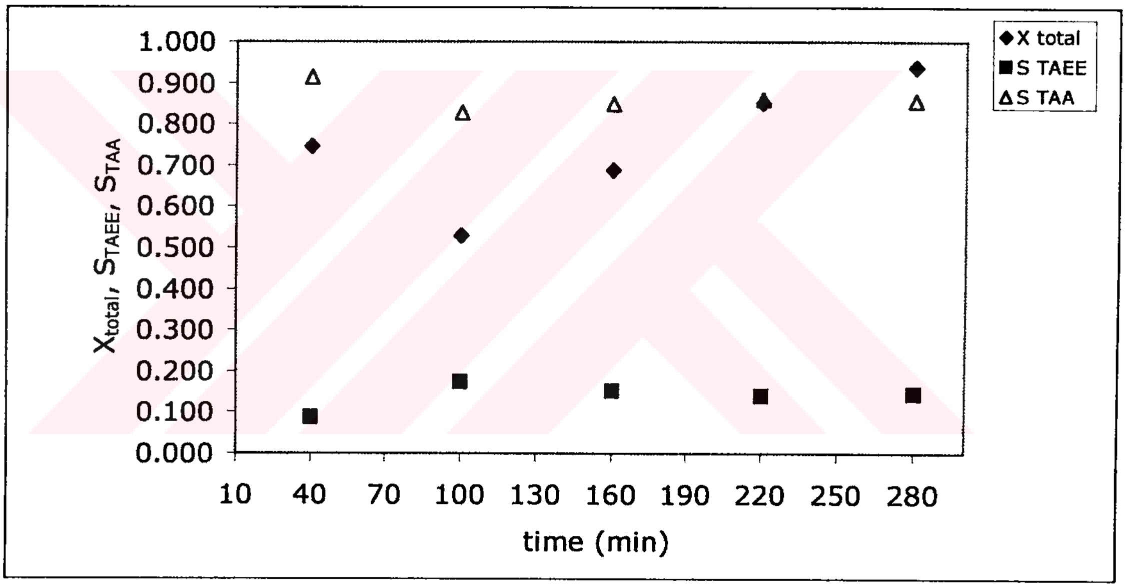


Figure 6.29 Total conversion of olefin, selectivity of TAEE and TAA at a feed composition of 10 mol% 2M2B (Exp No: 8)

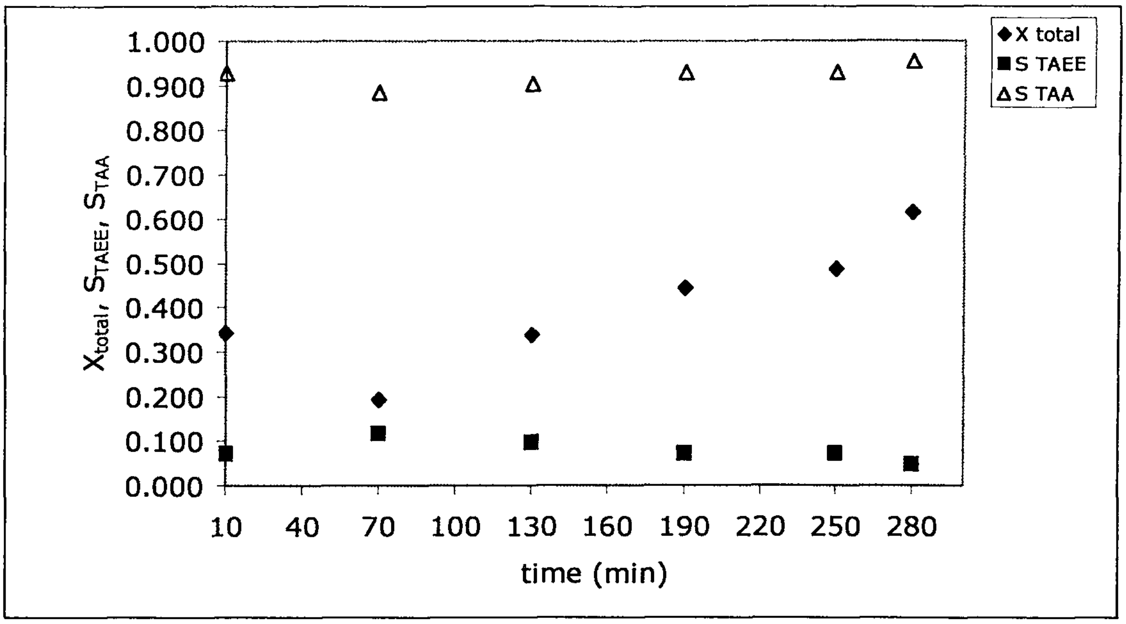


Figure 6.30 Total conversion of olefin, selectivity of TAEE and TAA at a feed composition of 18 mol% 2M2B (Exp No: 9)

Similar to first set of experiments, a maximum in TAEE selectivity and a corresponding minimum in TAA selectivity were observed at each composition. These are seen in Figure 6.31 and 6.32, respectively.

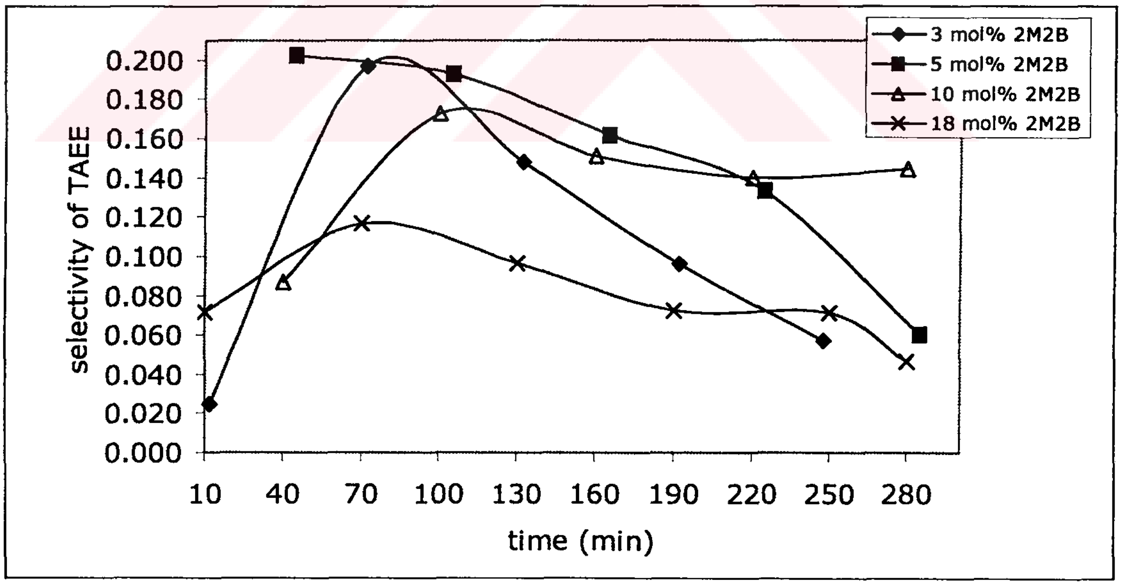


Figure 6.31 Variation of TAEE selectivities at different feed compositions (Exp No: 6-9)

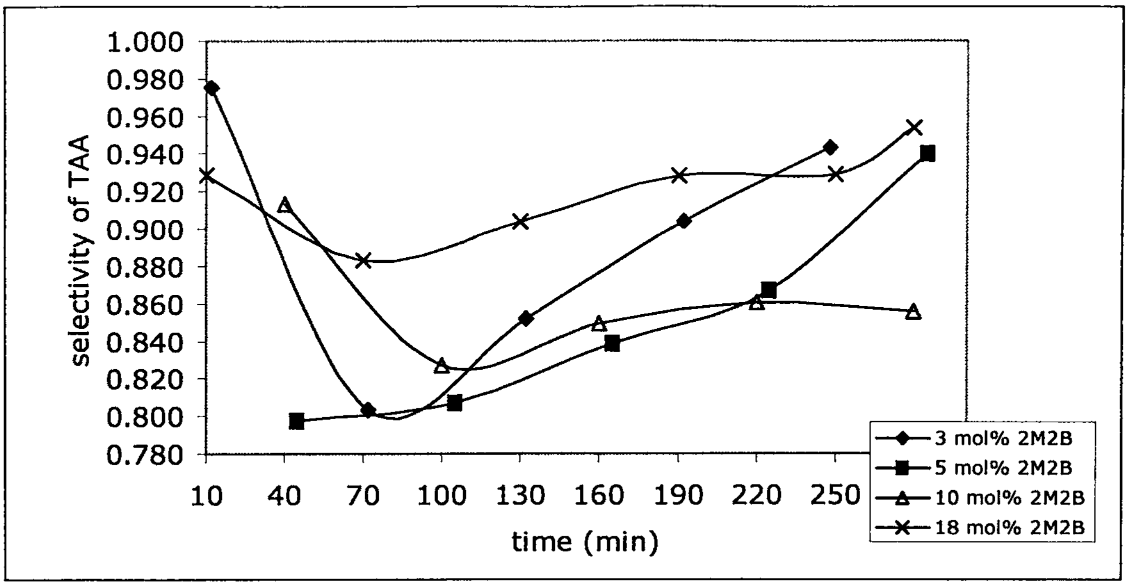


Figure 6.32 Variation of TAA selectivities at different feed compositions (Exp No: 6-9)

As in the case of first set, comparison of the final instantaneous conversion and selectivity values with the corresponding values obtained after the shutdown of the apparatus, are made in Figure 6.33 and 6.34, respectively. These figures show negligible differences for these two situations.

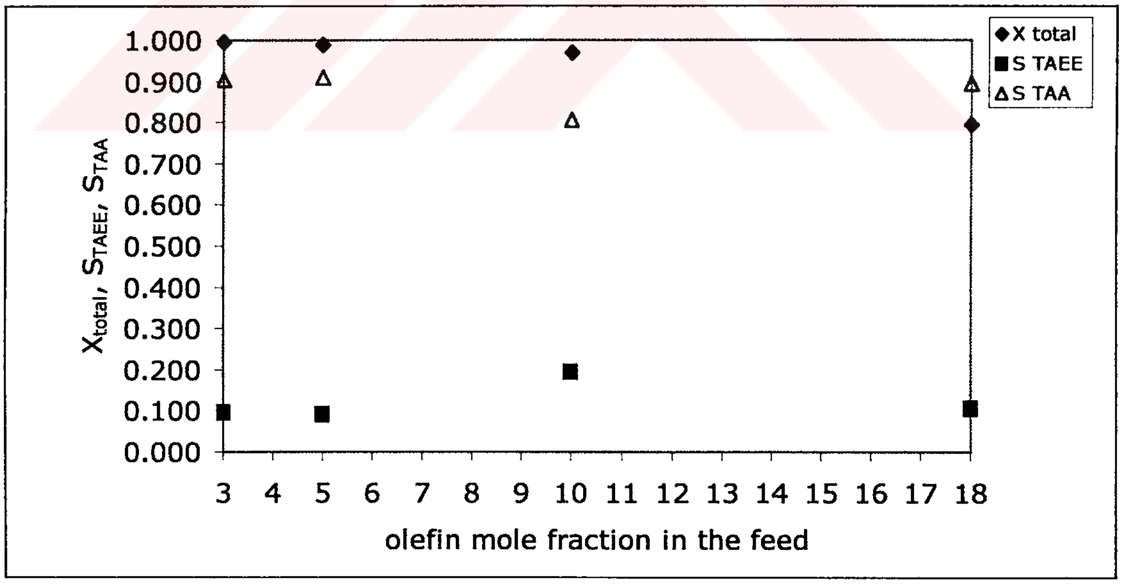


Figure 6.33 Total conversion of olefin and selectivities of TAEE and TAA for different feed mixtures using the reboiler data (Exp No: 6-9)

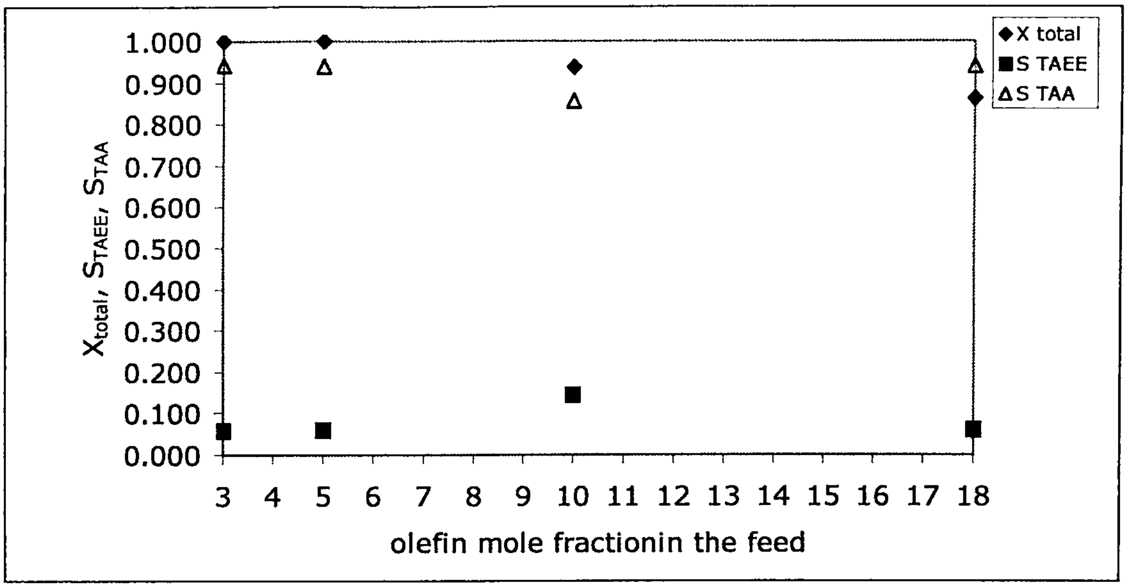


Figure 6.34 Total conversion of olefin and selectivities of TAEE and TAA for different feed mixtures using the final experimental data (Exp No: 6-9)

6.3 Effect of Reactive Zone Location

To investigate the effect of reactive zone, experiments were carried out selecting two different places for the catalyst section. In the first part, the catalyst pockets were located on the 4th and 5th plates. In the second part, the 7th and 8th plates were selected as the reactive plates, which were the top two plates. Other experimental parameters, such as amount of catalyst were the same as the previous experiments. The feed composed of 5 mol% 2M2B and the water/ethanol molar ratio was 0.1346. The reboiler temperature was adjusted as 111°C, 114°C for middle and top sections, respectively, which corresponds to reaction zone temperatures of 90°C.

It was observed that total conversion was increased by changing the catalyst zone from 4&5th plates to 7&8th plates, as given in the Figure 6.35. Also, this situation was supported by the evaluation of the reboiler data, given in Table 6.6. In addition, the most pronounced effect of changing reactive zone location was observed on the TAA conversion.

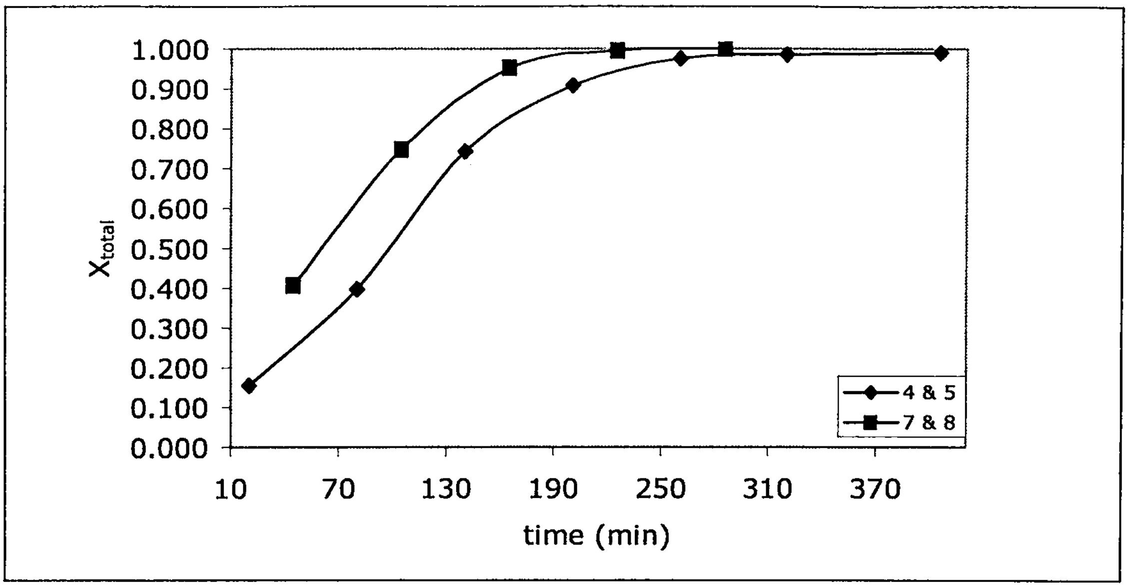


Figure 6.35 Variation of total conversion of olefin at different reactive zone (Exp No: 8,13)

Table 6.6 The Experimental and Equilibrium Conversion Values at Different Feed Compositions Calculated After Shut-Down.

Reactive Plates	Experimental Values			Equilibrium Values	
	X_{TAEE}	X_{TAA}	X_{TOTAL}	$X_{TAEE,eqb}$	$X_{TAA,eqb}$
4 & 5	0.107	0.786	0.893	0.388	0.081
7 & 8	0.091	0.898	0.989	0.365	0.079

Also, the selectivities of TAEE and TAA were investigated for these two cases. The results were given in Figure 6.36 and 6.37, for TAEE and TAA, respectively. It could be said that changing the reactive plates from the middle section to top, increased the selectivity of TAA but decreased the selectivity of TAEE.

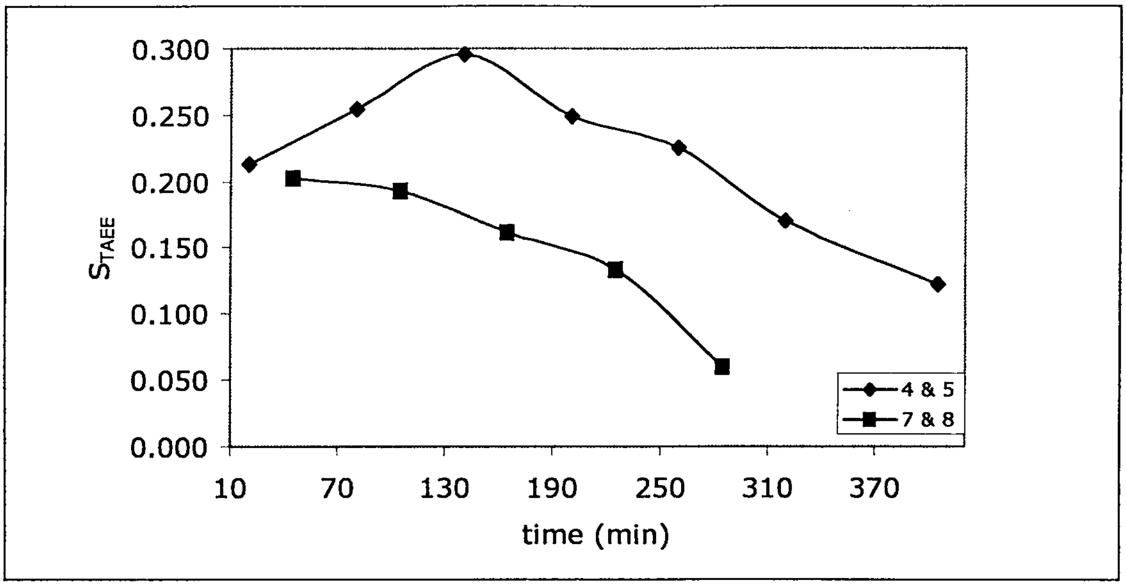


Figure 6.36 Variation of TAEE selectivity at different reactive zone
(Exp No: 8,13)

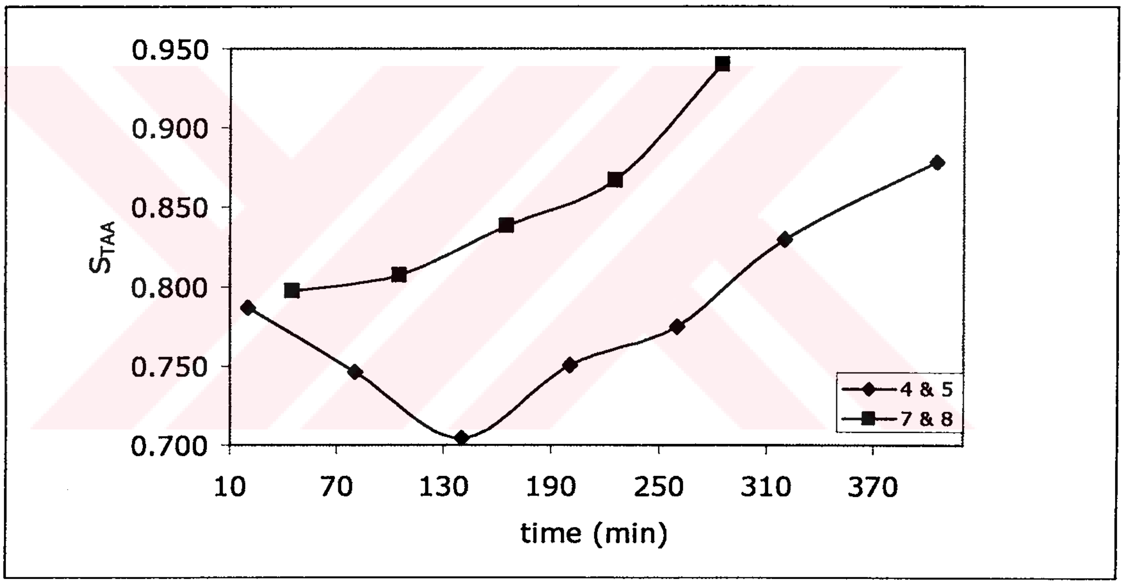


Figure 6.37 Variation of TAA selectivity at different reactive zone
(Exp No: 8,13)

When the reflux sample was investigated, the amount of TAA was higher than TAEE at least one order of magnitude. Indeed, at the same time the mole fraction of the TAA in the reboiler was also higher than that of TAEE. So, the effect of changing position was more efficient for TAA formation.

6.4 Effect of Water/Ethanol Ratio

The effect of ethanol mole fraction in the feed was investigated in this part. Keeping the reactive plates at the 4&5th plates, 5 mol% 2M2B feed mixture was used. In the first experiment the water/ethanol molar ratio was 0.135, in the second case it was 0.0065.

The conversion of olefin to TAEE was expected to be higher in the second case and it was shown in Figure 6.38. (In all the related figures, 96 vol % and 99.8 vol % refers to the mixtures of 0.135 and 0.0065 water/ethanol mole ratio) Although, there were a little amount of water was in the feed, it gave competitive reaction immediately, Figure 6.39. So these results also supported that the tendency of water molecules to be adsorbed on the catalyst surface was higher than the alcohol. For this reason, the conversion values for TAEE reached to 85 % and could not exceed beyond this value.

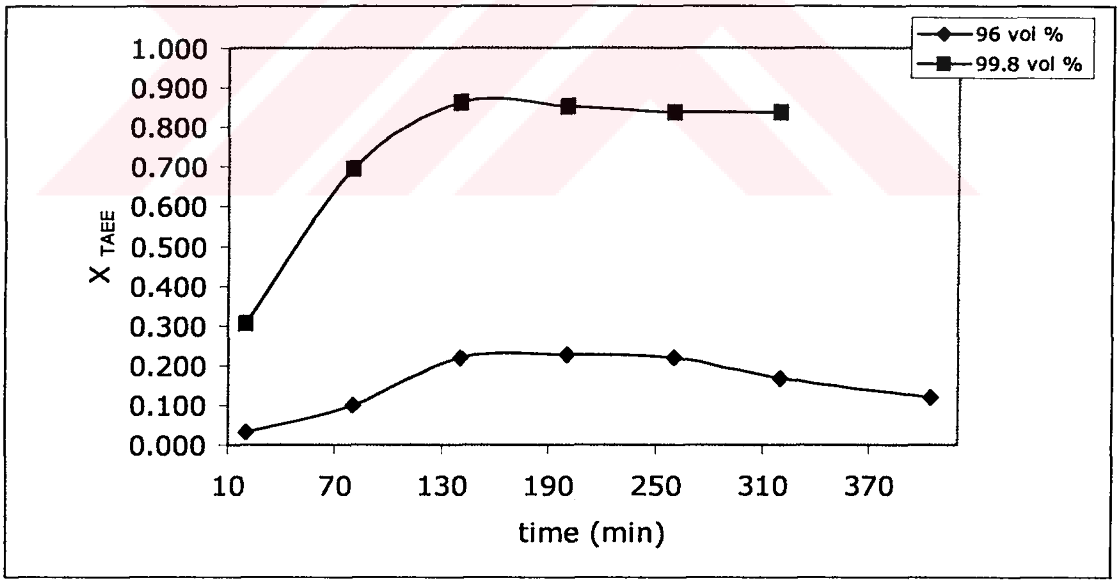


Figure 6.38 Variation of conversion to TAEE at different EtOH-Water mixtures (Exp No: 8,19)

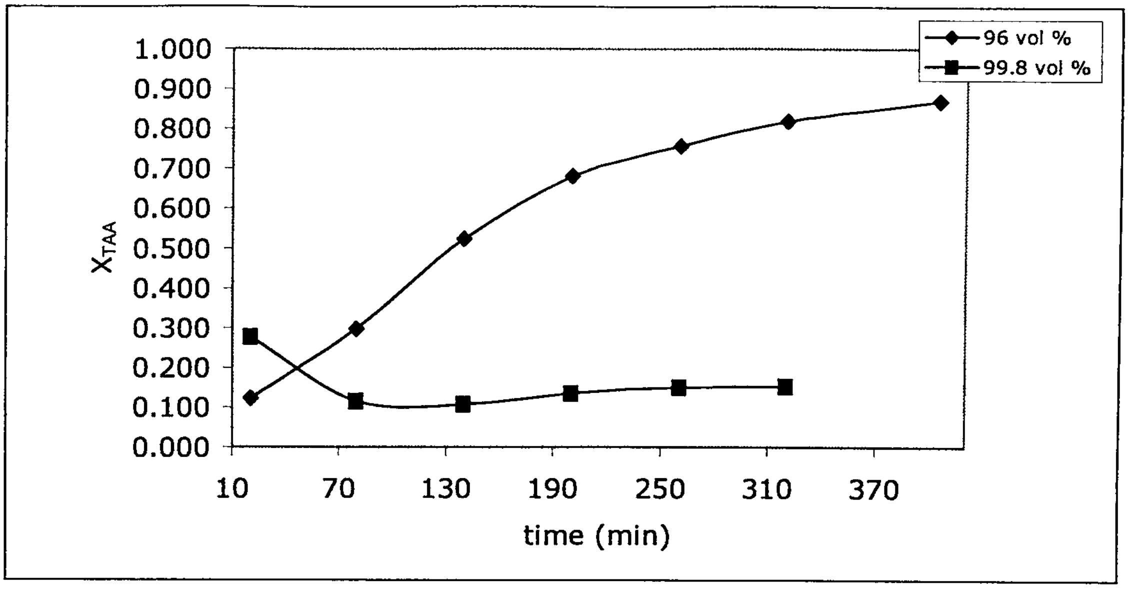


Figure 6.39 Variation of conversion to TAA at different EtOH-Water mixtures (Exp No: 8,19)

When the total conversion of olefin during the reaction considered in both cases, after 300 min, conversion was almost completed as given in Figure 6.40. The time needed to reach the conversion values higher than 90% became shorter by decreasing the molar ratio of water.

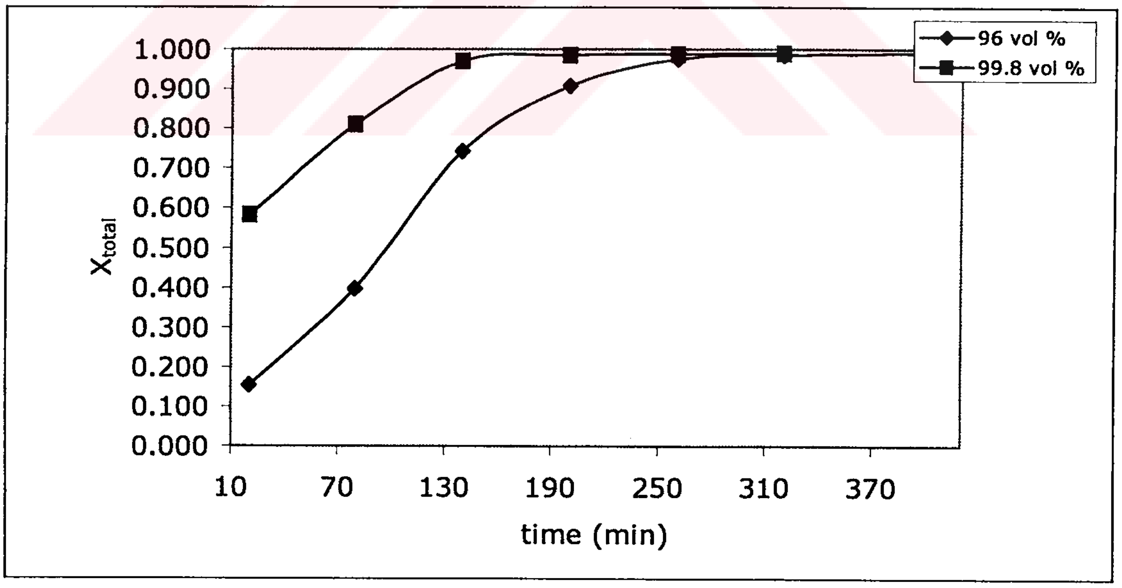


Figure 6.40 Variation of total conversion of olefin at different EtOH-Water mixtures (Exp No: 8,19)

The differences in the conversion values were also followed by the selectivity figures plotted for TAEE and TAA at different ethanol content of feed, the related Figures 6.41 and 6.42.

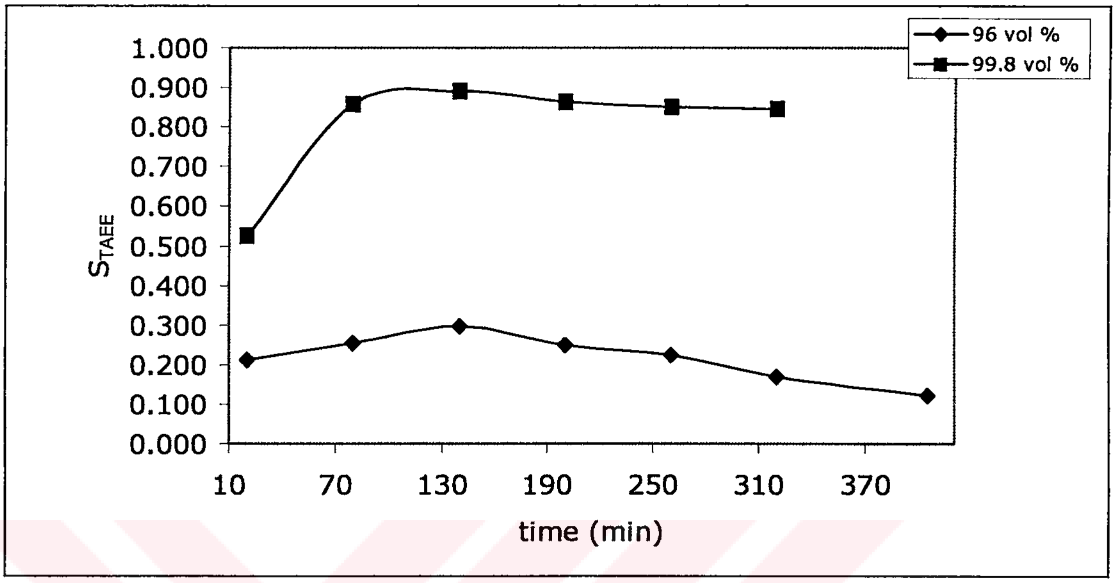


Figure 6.41 Variation of selectivity of TAEE at different EtOH-Water mixtures (Exp No: 8,19)

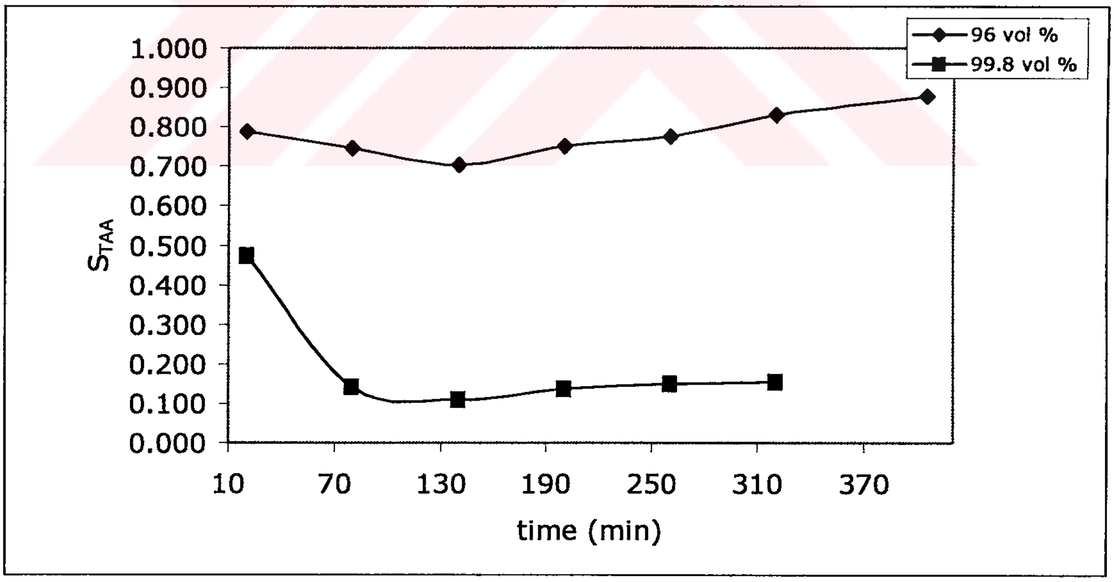


Figure 6.42 Variation of selectivity of TAA at different EtOH-Water mixtures (Exp No: 8,19)

6.5 Effect of Isomerization

As it was discussed previously, there are three reversible reactions that occur simultaneously in TAEE production from ethanol and isoamylene, 2M1B and 2M2B. All three reactions involved in this network are reversible and exothermic, although the exothermicity of the etherification reactions is considerably greater than that of the isomerization reaction as indicated by Kitchaiya and Datta (1995). They also presented expressions for equilibrium constants as a function of temperature. In the study of Oktar et al. (1999), 2M1B was shown to be more reactive than 2M2B in the etherification with ethanol and the activation energy of 2M1B etherification was also found to be less than the corresponding value for the more stable isoamylene, 2M2B.

In the present study, isoamylene mixture of 2-methyl-2-butene (95 mol%) and 2-methyl-1-butene was used in all experiments. In the calculations, the properties of isoamylene mixture were assumed to be equal to properties of 2-methyl-2-butene only. Actually, there were 5 reactions in this system, one of them was isomerization, two of them came from etherification and the last two was written for the hydrations reactions.

$$\begin{aligned}
&\text{2M1B} + \text{EtOH} \xrightarrow{x_{11}} \text{TAEE}\\
&\text{2M2B} + \text{EtOH} \xrightarrow{x_{21}} \text{TAEE}\\
&\text{2M1B} + H_2O \xrightarrow{x_{12}} \text{TAA}\\
&\text{2M2B} + H_2O \xrightarrow{x_{22}} \text{TAA}\\
&\qquad\qquad \text{2M1B} \rightarrow \text{2M2B}
\end{aligned}$$

In the previous calculations the equilibrium conversions were calculated considering the reaction of 2M2B with ethanol and water simultaneously; the reactions related with 2M1B were neglected. To see how the presence of 2M1B effected the equilibrium conversion, a theoretical study was carried out. The details of these calculations were given in Appendix D.5, and the result for one experimental condition was tabulated in Table 6.7. In this table, the first column presented the equilibrium conversion at a reaction temperature of 80°C and at a feed composition of 5 mol% 2M2B assuming all the reactions were carried out simultaneously. In the second column, only the hydration and etherification reaction of 2M2B was considered at the same conditions. Looking at these results, it was concluded that, the assumption of taking only 2M2B in the calculations and considering only the reaction of 2M2B was acceptable. This was majorly due to the low mole fraction of 2M1B in the feed mixture.

Table 6.7 The Experimental and Equilibrium Conversion Values at Different Feed Compositions

Reactions	Considering isomerization	Neglecting isomerization
2M1B + EtOH ⇒ TAEE	0.188	-
2M2B + EtOH ⇒ TAEE	0.535	0.535
2M1B + H_20 ⇒ TAA	0.079	-
2M2B + H_20 ⇒ TAA	0.111	0.113
2M1B ⇒ 2M2B	-	-

6.6 VLE Data for the Binary Pairs

Generally the final step in the synthesis process is the separation of the ether from both unreacted hydrocarbons and the alcohol. As indicated in the previous sections, in all experiments all reactants and products were present in the reboiler. In the first set of experiment (Exp No: 1-5), the sample taken from the reflux was composed of olefin, ethanol and water. For the second set (Exp No: 6-9), the reflux sample contained all the components in different ratios. So it might be important to have some information on the VLE data for different binary pairs in this system.

In the literature the experimental VLE data in the system MeOH-TAME at 288.15, 308.15, 328.15 K (Mössner et al., 1996), MeOH-MTBE, MeOH-TAME at temperature ranging from 288.15 to 338.15 K (Coto et al., 1997), 2M2B-MeOH,

MeOH-TAME, 2M2B-TAME at 100kPA, EtOH-Water at 50kPA (Reichl et al., 1998), EtOH-TAEE, 2M1B-EtOH, 2M1B-TAEE, and EtOH-2M2B-TAEE at 87 kPa (Everson and Jansen, 2001) were presented.

Predictions of VLE data and azeotrope coordinates have been made by means of the group contribution UNIFAC model. Previously, Coto et al. (1997), accurately predicted VLE data and azeotrope coordinates by means of several versions of the UNIFAC model.

In this study, by using UNIFAC model, it was theoretically shown that, the binary mixture consisting of EtOH with TAEE, 2M2B with EtOH and TAEE with TAA had a minimum boiling azeotrope (Figures 6.43, 6.44 and 6.45, respectively). Also, the mixture of 2M2B with TAEE and EtOH with TAA had properties close to that of an ideal mixture (Figure 6.46 and 6.47, respectively). This theoretical study could be supported with the study of Everson and Jansen (2001). Since, Everson and Jansen (2001) showed experimentally, that of the binary mixtures consisting of EtOH with TAEE and 2M1B with EtOH had minimum boiling azeotropes; the mixture of 2M1B with TAEE had the properties close to that of an ideal mixture.

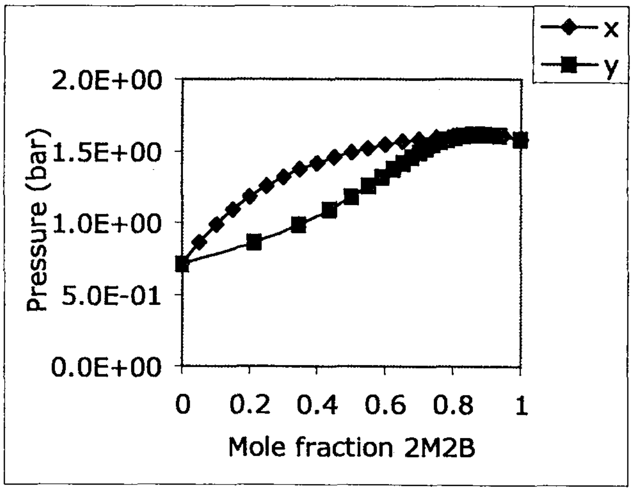


Figure 6.43 Pressure-composition diagram for EtOH-TAEE system at fixed temperature, T=90 °C

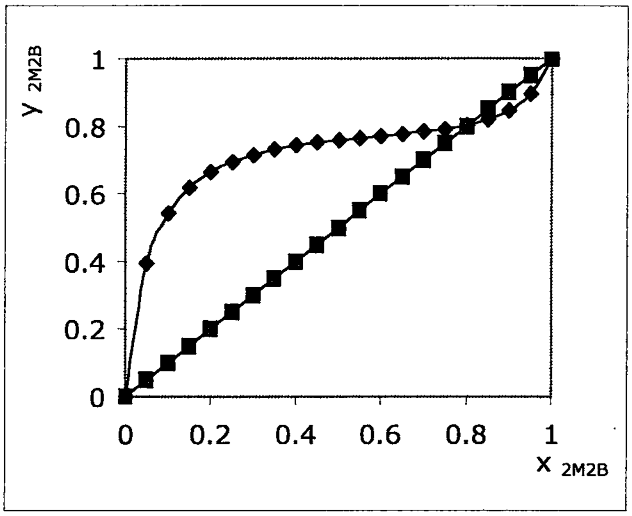


Figure 6.44 The x-y diagram for the 2M2B-EtOH system at T=90°C

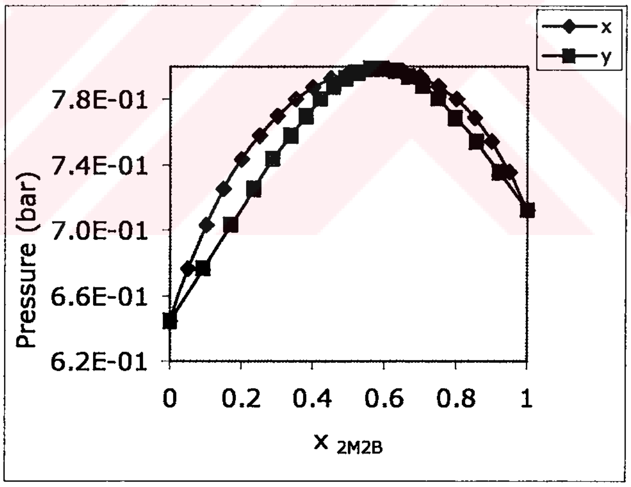


Figure 6.45 Pressure-composition diagram for TAEE-TAA system at fixed temperature, T=90 °C

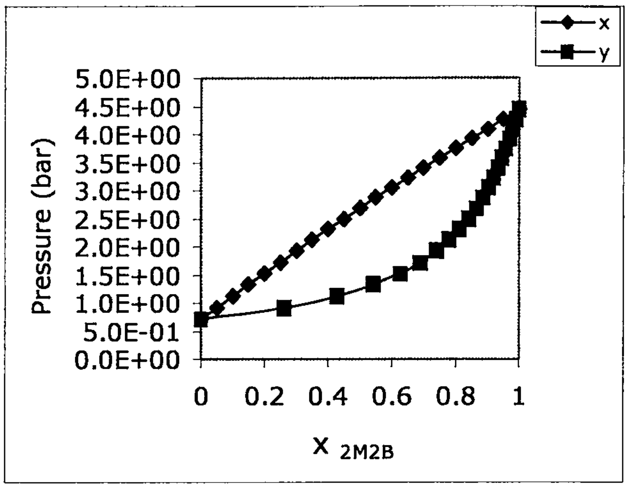


Figure 6.46 Pressure-composition diagram for 2M2B-TAEE system at fixed temperature, T=90 °C

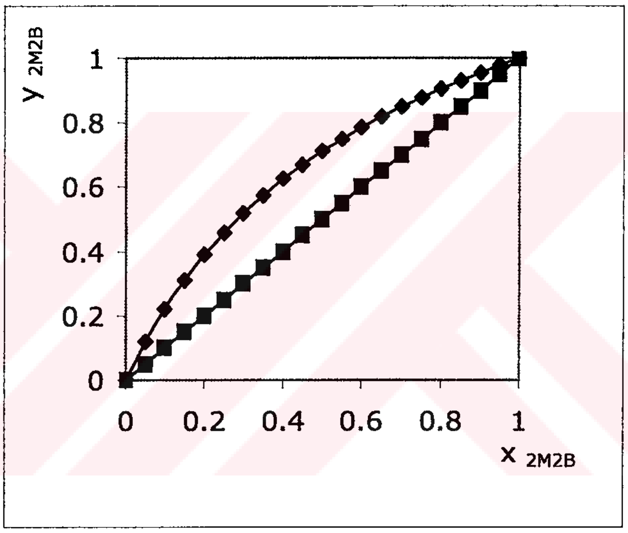


Figure 6.47 The x-y diagram for the EtOH-TAA system at T=90°C

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

In this study, simultaneous production of tert-amyl alcohol and tert-amyl-ethyl ether was investigated in a reactive distillation column. Major conclusions reached as a result of this work are,

1. Very high overall olefin conversions over 99% could be achieved in reaction olefin with ethanol-water mixtures. These conversion values are higher than the calculated equilibrium conversions.

2. Overall conversion of olefin was significantly increased with an increase in temperature. For a feed mixture of 5% isoamylene, total conversion of olefin increased from 0.72 to 0.93 by increasing the reboiler temperature from 90°C to 125°C. Increasing temperature favors the reaction to be complete at a shorter time interval.

3. Selectivity values of TAEE passed through a maximum at all temperatures. However, selectivity values of passed through a minimum showing significant increase at longer times. Selectivity of TAA with respect to TAEE was significantly increased with an increase in temperature. For a feed mixture containing 5% isoamylene, this selectivity ratio increased from 2.3 to 10.8 by increasing the reboiler temperature from 90°C to 124°C.

4. Conversion of olefin to TAA is higher than the equilibrium conversion of this reaction calculated at reboiler temperature. So, reactive distillation is appropriate for this process.

5. Increase of olefin content of feed mixture causes increase in selectivity of TAEE reaction but decrease in selectivity of TAA reaction.

6. Total conversion of olefin increases by changing the position of reactive zone from the middle to top of the column. At longer times in either case, the obtained conversion value higher than 99 %.

7. Changing the plate location from 4 & 5 to 7& 8, the selectivity of TAEE decreased while that of TAA increased.

8. Decreasing the water composition of the feed, as it was expected, increased the olefin conversion to TAEE while overall conversion of olefin increased. Water molecules were strongly adsorbed on the $-SO_3H$ sites of Amberlyst-15 than alcohols and cause a poisoning effect on the catalyst for TAEE production.

9. The equilibrium calculation is carried out neglecting the isomerisation effect. It is showed that the isomerization reaction between the 2-methyl-2- butene and the 2-methyl-1-butene did not effect the equilibrium conversion values.

10. It was theoretically shown that the binary mixture consisting of EtOH with TAEE, 2M2B with EtOH and TAEE with TAA have minimum boiling azeotrope. Also the mixture of 2M2B with TAEE and EtOH with TAA have properties close to that of an ideal mixture.

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APPENDIX A

GAS CHROMATOGRAPH CALIBRATION FACTORS

During the analysis of reactants and products, to evaluate the peak read from the computer that is connected to the gas chromatography or integrator, and to calculate concentrations of the species using these peaks, it is necessary to calculate the calibration factors for gas chromatography. By this way, the errors due to injection and the probable errors come from the detector can be eliminated.

In this study, the calibration factors for 2M2B, TAA and TAME were calculated to obtain quantitative results from the GC trace. The calibration factor of ethanol was taken as a unit and the ratio between each of these species and ethanol were found.

Firstly, 2M2B-EtOH, TAME-EtOH and TAA-EtOH mixtures were prepared concerning the composition range of experiments and these mixtures were injected to the column at different amounts. According to the results, it is concluded that the differences in concentration and injection amount do not affect the value of calibration factor of that species.

A.1 Sample calculation for finding calibration factor:

To find out the calibration factor, for each species, mixtures of different volume fraction were prepared, and different amounts of samples from these mixtures were injected to the gas chromatograph. The calculation procedure for calibration factor was given in the following.

A_A : Area belongs to C_5 reactive olefin, 2M2B

A_B : Area belongs to EtOH

A_C : Area belongs to TAME

A_D : Area belongs to TAA

y_i : Volume fraction belongs to i'th component

x_i : Molar fraction belongs to i'th component

α_i : Relative calibration factor belongs to i'th component

$$A_A\beta_A + A_B\beta_B = 1$$

$$x_A = \frac{A_A\beta_A}{A_A\beta_A + A_B\beta_B} = \frac{\frac{A_A\beta_A}{A_B\beta_B}}{\frac{A_A\beta_A}{A_B\beta_B} + \frac{A_B\beta_B}{A_B\beta_B}} \quad \text{and} \quad \alpha_i = \frac{\beta_A}{\beta_B}$$

$$x_A = \frac{\frac{A_A}{A_B}\alpha_A}{\frac{A_A}{A_B}\alpha_A + 1} \quad \text{and} \quad \alpha_A = \frac{x_A}{\frac{A_A}{A_B}(1 - x_A)}$$

$$\frac{x_A}{x_B}=\frac{y_A}{y_B}\times\frac{\frac{\rho_A}{M_A}}{\frac{\rho_B}{M_B}} \qquad x_A+x_B=1.0$$

Solving these equations simultaneously, calibration factor for species A can be found. Results of calibration experiments using 2M2B and EtOH were given in Table A.1. The calibration factors for TAEE & EtOH and TAA & EtOH were calculated in the same way.

Table A.1 The evaluation of calibration factor α of 2M2B

Injection amount,µl	y_A/y_B	AA	AB	AA/AB	x_B	x_A	α
1	0,20	399	867	0.460	0.901	0.099	0.238
1	0.20	363	786	0.462	0.901	0.099	0.237
2	0.20	797	1712	0.466	0.901	0.099	0.235
2	0.20	753	1641	0.459	0.901	0.099	0.239
5	0.20	2049	4145	0.494	0.901	0.099	0.234
5	0.20	2035	4206	0.484	0.901	0.099	0.227
1	0.10	135	583	0.232	0.948	0.052	0.237
1	0.10	135	650	0.208	0.948	0.052	0.264
2	0.10	358	1653	0.217	0.948	0.052	0.253
2	0.10	394	1849	0.213	0.948	0.052	0.257
5	0.10	909	4188	0.217	0.948	0.052	0.253
5	0.10	896	3974	0.225	0.948	0.052	0.243
						$\alpha_{2M2B.avg}$:	0.241

A.2 Sample Calculation for finding Concentration from GC

The mole fraction of components was calculated by using the following method.

$$A_A\beta_A+A_B\beta_B+A_C\beta_C+A_D\beta_D=1.0$$

$$x_{A}' = \frac{A_A\beta_A}{A_A\beta_A + A_B\beta_B + A_C\beta_C + A_D\beta_D}$$

$$x_{A}' = \frac{\dfrac{A_A\beta_A}{A_B\beta_B}}{\dfrac{A_A\beta_A}{A_B\beta_B} + \dfrac{A_B\beta_B}{A_B\beta_B} + \dfrac{A_C\beta_C}{A_B\beta_B} + \dfrac{A_D\beta_D}{A_B\beta_B}}$$

and defining, $\alpha_i = \dfrac{\beta_i}{\beta_B}$

$$x_{A}' = \frac{\left(\dfrac{A_A}{A_B}\right) \times \alpha_A}{\left(\dfrac{A_A}{A_B} \times \alpha_A + 1 + \dfrac{A_C}{A_B} \times \alpha_C + \dfrac{A_D}{A_B} \times \alpha_D\right)}$$

The mole fraction of other components is calculated in the same way. The final form of the equations are given in the following:

$$x_{B}' = \frac{1}{\left(\dfrac{A_A}{A_B} \times \alpha_A + 1 + \dfrac{A_C}{A_B} \times \alpha_C + \dfrac{A_D}{A_B} \times \alpha_D\right)}$$

$$x_{C}'' = \frac{\left(\dfrac{A_C}{A_B}\right) \times \alpha_C}{\left(\dfrac{A_A}{A_B} \times \alpha_A + 1 + \dfrac{A_C}{A_B} \times \alpha_C + \dfrac{A_D}{A_B} \times \alpha_D\right)}$$

$$x_{D}' = \frac{\left(\dfrac{A_D}{A_B}\right) \times \alpha_D}{\left(\dfrac{A_A}{A_B} \times \alpha_A + 1 + \dfrac{A_C}{A_B} \times \alpha_C + \dfrac{A_D}{A_B} \times \alpha_D\right)}$$

APPENDIX B

THE PROPERTIES OF CHEMICALS

Table B.1 Properties of Chemicals Used in the Reactive Distillation Experiments

Chemical	Chemical Formula	Boiling Point (°C)	Purity	Density	Molecular Weight	Firm
2M2B	C_5H_{10}	38	95%	0.66	70.14	Merck
Ethanol	C_2H_5OH	78-79	Min99.8 Vol%	0.790	32.04	Sigma-Aldrich
Ethanol	C_2H_5OH	78	96 Vol%	0.800	32.04	Birpa
TAME	$C_6H_{14}O$	85-86	97 %	0.770	102.18	Aldrich
TAA	$C_5H_{12}O$	102	99%	0.808	88.15	Merck

(*) Taken from Arce et al., 2001.

Table B.2 Properties of components necessary for the programs

Components	T_C, K	P_C, bar	ω	κ_1
2M2B	470	38.6	0.339	-0.2086
EtOH	513.92	61.48	0.64439	-0.03374
TAEE	552.67	28.036	0.301215	0.1254
TAA	545	37.9	0.478	0.7013
H_2O	647.29	220.90	0.34380	-0.06635

Table B.3 Coefficients of the Antoine Equations

Components	A	B	C
2M2B	4.09149	1124.330	236.630
EtOH	5.33675	1648.220	230.918
TAEE (*)	5.926451	-1218.389	-63.940
TAA	3.64420	863.400	135.30
H2O	5.11564	1687.537	230.17

Vapor pressures of 2M2B,EtOH, TAA and H_2O were calculated using the following equation and Antoine constants, taken from Poling, Prausnitz and O'Connell, 2001:

$$\log_{10}(P_{vap}) = A - B/(T + C - 273.15)$$

where, P_{vap} is in bar and T is in K.

To calculate the vapor pressure of TAEE, the equation and the Antoine coefficients taken from Krähenbühl and Gmehling, 1994, was used. This equation was given in the following:

$$\log(P_i^s / kPa) = A + \frac{B}{(T/K) + C}$$

APPENDIX C

EXPERIMENTAL DATA

For each experiment, samples were taken from the reboiler and reflux sections at the same time. In the following tables, data analyzed with GC for both reboiler and reflux samples are presented. It is necessary to note that, for the reflux data, sometimes two-phase occurrence was observed. In tables the reflux section was divided into 3 parts for two-phase samples. In the first row, the lower layer, in the second row the upper layer and the third row represents the mixture obtained from the analysis.

Table C.1 Experimental data of components without water Experiment No:1 at $T_{reboiler}$:90°C

EXPERIMENT: 1
Feed:5 mol % 2M2B, 84 mol % EtOH, 11 mol% H_2O
Reboiler Temperature (°C):90
Operating Gauge Pressure Range (bar): 1.35-1.10
Reaction Plates: 4 & 5
Catalyst Amount (gr/plate): 10
Water/Ethanol mole ratio: 0.135

Feed: x_{2M2B} : 0.0581, x_{EtOH} :0.9419

Time (min)	Reboiler data				Reflux Data			
	x_{2M2B}	x_{EtOH}	x_{TAEE}	x_{TAA}	x_{2M2B}	x_{EtOH}	x_{TAEE}	x_{TAA}
20	0.0241	0.9548	0.0055	0.0156	0.1925	0.8075	0.0000	0.0000
					0.8010	0.1990	0.0000	0.0000
					0.6401	0.3599	0.0000	0.0000
80	0.0350	0.9520	0.0045	0.0085	0.0254	0.9746	0.0000	0.0000
					0.6997	0.3003	0.0000	0.0000
					0.0821	0.9179	0.0000	0.0000
140	0.0331	0.9499	0.0065	0.0106	0.0183	0.9817	0.0000	0.0000
					0.2933	0.7067	0.0000	0.0000
					0.0673	0.9327	0.0000	0.0000
200	0.0254	0.9504	0.0091	0.0151	0.0152	0.9848	0.0000	0.0000
290	0.0210	0.9464	0.0117	0.0209	0.0164	0.9836	0.0000	0.0000
350	0.0164	0.9460	0.0125	0.0251	0.0184	0.9816	0.0000	0.0000
					0.4358	0.5642	0.0000	0.0000
					0.0668	0.9332	0.0000	0.0000
Reboiler	0.0166	0.9398	0.0135	0.0301				

Table C.2 Experimental data of components without water Experiment No: 2 at $T_{reboiler}$:101°C

EXPERIMENT: 2

Feed:5 mol % 2M2B, 84 mol % EtOH, 11 mol% H_2O

Reboiler Temperature (°C):101

Operating Gauge Pressure Range (bar): 2.40-1.50

Reaction Plates: 4 & 5

Catalyst Amount (gr/plate): 10

Water/Ethanol mole ratio: 0.135

Feed: x_{2M2B} : 0.0597, x_{EtOH} :0.9403

Time (min)	Reboiler data				Reflux Data			
	x_{2M2B}	x_{EtOH}	x_{TAEE}	x_{TAA}	x_{2M2B}	x_{EtOH}	x_{TAEE}	x_{TAA}
25	0.0424	0.9540	0.0005	0.0031	0.0525	0.9475	0.0000	0.0000
					0.8098	0.1902	0.0000	0.0000
					0.2704	0.7296	0.0000	0.0000
145	0.0161	0.9702	0.0059	0.0079	0.0252	0.9746	0.0001	0.0000
					0.8036	0.1964	0.0000	0.0000
					0.3743	0.6257	0.0000	0.0000
205	0.0065	0.9739	0.0071	0.0125	0.0253	0.9745	0.0001	0.0000
265	0.0035	0.9666	0.0088	0.0211	0.0111	0.9885	0.0004	0.0000
325	0.0017	0.9602	0.0103	0.0278	0.0078	0.9906	0.0015	0.0000
385	0.0019	0.9576	0.0100	0.0305	0.0051	0.9940	0.0009	0.0000
Reboiler	0.0159	0.9435	0.0092	0.0314				

Table C.3 Experimental data of components without water Experiment No:3 at $T_{reboiler}$:111°C

EXPERIMENT: 3
Feed:5 mol % 2M2B, 84 mol % EtOH, 11 mol% H_2O
Reboiler Temperature (°C):111
Operating Gauge Pressure Range (bar): 3.40-1.00
Reaction Plates: 4 & 5
Catalyst Amount (gr/plate): 10
Water/Ethanol mole ratio: 0.135

Feed: x_{2M2B} : 0.0512, x_{EtOH} :0.9488

Time (min)	Reboiler data				Reflux Data			
	x_{2M2B}	x_{EtOH}	x_{TAEE}	x_{TAA}	x_{2M2B}	x_{EtOH}	x_{TAEE}	x_{TAA}
20	0.0162	0.9808	0.0006	0.0023	0.0078	0.9922	0.0000	0.0000
80	0.0097	0.9839	0.0016	0.0048	0.0084	0.9912	0.0004	0.0000
140	0.0050	0.9805	0.0043	0.0102	0.0078	0.9917	0.0005	0.0000
200	0.0023	0.9753	0.0056	0.0168	0.0053	0.9938	0.0003	0.0007
260	0.0007	0.9735	0.0058	0.0200	0.0080	0.9909	0.0006	0.0006
320	0.0003	0.9770	0.0039	0.0188	0.0232	0.9635	0.0073	0.0059
405	0.0003	0.9766	0.0028	0.0203	0.2347	0.7406	0.0225	0.0022
Reboiler	0.0024	0.9775	0.0024	0.0177	-	-	-	-

Table C.4 Experimental data of components without water Experiment No:4 at $T_{reboiler}$:119°C

EXPERIMENT: 4

Feed:5 mol % 2M2B, 84 mol % EtOH, 11 mol% H_2O

Reboiler Temperature (°C): 119

Operating Gauge Pressure Range (bar): 4.00-3.60

Reaction Plates: 4 & 5

Catalyst Amount (gr/plate): 10

Water/Ethanol mole ratio: 0.135

Feed: x_{2M2B} : 0.0625, x_{EtOH} :0.9375

Time (min)	Reboiler Data				Reflux Data			
	x_{2M2B}	x_{EtOH}	x_{TAEE}	x_{TAA}	x_{2M2B}	x_{EtOH}	x_{TAEE}	x_{TAA}
15	0.0177	0.9682	0.0026	0.0114	0.0350	0.9650	0.0000	0.0000
					0.7263	0.2737	0.0000	0.0000
					0.2004	0.7996	0.0000	0.0000
75	0.0099	0.9762	0.0038	0.0100	0.0541	0.9449	0.0009	0.0000
135	0.0028	0.9707	0.0074	0.0190	0.0619	0.9374	0.0007	0.0000
195	0.0014	0.9652	0.0087	0.0248	0.0334	0.9665	0.0001	0.0000
					0.7220	0.2780	0.0000	0.0000
					0.1216	0.8783	0.0001	0.0000
255	0.0007	0.9554	0.0093	0.0346	0.0559	0.9436	0.0006	0.0000
					0.7578	0.2420	0.0001	0.0000
					0.3002	0.6996	0.0002	0.0000
Reboiler	0.0042	0.9485	0.0061	0.0411	-	-	-	-

Table C.5 Experimental data of components without water Experiment No:5 at $T_{reboiler}$:125°C

EXPERIMENT: 5
Feed:5 mol % 2M2B, 84 mol % EtOH, 11 mol% H_2O
Reboiler Temperature (°C): 125
Operating Gauge Pressure Range (bar): 5.00-1.00
Reaction Plates: 4 & 5
Catalyst Amount (gr/plate): 10
Water/Ethanol mole ratio: 0.135

Feed: x_{2M2B} : 0.0585, x_{EtOH} :0.9415

Time (min)	Reboiler Data				Reflux Data			
	x_{2M2B}	x_{EtOH}	x_{TAEE}	x_{TAA}	x_{2M2B}	x_{EtOH}	x_{TAEE}	x_{TAA}
45	0.0053	0.9735	0.0060	0.0151	0.0154	0.9845	0.0001	0.0000
					0.0438	0.9561	0.0001	0.0000
					0.0255	0.9744	0.0001	0.0000
105	0.0021	0.9704	0.0068	0.0207	0.0100	0.9899	0.0001	0.0000
165	0.0005	0.9663	0.0062	0.0270	0.0315	0.9684	0.0001	0.0000
					0.7872	0.2128	0.0000	0.0000
					0.2671	0.7329	0.0000	0.0000
225	0.0007	0.9671	0.0050	0.0272	0.3271	0.6687	0.0041	0.0000
285	0.0006	0.9668	0.0040	0.0266	0.2280	0.7603	0.0117	0.0000
345	0.0001	0.9749	0.0021	0.0229	0.1660	0.8187	0.0153	0.0000
Reboiler	0.0017	0.9750	0.0020	0.0213	-	-	-	-

Table C.6 Experimental data of components without water Experiment No:6 at a olefin mole fraction of 3 %

EXPERIMENT: 6

Feed: 3 mol % 2M2B, 85.5 mol % EtOH, 11.5 mol% H_2O

Reboiler Temperature (°C): 111

Operating Gauge Pressure Range (bar): 4.50-1.50

Reaction Plates: 7 & 8

Catalyst Amount (gr/plate): 10

Water/Ethanol mole ratio: 0.135

Feed: x_{2M2B} : 0.0413, x_{EtOH} :0.9587

Time (min)	Reboiler Data				Reflux Data			
	x_{2M2B}	x_{EtOH}	x_{TAEE}	x_{TAA}	x_{2M2B}	x_{EtOH}	x_{TAEE}	x_{TAA}
12	0.0051	0.9398	0.0014	0.0538	0.0292	0.9708	0.0000	0.0000
					0.7876	0.2124	0.0000	0.0000
					0.1438	0.8562	0.0000	0.0000
72	0.0038	0.9617	0.0068	0.0277	0.4160	0.5242	0.0496	0.0102
132	0.0004	0.9430	0.0084	0.0483	0.3132	0.6080	0.0708	0.0080
192	0.0001	0.9406	0.0057	0.0536	0.2508	0.6797	0.0695	0.0000
248	0.0000	0.9357	0.0037	0.0606	0.2282	0.7097	0.0568	0.0053
Reboiler	0.0002	0.9565	0.0041	0.0392	-	-	-	-

Table C.7 Experimental data of components without water Experiment No:7 at a olefin mole fraction of 5 %

EXPERIMENT: 7

Feed: 5 mol % 2M2B, 83.7 mol % EtOH, 11.3mol% H_2O

Reboiler Temperature (°C): 114

Operating Gauge Pressure Range (bar): 4.50-1.50

Reaction Plates: 7 & 8

Catalyst Amount (gr/plate): 10

Water/Ethanol mole ratio: 0.135

Feed: x_{2M2B} : 0.0413, x_{EtOH} :0.9587

Time (min)	Reboiler Data				Reflux Data			
	x_{2M2B}	x_{EtOH}	x_{TAEE}	x_{TAA}	x_{2M2B}	x_{EtOH}	x_{TAEE}	x_{TAA}
45	0.0194	0.9673	0.0027	0.0106	0.0072	0.9741	0.0005	0.0182
105	0.0125	0.9500	0.0072	0.0302	0.0048	0.9753	0.0037	0.0162
165	0.0031	0.9364	0.0098	0.0508	0.0773	0.9017	0.0121	0.0089
					0.5815	0.2920	0.1265	0.0000
					0.3325	0.5937	0.0615	0.0123
225	0.0003	0.9332	0.0089	0.0577	0.2726	0.6400	0.0791	0.0082
Reboiler	0.0011	0.9286	0.0049	0.0654	-	-	-	-

Table C.8 Experimental data of components without water Experiment No:8 at a olefin mole fraction of 10 %

EXPERIMENT: 8
Feed: 10 mol % 2M2B, 79.3 mol % EtOH, 10.7 mol% H_2O
Reboiler Temperature (°C): 118
Operating Gauge Pressure Range (bar): 4.20-3.20
Reaction Plates: 7 & 8
Catalyst Amount (gr/plate): 10
Water/Ethanol mole ratio: 0.135

Feed: x_{2M2B} : 0.0413, x_{EtOH} :0.9587

Time (min)	Reboiler Data				Reflux Data			
	x_{2M2B}	x_{EtOH}	x_{TAEE}	x_{TAA}	x_{2M2B}	x_{EtOH}	x_{TAEE}	x_{TAA}
40	0.0198	0.9224	0.0050	0.0528	0.0061	0.9845	0.0006	0.0088
100	0.0397	0.9158	0.0077	0.0368	0.0034	0.9884	0.0003	0.0078
160	0.0334	0.8932	0.011	0.0623	0.0031	0.9917	0.0003	0.0049
220	0.0169	0.8859	0.0136	0.0836	0.0036	0.9891	0.0005	0.0068
280	0.0081	0.8683	0.0179	0.1057	0.2753	0.6606	0.0641	0.0000
Reboiler	0.0037	0.8818	0.0223	0.0922	-	-	-	-

Table C.9 Experimental data of components without water Experiment No:9 at a olefin mole fraction of 18 %

EXPERIMENT: 9

Feed: 18 mol % 2M2B, 72.3 mol % EtOH, 9.7 mol% H_2O

Reboiler Temperature (°C): 118

Operating Gauge Pressure Range (bar): 4.20-3.20

Reaction Plates: 7 & 8

Catalyst Amount (gr/plate): 10

Water/Ethanol mole ratio: 0.135

Feed: x_{2M2B} : 0.2018, x_{EtOH} :0.7983

Time (min)	Reboiler Data				Reflux Data			
	x_{2M2B}	x_{EtOH}	x_{TAEE}	x_{TAA}	x_{2M2B}	x_{EtOH}	x_{TAEE}	x_{TAA}
10	0.0726	0.8895	0.0027	0.0352	0.0137	0.9862	0.0001	0.0000
					0.8359	0.1605	0.0000	0.0000
					0.2861	0.7140	0.0000	0.0000
70	0.1099	0.8641	0.0030	0.0229	0.0102	0.9867	0.0001	0.0030
130	0.1044	0.8422	0.0051	0.0483	0.0060	0.9939	0.0000	0.0000
190	0.1015	0.8175	0.0058	0.0751	0.0043	0.9940	0.0002	0.0015
250	0.1008	0.8040	0.0068	0.0884	0.0040	0.0057	0.0002	0.0000
310	0.0800	0.7943	0.0059	0.1202	0.0049	0.9935	0.0016	0.0000
Reboiler	0.1309	0.7575	0.0060	0.1055	-	-	-	-

Table C.10 Experimental data of components without water Experiment No:10 at a water/ethanol mole ratio of 0.0065

EXPERIMENT: 10

Feed: 5 mol % 2M2B, 94.4 mol % EtOH, 0.6 mol% H_2O

Reboiler Temperature (°C): 110

Operating Gauge Pressure Range (bar): 2.4

Reaction Plates: 4 & 5

Catalyst Amount (gr/plate): 10

Water/Ethanol mole ratio: 0.0065

Feed: x_{2M2B} : 0.0434, x_{EtOH} :0.9566

Time (min)	Reboiler Data				Reflux Data			
	x_{2M2B}	x_{EtOH}	x_{TAEE}	x_{TAA}	x_{2M2B}	x_{EtOH}	x_{TAEE}	x_{TAA}
20	0.0037	0.9913	0.0027	0.0024	0.6676	0.3285	0.0031	0.0008
80	0.0016	0.9913	0.0061	0.0010	0.8397	0.1593	0.0009	0.0000
140	0.0003	0.9888	0.0096	0.0012	0.8168	0.1827	0.0005	0.0000
200	0.0001	0.9892	0.0092	0.0015	0.8313	0.1684	0.0003	0.0000
260	0.0001	0.9912	0.0074	0.0013	0.8259	0.1738	0.0002	0.0000
320	0.0001	0.9924	0.0064	0.0012	0.8219	0.1777	0.0003	0.0000
Reboiler	0.0033	0.9900	0.0057	0.0010	-	-	-	-

APPENDIX D

CALCULATIONS

D.1 Calculations of water concentration from the concentration data obtained without water

FID (Flame Ionization Detector) can not perceive the water molecule. Since the mole fractions of other components unlike water were calculated by using the gas chromatography data, the amount of water could be calculated using these data and material balances.

At the beginning of the experiment: x_{2M2M}', x_{EtOH}' which are the mole fraction are known.

$$x_{2M2B'} = \frac{x_{2M2B}}{1 - x_{H_2O}} \quad \text{and} \quad x_{EtOH'} = \frac{x_{EtOH}}{1 - x_{H_2O}}$$

The ethanol water mixture used in the experiments was 96% purity so,

$$\left(\frac{H_2O}{EtOH}\right)_{vol} = \frac{4}{96} \Rightarrow \frac{x_{H_2O}}{x_{EtOH}} = \frac{4}{96} * \frac{\frac{1}{18.0152}}{\frac{0.7914}{46.069}} \Rightarrow \frac{x_{H_2O}}{x_{EtOH}} = 0.1346 \quad \text{and}$$

$$x_{2M2B} + x_{EtOH} + x_{H_2O} = 1.0$$

Simultaneous solution of these equations gives x_{H_2O}.

Sample calculations;

Using chromatographic analysis the mol fraction of olefin and ethanol was found like these,

$$x_{2M2B'} = 0.0581, x_{EtOH'} = 0.9419$$

$$\frac{x_{2M2B}}{1-x_{H_2O}} = 0.0581, \frac{x_{EtOH}}{1-x_{H_2O}} = 0.9419, \frac{x_{H_2O}}{x_{EtOH}} = 0.1346$$

Using total material balances,

$$0.0581*(1-x_{H_2O}) + \frac{x_{H_2O}}{0.1346} + x_{H_2O} = 1.0$$

$$0.0581 - 0.0581*x_{H_2O} + 7.4294*x_{H_2O} + x_{H_2O} = 1.0$$

it was founded: $x_{H_2O} = 0.1125$, $x_{2M2B} = 0.0516$, $x_{EtOH} = 0.8359$

Final Condition:

This procedure is applicable to any time including final form. In this case, $x_{2M2B'}$, $x_{EtOH'}$, $x_{TAEE'}$ and $x_{TAA'}$ are known.

$$x_{2M2B'} = \frac{x_{2B2B}}{1-x_{H_2O}}, x_{EtOH'} = \frac{x_{EtOH}}{1-x_{H_2O}}, x_{TAEE'} = \frac{x_{TAEE}}{1-x_{H_2O}}, \text{and } x_{TAA'} = \frac{x_{TAA}}{1-x_{H_2O}}$$

Reactions can be written as,

2M2B + EtOH → TAEE
2M2B + H_2O → TAA

$$\frac{n_{EtOH}+n_{TAEE}}{n_{H_2O}+n_{TAA}}=\frac{x_{EtOH}+x_{TAEE}}{x_{H_2O}+x_{TAA}}=\frac{1}{0.1346}\Rightarrow\frac{x_{TAA}+x_{H_2O}}{x_{TAEE}+x_{EtOH}}=0.1346$$

$$x_{2M2B}+x_{EtOH}+x_{TAEE}+x_{TAA}+x_{H_2O}=1.0$$

Simultaneous solution of these equations gives the mole fraction of component with water.

Sample Calculations:

$x_{2M2B'}=\frac{x_{2M2B}}{1-x_{H_2O}}=0.0166$, $x_{EtOH'}=\frac{x_{EtOH}}{1-x_{H_2O}}=0.9398$, $x_{TAEE'}=\frac{x_{TAEE}}{1-x_{H_2O}}=0.0135$,

$x_{TAA'}=\frac{x_{TAA}}{1-x_{H_2O}}=0.0301$, and $\frac{x_{EtOH}+x_{TAEE}}{x_{H_2O}+x_{TAA}}=\frac{1}{0.1346}$

$$0.0166*(1-x_{H_2O})+0.9398*(1-x_{H_2O})+0.0135*(1-x_{H_2O})+x_{H_2O}+x_{TAA}=1.0$$

$$\frac{x_{EtOH}+x_{TAEE}}{x_{TAA}+x_{H_2O}}=\frac{1}{0.1346}\Rightarrow x_{TAA}+x_{H_2O}=0.1346*(x_{EtOH}+x_{TAEE})$$

Solving these equations it was founded that,

$x_{H_2O}=0.0894$

$x_{2M2B}=0.0166*(1-x_{H_2O})=0.0151$

$x_{EtOH}=0.9398*(1-x_{H_2O})=0.856$

$x_{TAEE}=0.90135*(1-x_{H_2O})=0.0123$

$x_{TAA}=0.0301*(1-x_{H_2O})=0.0274$

In Table D.1, the application of this calculation produce for Experiment was presented.

Table D.1 Sample Calculation from the composition of components including water for an experiment

	x_{2M2B}	x_{EtOH}	x_{TAEE}	x_{TAA}	$x_{2M2B'}$	$x_{EtOH'}$	$x_{TAEE'}$	$x_{TAA'}$	$x_{H_2O'}$
Feed	0.0581	0.9419	0.0000	0.0000	0.0516	0.8359	0.0000	0.0000	0.1125
BP 1	0.0241	0.9548	0.0055	0.0156	0.0216	0.8574	0.0049	0.1404	0.1021
BP 2	0.0350	0.9520	0.0045	0.0085	0.0313	0.8498	0.0040	0.0076	0.1074
BP 3	0.0331	0.9499	0.0065	0.0106	0.0296	0.8495	0.0058	0.0094	0.1057
BP 4	0.0254	0.9504	0.0091	0.0151	0.0228	0.8531	0.0082	0.0136	0.1024
BP 5	0.0210	0.9464	0.0117	0.0209	0.0190	0.8541	0.0105	0.0189	0.0975
BP 6	0.0164	0.9460	0.0125	0.0251	0.0148	0.8569	0.0113	0.0228	0.0942
BP 7	0.0119	0.9487	0.0121	0.0273	0.0108	0.8609	0.0109	0.0248	0.0926
R	0.0166	0.9398	0.0135	0.0301	0.0151	0.8557	0.0123	0.0274	0.0895

D.2 Calculations of Volume Fraction

$$(2M2B)_{volumefraction} = \frac{\left(x_{2M2B} \times \dfrac{MW_{2M2B}}{\rho_{2M2B}}\right)}{\left(x_{2M2B} \times \dfrac{MW_{2M2B}}{\rho_{2M2B}}\right) + \left(x_{EtOH} \times \dfrac{MW_{EtOH}}{\rho_{EtOH}}\right) + \left(x_{H_2O} \times \dfrac{MW_{H_2O}}{\rho_{H_2O}}\right)}$$

For 2M2B: $y_{2M2B} = x_{2M2B} \times \dfrac{MW_{2M2B}}{\rho_{2M2B}} \Rightarrow y_{2M2B} = x_{2M2B} \times \dfrac{70.135 g/mol}{0.6604 g/cm^3}$

For EtOH: $y_{EtOH} = x_{EtOH} \times \dfrac{MW_{EtOH}}{\rho_{EtOH}} \Rightarrow y_{EtOH} = x_{Etoh} \times \dfrac{46.069 g/mol}{0.7914 g/cm^3}$

For H₂O: $y_{H_2O} = x_{H_2O} \times \dfrac{MW_{H_2O}}{\rho_{H_2O}} \Rightarrow y_{H_2O} = x_{H_2O} \times \dfrac{18.015 g/nol}{1 g/cm^3}$

D.3 Calculations of Mol Numbers

$$n_i = V_{total} \times y_i \times \frac{\rho_i}{MW_i}$$

D.4 Calculations of Equilibrium Conversion

Reactions considered to calculate equilibrium

$$2M2B + EtOH \Leftrightarrow TAEE \qquad (Q_1)$$
$$2M2B + H_2O \Leftrightarrow TAA \qquad (Q_2)$$

Concentration were written as,

Olefin $\Rightarrow$ $C_{2M2B} = C^0_{2M2B} * (1 - X_1 - X_2)$

Ethanol $\Rightarrow$ $C_{EtOH} = C^0_{EtOH} - C^0_{2M2B} * X_1$

TAEE $\Rightarrow$ $C_{TAEE} = C^0_{2M2B} * X_1$

TAA $\Rightarrow$ $C_{TAA} = C^0_{2M2B} * X_2$

H_2O $\Rightarrow$ $C_{H_2O} = C^0_{H_2O} - C^0_{2M2B} * X_2$

C $_{TOTAL}$ $\Rightarrow$ $C_{TOTAL} = C^0_{2M2B} * (1 - X_1 - X_2) + C^0_{H_2O} + C^0_{EtOH}$

Mole Fractions were written as;

$$x_{2M2B} = \frac{C^0_{2M2B} * (1 - X_1 - X_2)}{C^0_{2M2B} * (1 - X_1 - X_2) + C^0_{H_2O} + C^0_{EtOH}}$$

$$x_{EtOH} = \frac{C^0_{EtOH} - C^0_{2M2B} * X_1}{C^0_{2M2B} * (1 - X_1 - X_2) + C^0_{H_2O} + C^0_{EtOH}}$$

$$x_{TAEE} = \frac{C^0_{2M2B} * X_1}{C^0_{2M2B} * (1 - X_1 - X_2) + C^0_{H_2O} + C^0_{EtOH}}$$

$$x_{TAA} = \frac{C^0_{2M2B} * X_2}{C^0_{2M2B} * (1 - X_1 - X_2) + C^0_{H_2O} + C^0_{EtOH}}$$

$$x_{H_2O} = \frac{C^0_{H_2O} - C^0_{2M2B} * X_2}{C^0_{2M2B} * (1 - X_1 - X_2) + C^0_{H_2O} + C^0_{EtOH}}$$

Writing K_1 and K_2 for TAEE reaction and TAA reaction respectively;

$$K1 = \frac{\gamma_{TAEE}}{\gamma_{EtOH} \times \gamma_{2M2B}} \times \frac{x_{TAEE}}{x_{EtOH} \times x_{2M2B}}$$

$$K2 = \frac{\gamma_{TAA}}{\gamma_{H2O} \times \gamma_{2M2B}} \times \frac{x_{TAA}}{x_{H2O} \times x_{2M2B}}$$

substituting the mole fractions,

$$K1 = \frac{\gamma_{TAEE}}{\gamma_{EtOH} \times \gamma_{2M2B}} \times \frac{C_{2M2B,0} \times X_1 \times C_T}{\left(C_{EtOH,0} - C_{2M2B,0} \times X_1\right) \times \left(C_{2M2B,0} \times \left(1 - X_1 - X_2\right)\right)}$$

$$K_2 = \frac{\gamma_{TAA}}{\gamma_{H2O} \times \gamma_{2M2B}} \times \frac{C_{2M2B,0} \times X_2 \times C_T}{\left(C_{H2O,0} - C_{2M2B,0} \times X_2\right) \times \left(C_{2M2B,0} \times \left(1 - X_1 - X_2\right)\right)}$$

Equilibrium constants, K_1 and K_2 were calculated from literature.

For TAEE: (Kitchaiya and Datta, 1995)

$$\ln K2 = 26.779 + \frac{2078.6}{T} - 6.5925 \times \ln T + 0.0231 \times T - 1.126 \times 10^{-5} \times T^2 - 1.414 \times 10^{-8} \times T^3$$

For TAA: (Gonzalez and Fair, 1999)

$$Ke = Ke_o \times \exp\left(\frac{-\Delta H_r}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right)$$

for $T_0 = 70.1 \Rightarrow K_e = 0.33$ substituting into eqn (*)

$$K_e = 0.33 \times \exp\left(\frac{26500}{8.314}\left(\frac{1}{T} - \frac{1}{343.25}\right)\right)$$

For finding the equilibrium constant for TAA formation, Aioache and Goto (2003) present an equation obtained from experimental data as

$$\ln K = 5.75 - \frac{1376}{T}$$

This equation gives nearly the same value with the found from Gonzalez and Fair (1999).

D.5 Calculations of Equilibrium Conversion Considering 2M1B

Reactions ,

$$\text{2M1B} + \text{EtOH} \xrightarrow{X_{11}} \text{TAEE}$$
$$\text{2M2B} + \text{EtOH} \xrightarrow{X_{21}} \text{TAEE}$$
$$\text{2M1B} + H_2O \xrightarrow{X_{12}} \text{TAA}$$
$$\text{2M2B} + H_2O \xrightarrow{X22} \text{TAA}$$
$$\text{2M1B} \rightarrow \text{2M2B}$$

Concentration were written as,

2M1B $\Rightarrow$ $C_{2M1B} = C^0_{2M1B} * (1 - X_{11} - X_{12})$

2M2B $\Rightarrow$ $C_{2M2B} = C^0_{2M2B} * (1 - X_{21} - X_{22})$

EtOH $\Rightarrow$ $C_{EtOH} = C^0_{EtOH} - C^0_{2M1B} * X_{11} - C^0_{2M2M} * X_{21}$

TAEE $\Rightarrow$ $C_{TAEE} = C^0_{2M1B} * X_{11} + C^0_{2M2B} * X_{21}$

TAA $\Rightarrow$ $C_{TAA} = C^0_{2M1B} * X_{12} + C^0_{2M2B} * X_{22}$

H_2O $\Rightarrow$ $C_{H_2O} = C^0_{H_2O} - C^0_{2M1B} * X_{12} - C^0_{2M2B} * X_{22}$

C_{TOTAL} $\Rightarrow$ $C_{TOTAL} = C^0_{2M1B} * (1 - X_{11} - X_{12}) + C^0_{2M2B} * (1 - X_{21} - X_{22}) + C^0_{H_2O} + C^0_{EtOH}$

Mole Fractions were written as;

$$x_{2M1B} = \frac{C^0_{2M1B} * (1 - X_{11} - X_{12})}{C^0_{2M1B} * (1 - X_{11} - X_{12}) + C^0_{2M2B} * (1 - X_{21} - X_{22}) + C^0_{H_2O} + C^0_{EtOH}}$$

$$x_{2M2B} = \frac{C^0_{2M2B} * (1 - X_{21} - X_{22})}{C^0_{2M1B} * (1 - X_{11} - X_{12}) + C^0_{2M2B} * (1 - X_{21} - X_{22}) + C^0_{H_2O} + C^0_{EtOH}}$$

$$x_{EtOH} = \frac{C^0_{EtOH} - C^0_{2M1B} * X_{11} - C^0_{2M2B} * X_{21}}{C^0_{2M1B} * (1 - X_{11} - X_{12}) + C^0_{2M2B} * (1 - X_{21} - X_{22}) + C^0_{H_2O} + C^0_{EtOH}}$$

$$x_{TAEE} = \frac{C^0_{2M1B} * X_{11} - C^0_{2M2B} * X_{21}}{C^0_{2M1B} * (1 - X_{11} - X_{12}) + C^0_{2M2B} * (1 - X_{21} - X_{22}) + C^0_{H_2O} + C^0_{EtOH}}$$

$$x_{TAA} = \frac{C^0_{2M1B} * X_{12} - C^0_{2M2B} * X_{22}}{C^0_{2M1B} * (1 - X_{11} - X_{12}) + C^0_{2M2B} * (1 - X_{21} - X_{22}) + C^0_{H_2O} + C^0_{EtOH}}$$

$$x_{H_2O} = \frac{C^0_{H_20} - C^0_{2M1B} * X_{12} - C^0_{2M2B} * X_{22}}{C^0_{2M1B} * (1 - X_{11} - X_{12}) + C^0_{2M2B} * (1 - X_{21} - X_{22}) + C^0_{H_2O} + C^0_{EtOH}}$$

Writing equilibrium constants for each species

$$K_{E1} = \frac{\gamma_{TAEE}}{\gamma_{EtOH} \times \gamma_{2M1B}} \times \frac{x_{TAEE}}{x_{EtOH} \times x_{2M1B}}$$

$$K_{E2} = \frac{\gamma_{TAEE}}{\gamma_{EtOH} \times \gamma_{2M2B}} \times \frac{x_{TAEE}}{x_{EtOH} \times x_{2M2B}}$$

$$K_{H2} = \frac{\gamma_{TAA}}{\gamma_{H2O} \times \gamma_{2M2B}} \times \frac{x_{TAA}}{x_{H2O} \times x_{2M2B}}$$

$$K_I = \frac{\gamma_{T2M2B}}{\gamma_{2M1B}} \times \frac{x_{2M2B}}{x_{2M1B}}$$

substituting the mole fractions,

$$K_{E1} = \frac{\gamma_{TAEE}}{\gamma_{EtOH} \times \gamma_{2M1B}} \times \frac{(C_{2M1B,0} * X_{11} + C^0_{2M2B} * X_{21}) * C_T}{C^0_{2M1B} * (1 - X_{11} - X_{12}) * \left(C_{EtOH,0} - C^0_{2M1B} * X_{11} - C^0_{2M2B} * X_{21}\right)}$$

$$K_{E2} = \frac{\gamma_{TAEE}}{\gamma_{EtOH} \times \gamma_{2M2B}} \times \frac{(C_{2M1B,0} * X_{11} + C^0_{2M2B} * X_{21}) * C_T}{C^0_{2M2B} * (1 - X_{21} - X_{22}) * \left(C_{EtOH,0} - C^0_{2M1B} * X_{11} - C^0_{2M2B} * X_{21}\right)}$$

$$K_{H2} = \frac{\gamma_{TTAA}}{\gamma_{EtOH} \times \gamma_{2M2B}} \times \frac{(C_{2M1B,0} * X_{12} + C^0_{2M2B} * X_{22}) * C_T}{C^0_{2M2B} * (1 - X_{21} - X_{22}) * \left(C_{H_20,0} - C^0_{2M1B} * X_{12} - C^0_{2M2B} * X_{22}\right)}$$

$$K_I = \frac{\gamma_{2M2B}}{\gamma_{2M1B}} \times \frac{C_{2M2B,0} * (1 - X_{21} - X_{22})}{C^0_{2M1B} * (1 - X_{11} - X_{12})}$$

The values of equilibrium constants were taken from the literature,

$$\ln K_{E1} = 22.809 + \frac{3136.3}{T} - 5.8227 * \ln T + 0.0179 * T - 6.395 \times 10^{-6} * T^2 - 1.672 \times 10^{-8} * T^3$$

$$\ln K_{E2} = 22.779 + \frac{2078.6}{T} - 6.5925 * \ln T + 0.0231 * T - 1.126 \times 10^{-5} * T^2 - 1.414 \times 10^{-8} * T^3$$

$$\ln K_I = -3.97 + \frac{1057.7}{T} + 0.7698 * \ln T - 0.0052 * T + 4.865 \times 10^{-6} * T^2 - 2.58 \times 10^{-9} * T^3$$

$$K_{H2} = 0.33 * \exp(\frac{26500}{8.314} * (\frac{1}{T} - \frac{1}{343.25}))$$

Solving these 4 equations simultaneously the equilibrium conversion was obtained.

For a feed composition 5 mol% 2M2B and at a reaction temperature of 80°C, the mol fractions and activity coefficients at the given temperatures were tabulated as the following;

Components	C_i^0 (mol)	x_i	γ_i
2M1B	0.33	0.0138	5.3093
2M2B	6.26	0.000693	5.2183

Components	C_i^0 (mol)	x_i	γ_i
EtOH	103.89	0.8601	1.0050
TAEE	0	0.0084	3.2177
TAA	0	0.0286	1.1204
H_2O	13.99	0.0883	2.4847

Equilibrium Constants calculated at the reaction temperature;

Reactions	K_i
2M1B +EtOH $\xrightarrow{X_{11}}$ TAEE	5.244
2M2B +EtOH $\xrightarrow{X_{21}}$ TAEE	0.690
2M1B +H_2O $\xrightarrow{X_{12}}$ TAA	-
2M2B +H_2O $\xrightarrow{X_{22}}$ TAA	0.157
2M1B→2M2B	7.595

Conversions	Values
X_{11}	0.188
X_{12}	0.079
X_{21}	0.535
X_{22}	0.111

Finally, to check the isomerization effect,

$$X_{OLEFIN} * C^0_{OLEFIN} = C^0_{2M1B} * (X_{11} + X_{12}) + C^0_{2M2B} * (X_{21} + X_{22})$$

RHS ⇒ 0.33*(0.188+0.079)+6.26*(0.535+0.111)

⇒4.1321

LHS ⇒(0.535+0.113)*6.59

⇒4.2703

So it could be said that neglecting the reactions of 2M1B did not effect the result.

APPENDIX E

OUTPUT FILES OF PROGRAMS

E.1 Program KOPT: Evaluation of the κ_1 Parameter for the PRSV Equation of State

The sample output file of KOPT program to calculate the κ_1 value for water was given in the following. T_C, P_C and ω was given as 647.29, 220.9 and 0.3438, respectively. Saturation pressures were calculated at different temperatures by using Antoine equations. −0.0663 was found from this program, in the literature, this value was reported being -0.06635 by Orbey and Sandler.

```
PROGRAM :KOPT: KAPPA-1 OPTIMIZATION FOR THE PRSV EQUATION
 c:water.dat

 Water kappa

 KAPPA-1= -.0663

   T(K)         PEXP(BAR)    PCAL        AAD       VL(CM3/MOL)       VV
   290.0000  .0192        .0192        .2625      21.1487      1256451.4
   328.0000  .1566        .1563        .1990      21.6951       174130.2
   343.0000  .3097        .3097        .0001      21.9445        91789.0
   353.0000  .4702        .4708        .1184      22.1223        62049.4
   357.0000  .5516        .5525        .1590      22.1961        53436.
   363.0000  .6957        .6972        .2113      22.3100        43013.9
   373.0000 1.0051       1.0078        .2729      22.5086        30506.1
   383.0000 1.4210       1.4253        .3015      22.7189        22087.8

 PERCENT AAD (OVERALL), SUM(ABS(PEXP-PCAL)/PEXP)*100/NP:      .191
```

E.2 Program VDW: Binary VLE with the van der Waals One-Fluid Mixing Rules

This program could be run either by supplying experimental isothermal VLE data or not. Since, only liquid composition of the components could be obtained in this study, the isothermal VLE of each pairs were prepared by using UNIFAC prediction method. UNIFAC program was run for the temperature range studied in the experimental section; the liquid and vapor composition, also the pressure were taken from the results of this program. The sample output file for 2M2B-EtOH at 90°C was given in the following.

```
PROGRAM: VDW - VAN DER WAALS MODEL(S), 1-PARAMETER (CONVENTIONAL,
1PDW) OR
 2-PARAMETER, 2PDW
 c:2m2betoh.dat
 2m2b etoh at 90C

 K12=  .1513   K21=  .0988
 T(K)=  363.00

  PHASE VOLUMES ARE IN CC/MOL, PRESSURE IS IN UNITS OF THE DATA.


   X-EXP  P-EXP      P-CAL       Y-EXP     Y-CAL      VL-CAL   VV-CAL
   .0000   1.579      1.572     .00000    .00002      67.93  18580.9
   .5000   4.807      4.807     .75890    .71894      90.76   5626.3
  1.0000   4.443      4.546    1.00000   1.00000     110.32   5924.8

 AAD-Y=     1.755
 AAD-P=      .913

 AAD=SUM[ABS(EXP-CAL)/EXP]*100/(NO. OF DATA POINTS)
```

E.3 Program AC: VLE From Activity Coefficient Models-The NRTL Model

The isothermal VLE data was predicted by UNIFAC model. The program was repeated for the temperature range that was studied in the experimental section. The sample output file for the 2M2B-EtOh binary pairs at 90°C was given in the following.

```
AC - VLE FROM ACTIVITY COEFFICIENT MODELS
  THE NRTL MODEL

 ALPHA=  .300
 P12, P21 (PIJ=AIJ/RT, AIJ IN CAL/MOL)    1.7739    .4395
 A12, A21 (IN CAL/MOL)  1279.6426  317.0561

 DATA FILE NAME: 2m2betoh.act

 2m2betoh

 TEMPERATURE (K):  363.00

 PRESSURE IS IN THE UNITS OF THE DATA.
```

```
 XEXP     YEXP    YCAL      PEXP         PCAL    ACT1    ACT2     SUM
.0000   .0000   .0000     1.5790       1.5790  4.4606  1.0000  1.0000
.1000   .5419   .5247     3.1500       3.0252  3.5724  1.0119  1.0000
.2000   .6637   .6598     3.9890       3.8998  2.8957  1.0502  1.0000
.3000   .7151   .7186     4.4390       4.4068  2.3757  1.1221  1.0000
.4000   .7423   .7491     4.6790       4.6825  1.9736  1.2403  1.0000
.5000   .7589   .7661     4.8070       4.8201  1.6622  1.4280  1.0000
.6000   .7710   .7765     4.8780       4.8842  1.4227  1.7284  1.0000
.7000   .7831   .7854     4.9210       4.9173  1.2418  2.2274  1.0000
.8000   .8016   .8009     4.9410       4.9340  1.1118  3.1101  1.0000
.9000   .8445   .8440     4.8890       4.8793  1.0299  4.8203  1.0000
1.0000 1.0000  1.0000     4.4430       4.4430  1.0000  8.5810  1.0000
```

E.4 Program WSMMAIN: Multicomponent VLE calculations with Wong-Sandler mixing Rules

```
WSM: MULTICOMPONENT VLE CALCULATIONS WITH THE WONG-SANDLER-NRTL
MIXING RULE
 c:exp8bp.wsn
 exp 8 BP, 111C


  SET NO.      TEMP(K)      PEXP(BAR)     PCAL    VLIQ(CM3/MOL)    VVAP
 ------------------------------------------------------------------------
      1        384.00           -         3.513       63.971      8569.4
      2        384.00           -         3.366       63.999      8966.6
      3        384.00           -         3.251       64.508      9300.7
      4        384.00           -         3.183       65.099      9504.9
      5        384.00           -         3.142       65.334      9635.3
      6        384.00           -         3.137       65.066      9651.4
      7        384.00           -         3.134       65.112      9662.7



       PHASE COMPOSITIONS (IN MOLE FRACTION)

  SET NO.     COMPONENT     XEXP          YEXP         YCAL
 ---------------------------------------------------------------
      1            1       .0144           -          .1103
                   2       .8680           -          .7987
                   3       .0006           -          .0004
                   4       .0021           -          .0009
                   5       .1149           -          .0898

      2            1       .0086           -          .0692
                   2       .8724           -          .8359
                   3       .0014           -          .0010
                   4       .0042           -          .0019
                   5       .1134           -          .0920

      3            1       .0044           -          .0364
                   2       .8737           -          .8650
                   3       .0038           -          .0029
                   4       .0091           -          .0043
                   5       .1090           -          .0914

      4            1       .0021           -          .0176
                   2       .8745           -          .8827
```

```
                    3         .0050          -         .0039
                    4         .0151          -         .0073
                    5         .1033          -         .0886

       5            1         .0006          -         .0051
                    2         .8756          -         .8946
                    3         .0052          -         .0041
                    4         .0180          -         .0088
                    5         .1006          -         .0875

       6            1         .0003          -         .0026
                    2         .8776          -         .8980
                    3         .0035          -         .0028
                    4         .0169          -         .0083
                    5         .1017          -         .0884

       7            1         .0002          -         .0017
                    2         .8787          -         .9000
                    3         .0025          -         .0020
                    4         .0183          -         .0090
                    5         .1003          -         .0874

  PARAMETER MATRIX FOR THE KIJ PARAMETER
               1            2            3            4            5
-----------------------------------------------------------------------
  1 |      .0000        .1044        .1005        .1014        .2268 |
  2 |      .1044        .0000        .1063        .0975        .1050 |
  3 |      .1005        .1063        .0000        .1104        .1490 |
  4 |      .1014        .0975        .1104        .0000        .1024 |
  5 |      .2268        .1050        .1490        .1024        .0000 |
-----------------------------------------------------------------------

  PARAMETER MATRIX FOR THE ALPHA PARAMETER
               1            2            3            4            5
-----------------------------------------------------------------------
  1 |      .0000        .3000        .3000        .3000        .3000 |
  2 |      .3000        .0000        .3000        .3000        .3000 |
  3 |      .3000        .3000        .0000        .3000        .3000 |
  4 |      .3000        .3000        .3000        .0000        .3000 |
  5 |      .3000        .3000        .3000        .3000        .0000 |
-----------------------------------------------------------------------

  PARAMETER MATRIX FOR THE NRTL ENERGY PARAMETER AIJ
  (IN CAL/MOLE)
               1            2            3            4            5
-----------------------------------------------------------------------
  1 |        .00      1139.76        22.13      1349.98      2989.29 |
  2 |     447.55          .00       756.54       -23.66       288.70 |
  3 |      75.36        84.83          .00       413.53      1492.09 |
  4 |    -264.32        73.70        79.67          .00       185.77 |
  5 |    3330.00       670.50      3508.01      2089.43          .00 |
-----------------------------------------------------------------------
```