SEPARATION OF THE XYLENE ISOMERS AND ETHYLBENZENE BY REACTIVE DISTILLATION

BY

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CERTIFICATION

This is to certify that the Thesis:

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For the award of the degree of
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By

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DEDICATION

TO GOD THE ALMIGHTY FATHER WHO MADE ALL THINGS POSSIBLE.

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ABSTRACT

During the last decade, there has been a rapid upturn of interest in reactive distillation. The chemical process industry recognizes the favorable economics of carrying out reaction simultaneously with distillation for certain systems and many new processes are being built based on this technology.

In this work, equations of a reactive distillation column were described and derived for a multi-component system. New sets of transformed composition variables were defined. These sets allow for the computation of the concentration profiles along the column and therefore a simple relationship between the reflux and reboil ratios. The system was assumed to be in both chemical and vapor-liquid equilibria. The new sets of transformed composition also help to eliminate the source term accounting for chemical reaction in the conservation equations; in other words, the transformed variables provide a way of reducing the dimensionality consistent with the Gibbs phase rule.

The complexity of the equations characterizing reactive distillation systems can be diminished by ensuring that, in the case of complex reacting systems, only the very minimum of reactions are considered. So, in the complex reactions where there are a myriad of single reactions to be considered, there is need to ensure that only independent set of reactions are considered. Therefore, there is need to consider how to achieve this objective. A computer-assisted procedure was developed for the determination of independent elementary steps in reactive schemes. The procedure facilitates the rapid reduction of large mechanistic and molecular reaction schemes into independent sets of reactions. The procedure was tested on some examples taken from the pyrolysis literature. These are the mechanisms for n-butane pyrolysis, cyclohexane pyrolysis' and some selected reactions of the mechanistic and molecular steps in n-heptane pyrolysis.

Although, the reaction system considered in this work is not complex enough to warrant the use of this concept of independent reaction, it is obvious that this topic is essential in any general kinetic schemes. For future developments of reactive distillation applicable to any reactive system, simple or complex, the role of the concept by independent reaction is assured.

Reactive distillation, a new separation process was employed to separate meta – and para – xylene mixture. A third component, di-tertiary butyl benzene was intentionally introduced (as a reactive entrainer) to react with m- xylene. The alkylation reaction complex, tertiary- butyl-m-xylene on reacting with more benzene liberated the m-xylene in another reaction step. The phase diagram in terms of the new composition variables was constructed. The residue curve maps in the transformed composition variables for the reactive mixture at equilibrium provide information on the feasibility of separation and even column sequencing of a desired separation.

The separation of C_8 close boiling aromatic compounds- a more complex system, using reactive distillation was done. A separation based on alkylation, separation of the alkylated products and their subsequent dealkylation and the final separation produced the high grade pure xylenes and ethylbenzene compounds. Meta, para, ortho – xylenes and ethylbenzene form a close boiling mixture and they are isomers of C_8 compound. A fifth component, di-tertiary butyl benzene, was intentionally introduced into the system (as a reactive entrainer) to react with o- xylene and ethylbenzene with the aid of the highly selective iron chloride ($FeCl_3$) catalyst in the first column. The separated alkylated complex, tertiary- butyl-o-xylene and tertiary- butyl-ethylbenzene, liberated the o-xylene and ethylbenzene in another reaction step on reacting with more benzene. $AlCl_3$ catalyst allows the reactive entrainer to react with m- xylene to form a complex : tertiary- butyl-m-xylene. This complex was separated and dealkylated in another step. The new variables represent the surfaces embedded within the mole fraction coordinate space in a simpler way, thus giving an easier visualization of the diagrams of the combined phase and

chemical equilibria. This made the determination of the feasibility and sequencing of the distillation columns easier.

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LIST OF SYMBOLS

A_i	reacting species
B	bottom flow rate
B	transformed bottom flow rate defined by equation 3.42
c	total number of reacting components
C	total number of reacting and inert components
D	distillate flow rate
D	transformed distillate flow rate defined by equation 3.41
F	degrees of freedom given by Gibbs phase rule
F	feed flow rate
F	transformed bottom flow rate defined by equation 3.40
I	total number of inert components
v	non square matrix of dimension (C,R) of stoichiometric coefficients for the C components in the R reactions
v_{Ref}	square matrix of dimension (R,R) of the stoichiometric coefficients for the R reference components in the R reactions
$v_{(c-R),R}$	non square matrix of dimension (C-R,R) of the stoichiometric coefficient for (C-R) components in R reactions
$x_{((C-ref)}$	column vector of dimension (C-R) of all the components except the reference components
x_B	column vector of the compositions of all the components in the bottom product stream
$x_{Ref,\,B}$	column vector of the compositions of all the reference components in the bottom product stream
x_D	column vector of the compositions of all the components in the distillate stream

$x_{Ref,D}$	column vector of the compositions of all the reference components in the distillate stream
x_F	column vector of the compositions of all the components in the feed stream
$x_{Ref,F}$	column vector of the compositions of all the reference components in the feed stream
$x_{Ref,}$	column vector of the mole fractions of the R reference components in the liquid phase
x_i	mole fraction of component I in the liquid phase at any time, t
X_i	transformed composition of component i in the liquid phase
$X_{i\,B}$	transformed composition of component i in the liquid bottom
$X_{i,F}$	transformed composition of component i in the liquid feed.
ε	column vector of the R molar extent of reaction
ε_r	column vector of the R molar extent of reaction
ν_{ir}	stoichiometric coefficient of component i in reaction r
ν_i^T	row vector of the stoichiometric coefficients for reaction r
ν^T_{TOT}	row vector of the sum of the stoichiometric coefficients for each reaction
TOT	total

CHAPTER ONE

1.0 INTRODUCTION

1.1 General Background

One of the major tasks of chemical engineering is the downstream processing of the effluents of chemical reactors. Since most chemical reactions are reversible, the feed components are not completely converted into the desired products and the effluents of a reactor are a mixture of feed components and products. The non-converted feed materials have to be separated from the products to enable an effective recycling and the product mixture must also be separated from the mixture for the production of pure chemicals. The separation of the reactor effluents, mostly homogenous mixture, into its individual components is in most cases achieved by distillation. Distillation is a widely used method for separating liquid mixtures into their components and had been called the workhorse separation of the petroleum, petrochemical, chemical and related industries (Stichlmair and Fair, 1998). There appeared to be no restriction in its dominance as a useful reliable and easily specified separation method for the economic separation of liquid mixtures.

Distillation utilizes a very simple separation principle. An intimate contact is created between the starting mixture and a second phase in order to enhance an effective mass transfer between these two phases. The phases are then separated into two phases with different compositions. . The three steps which are always involved in the implementation of this separation principle are; (i) creation of a two-phase system (ii) mass transfer between the phases and (iii) separation of the phases. These two-phase systems may be liquid and gas as in distillation, liquid-liquid as in extraction and solid-liquid as in adsorption (Stichlmair and Fair, 1998).

In practice, distillation requires intimate contacting of vapour and liquid under such conditions that the desired components of the liquid enters the vapour phase thus permitting mass transfer between the two phases. In addition, the two phases are not in thermodynamic equilibrium and the chemical species interact differently to environments offered by these phases. As the system moves towards equilibrium, each species establish a different concentration in each phase and this result in the separation desired. Total separation is obtained with ease when a large temperature difference exists between the boiling points of the components to be separated.

In a multi-component system, when the boiling temperature difference between the components is small, the components have a similar tendency to vaporize simultaneously and there will be no meaningful separation even as the process is controlled by heat supply, thus the impure vapour may contain fractions of all the species in the original mixture (Douglas, 1988, Muraki and Hayakawa, 1998).

The separation of isomeric mixtures such as the one used in this work is difficult to achieve due to the similarity in their volatility. Researchers have investigated their separation using other physical methods and processes such as freezing point difference, rate of adsorption and absorption difference in the mass separating agent (Malone, 2000, 1983, Maomi, *et al.*, 1982)

Enhanced distillation-based separation techniques have to be developed for the separation of close boiling or low relative volatility systems. Although these special techniques are ultimately based on the same differences in the vapor and liquid composition as ordinary distillation, they rely on some additional mechanism to further modify the vapor-liquid behavior of the components. Some of these enhanced techniques include extractive

distillation, extractive reaction and reactive distillation (Sylvestre and Doherty, 1995). Extractive reaction and extractive distillation however, cannot be successfully applied to the separation of isomers since the entrainer has almost the same effect on each of the components and therefore do not change their relative volatility.

Distillation columns can be used advantageously as a reactor for systems in which chemical reactions occur at temperatures and pressures suitable to the distillation of components. This combined unit operation is especially useful for those chemical reactions for which chemical equilibrium limits the conversion. By continuous separation of products from reactants while the reaction is in progress, the reaction can proceed to a much higher level of conversion than without separation. (Alejski, 1996)

1.1.1 Reactive Distillation

The process of reactive distillation, used in this work has a very good advantage over the other techniques as clearly suggested above. The close-boiling point components have different chemical properties and they react with the entrainer differently. These reversible alkylation reactions, which are further enhanced by the highly selective catalysts, help in the removal of some of the components from the liquid mixture in the first step. Dealkylating the products in the first step enables us to recover these components in these reverse reactions in the second step.(DeGermo, *et al.*,1992, Cisneroros, *et al.*, 1997).

In recent years, success has been attained in the development of commercial processes which combine reaction and separation in the same vessel (Grosser, *et al.*, 1987, Isla and Irazoqui, 1996) . Reactive distillation, the process of simultaneous reaction and distillation in a single unit, offers numerous advantages over conventional configuration of reactors

followed by separators. Unlike the conventional reactor-separator configuration, in reactive distillation, the reactant products are continuously separated from the liquid reaction phase into the non-reactive vapor phase. This causes the reaction to proceed in the forward direction according to Le Chatelier's principle (Harwood, *et al.*, 1989). This dramatically increases the overall conversion and selectivity in certain competitive reaction systems such as in the production of ethyl glycol (Ciric, *et al.*, 1994). The technology provides an efficient means of heat removal from the liquid phase for reactions with high heat of reaction (exothermic), this heat is used to vaporize the components in the liquid mixture. In reactive distillation, there is reduced emissions, improved economics in terms of reduced plant equipment and construction costs. The resulting flow sheet tends to be simpler and have fewer recycle streams. These advantages have motivated renewed interest in the use of reactive distillation technology for the production of important chemicals. The reduction in the number of equipment units leads to investment savings. Further, simultaneous reaction and separation provides the possibility of by-passing the equilibrium limitation imposed by reversible reactions. The use of reactive distillation in the production of methyl acetate and methyl tert-butyl ether (MTBE) clearly demonstrates the benefits (Degarmo, *et al.*, 1992, Doherty, *et al* ., 1992). Some examples of selected systems where reactive distillation has been successfully used for the equilibrium-limited reactions are listed in Table1. It is interesting to note the classic success story of the Eastman Chemical Company's methyl acetate reactive distillation process. Some of the improvements are so dramatic. Five times lower investment and five times lower energy use for the Eastman process (Malone and Doherty, 2000)

Table 1.1: Selected systems of reactive distillation.

System	Reference
Methyl acetate from methanol and acetic acid	Agreda, *et al.*, 1990.
Ethyl tertiary butyl ether from ethanol and isobutene	Thiel, *et al.*, 1997.
Ethylene glycol from ethylene oxide and water	Gu, , *et al.*, 1994.
Tert-amyl alcohol from iso-amylene and water	Gonzales, , *et al.*, 1997.
Methyl-tertiary-butyl-ether(MTBE) from methanol and Isobutene	Refinger et al,. 1990
Ethyl acetate from ethanol and Acetic acid	Komatsu, 1977

However, the interaction between the simultaneous reaction and distillation introduces a much more complex behavior compared to the conventional reactions and subsequent separation of the reactive mixture by ordinary distillation columns. This interaction leads to challenging problems in process synthesis, design, operations and control. The design issues for reactive distillation systems are significantly more complex than those involved in ordinary distillation. It is much more difficult to model, design and control reactive distillation because of the complicated interaction between reaction and distillation (Edgar et al., 2003) First, equations have to be derived for the system, catalyst must be chosen for the system, either heterogeneous or homogeneous. This will influence not only the type of internals (plates, packing, and catalyst baskets) of the column but also the liquid hold up and its distribution throughout the column. Secondly, the reaction zone has to be strategically placed within the column so as to get good performance. In some applications, the entire column is reactive while in others, only a part is. In some columns,

the non-reactive zone(s) provide product purification by ordinary distillation such as in the methyl-tertiary-butyl-ether (MTBE) production column but in others, it breaks an azeotrope with an entrainer (extractive distillation section). Other design problems include heat management (in the case of strongly exothermic reactions), reflux and re-boil ratios requirements and number of stages, positions of feed and control strategy (Espinosa, *et al.*, 1995, Dergamo, *et al.*, 1992, Ung and Doherty, *et al.*, 1995).

1.1.2 Independence of Chemical Reactions

The complexity of the equations characterizing reactive distillation systems can be diminished by ensuring that, in the case of complex reacting systems, only the very minimum numbers of reactions are considered. So, in the complex reactions where there are so many single reactions to be considered, there is need to ensure that only independent set of reactions are considered. In pyrolysis, for example, where hydrocarbons are subjected to relatively high temperatures(>600°C) over a period of time, complex reactions occur. The molecules of long chain hydrocarbon (paraffin) molecules break down in many ways to form small molecular compounds. The reactions at these high temperatures involve the transformation of C-C and C-H bonds in the hydrocarbons. In this process the number of hydrogen atoms present in the system becomes insufficient to provide the full complement for each carbon atom such that "unsaturated "compounds are formed . This is the key process for modern petro-chemistry where olefins, di-olefins, aromatics and acetylenic compounds are formed. The industrial use of pyrolysis is associated with high conversions and this in turn introduces secondary reactions (reactions among the radicals and products.(Albright, *et al.*. 1983). In fact, the two main dependent variables in the

cracking of hydrocarbons are selectivity and conversion. Conversion is a measure of the degree of cracking as indicated by the percentage disappearance of the feedstock while selectivity indicates the quantity of desired products such as ethylene and propylene that are obtained per unit of feedstock material converted. As conversion increases, the selectivity to lighter products (C_1-C_4) increases.(Albright, et al., 1983.).The heavier the reactant, the more complex the mix of products. Hexadecane molecule is heavier than that of butane hence, there are more products. The chain reactions become more complex in higher molecules as there are many places or points at which significant interference with the chain might be possible such that the reactant may undergo a series of free radical reactions leading to gaseous, liquid or solid products. With these reactions, important basic chemicals are formed and the petrochemical industry is advanced.

Unfortunately, the high level of technological advancement is not matched by an equal level of knowledge of the scientific fundamentals and correlations of the reactions taking place in the overall process (Albright, *et al.*, 1983). New pyrolysis reactors and technologies are being developed and these require reliable predictions of the effluent distribution which are in turn based on sound reaction models. Extensive and reliable reaction models are necessary because they improve on the prediction of results such as the product distribution, overall activation energy as well as reaction orders. These extensive reaction network indicate that many reaction paths contribute to a single product and they are of varying importance. To describe chemically reacting system, not all the reactions are necessarily required to adequately describe the reactions that can occur between the reactants species, only the independent reactions are required.. At least one reaction will be

a multiple of one of the others but also it may be a linear combination of others. Since it is certainly desirable to work with the fewest possible equations in any situation, it would therefore be useful to have a constructive test for the number of independent reactions as well as those reactions themselves and the reactive species. This is the smallest collections of result of reactions that on forming various linear combinations, includes all possible chemical reactions among the species present. Each of the sets of reactions is irreducible as it cannot be separated into sub mechanisms. The reaction-by-specie matrix gives a valid way to determine the maximum number of linearly independent reactions in the system. The final result consists of the minimal number of unique combinations necessary to describe the system in the detailed modeling of experimental data. Therefore, there is need to consider how to achieve this objective. This research work thus brings forth a computer algorithm that helps in the determination of independent reactions in any proposed mechanistic and molecular model consisting of I reactions and J species. The redundant reactions are identified.

Although, the reaction system considered in this work is not complex enough to warrant the use of this concept of independent reaction, it is obvious that this topic is essential in any general kinetic scheme. For future developments of reactive distillation applicable to any reactive system, simple or complex, the role of the concept by independent reaction is assured.

1.1.3 Xylene Mixture Separation

In his doctoral thesis, titled, Kinetic Analysis of N-octane Dehydrocyclization Reactions on Mono- and Bifunctional Platinum Alumina Catalyst, Ako, 1984 found out that the main products were mixed xylenes composed of ortho-xylene (OX), meta-xylene (MX), para-xylene (PX) and ethyl benzene (EB). They are all isomers and have similar or close boiling points as shown Table 2 Their separation by conventional distillation is therefore uneconomical. Extractive distillation cannot easily be used because adding a third non-reactive component does not shift their relative volatilities. Cryogenic separation (crystallization) utilising the difference in their melting points has been used (Mohammed, *et al.*,.2007). The Standard Oil Company had developed a commercial production process of PX from petroleum, based on cryogenic separation over five decades ago (Grosser, *et al.*, 1987).

Table 1.2. Components of mixed xylenes

Component	Ortho-xylene	Meta-xylene	Para-xylene	Ethylbenzene
Technical grade xylenes composition	20%	40%	20%	20%
Boiling Point(°C)	144.0	138.7	138.5	136.2
Melting Point(°C)	-25.2	- 47.9	13.3	-95.0
Use	Phthalic anhydride	Isophthalic acid	Ester production	Styrene production

Xylenes and ethylbenzene are used in many applications in the modern industry. Solvents and thinners for varnishes and paints often contain xylene. Paraxylene is in high demand for conversion to terephthalic acid(TPA) and then to dimethyl terephthalate (DMT).

Dimethyl terephthalate is then reacted with ethylene glycol to form polyethylene terephthalate PET). This is the raw material for most polyesters used in the production of fibers, packaging materials and containers.

However, with the rising costs of naphtha and energy, the world trend has been towards the replacement of cryogenic separation with adsorption separation. Adsorption method has been in use on a commercial scale since 1971 (Noeren *et al.,* 2003) There are numerous engineering difficulties associated with this method especially in relation to increasing the diameter of the adsorption column. Construction costs are also high since large-diameter, complex adsorption columns of the simulated moving bed design incorporating rotary valves are required. There is also the problem of low selectivity and small adsorption capacity of conventional catalyst and its loading. This necessitates the use of a long migrating distance to achieve sufficient separation. This results in a low concentration of xylene in the effluent solution and large fuel consumption for separation from the solution by distillation (Noeren, *et al.,* 2003). The advantage of combining chemical reaction with vapour-liquid equilibrium can be explained in part, by the way in which chemical reactions modify the phase behaviour. Barbosa and Doherty(1987) have studied the influence of a single chemical reaction on the structure and properties of phase diagrams for multicomponent mixtures. They showed that chemical reactions alone greatly changed the compositions and hence reactive phase and product compositions. The idea of distillation with reactive entrainers is to introduce a third component into the distillation column so that reversible chemical reaction(s) occurs. The reactive entrainer should be chosen so that it reacts preferentially with one of the isomers. The unreacted isomer will be taken off as distillate and the reaction products and unreacted entrainer will

be taken as bottoms. A second column can then be used to separate the bottoms into pure components. Some of the main areas in the chemical industry, in which combined distillation and chemical reaction occur are:

(i) Use of a distillation column as a chemical reactor in order to increase conversion of reactants especially for equilibrium limited reactions.

(ii) Improvement of separation in a column by using a chemical reaction in order to change unfavorable relations between component volatilities.(Barbosa *et al.*, 1998)

Separation is feasible by using reactive distillation, for the mixture of meta- and para-xylenes and a more complex mixture of ortho, meta, paraxylenes and ethylbenzene. This takes advantage of the fact that, in alkylation process, MX is selectively reacted whereas PX is left unreacted, for an example, in a mixture of MX and PX. Operating equilibrium-limited reactions in a distillation column displaces the reactions equilibria as one or more of the products are continuously removed, and this enhances the performance of the separation process as the reactive entrainer changes the relative volatilities of the compounds.

In this research work, we have developed the model equations and applied them first to a subsystem of the xylene mixture containing meta and paraxylenes and then to a more complex system of ortho, meta, paraxylenes and ethylbenzene mixture.

1.2 Statement of Problem

Most of the downstream processes contain reversible reactions. In the catalytic reformation of naphtha, dehydrocyclisation, steam cracking or catalytic cracking of

hydrocarbons, methylation of toluene , consist of reversible reactions. To describe chemically reacting systems, it is not necessary to consider all the chemical reactions that can occur between the reactants species, only the independent reactions. A computer-assisted algorithm or procedure is required for determining the number of independent reactions in a system and a perfect reactive process should afford the complete conversion of the reactants. However, for the reversible reactions, the composition of reaction mixture is limited by equilibrium. An effective reactive process is required to overcome this limitation.

The C_8 aromatics (orthoxylene, metaxylene, paraxylene and ethylbenzene) are important petrochemical raw materials in their pure states. The use of these chemicals is clearly stated earlier in this report(see Table 2). Because of their close boiling temperatures, their separation by distillation is impractical and uneconomical hence the mixture is mainly used as industrial solvent, extenders and carriers in the developing countries such as Nigeria while the pure xylenes are currently being imported. Due to a large demand and relative ease, p-xylene is being removed from the C_8 mixture and the rest of the stream is recycled to the isomerization unit for re-equilibrium. In the typical isomerization process, ethylbenzene conversion is more difficult and less selective to p-xylene than to ortho- and meta-xylenes. On the other hand, ethylbenzene has a ready market for styrene production. Unfortunately, it has been difficult to separate ethylbenzene from the mixtures along with p-xylene. In fact, p-xylene separation is limited by ethylbenzene contamination in the conventional separation based on elution chromatography (Mohammed, *et al.*, 2007).

Today, the downstream activity has increased as well as the amount of mixed xylenes being produced, the development of reactive distillation process and its application to the

separation of the xylenes seem to be the only viable solution to the production of these important chemicals.

This research work focuses on the development of the reactive distillation process for the separation of close boiling mixtures with emphasis on the xylenes and ethylbenzene mixture.

The following steps were used;

(i) Development of a computer-assisted procedure for determining the number of independent reactions in a scheme consisting of I reactions and J reactive species.

(ii). Development of the theoretical model for the reactive-distillation process of separating two- and four component mixtures.

(iii) Alkylation of the components

(iv) Separation of the alkylated products and

(v). Dealkylation of the complexes and

(vi) Final separation into pure components

to recover the xylenes and ethylbenzene compounds. Combining reaction with distillation in single apparatus is advantageous for liquid phase reactions that must be carried out in the presence of a large excess of one reactant. The target conversion in equilibrium-limited reactors can be achieved by means of an excess of one reactant in the feed stream, while higher conversion degree can be obtained using feed compositions closer to stoichiometric ratios in the reactant species.(Doherty, *et al.*, 1985). The idea of distillation with reactive entrainers is to introduce a component into the distillation column so that reversible chemical reactions occur. The reactive entrainer is always chosen so that it reacts preferentially with one or more of the isomers or compounds. A catalyst could be

used to enhance this process. Thus, the unreacted isomer and inerts will be taken off as distillate and the heavy alkylated products and isomers are taken off as bottoms. A second column can then be used to separate the bottoms into pure heavy isomers and pure alkylated products. The reverse reaction is made to occur using the alkylated products until complete recovery of the original pure components is accomplished (Le Chartelier Principle). The essential points of the process are:

(i) The reactions are fast and reversible. The alkylation/dealkylation reactions products exist only inside the columns and do not contaminate the pure output streams.

(ii) The reactive entrainer reacts selectively, and

(iii) The boiling point of the entrainer is always chosen higher than the least volatile isomer.

The theory of Friedel-Craft's Alkylation (FCA) was employed in this study. This is a part of the organic chemist's expertise in the ability to build larger molecules by using substitution reactions to attach groups to aromatic rings. Alkyl groups can be attached to benzene to build a more extensive network of carbon atoms using FCA. In the present study, ferric chloride in addition to the aluminum chloride, were used as the catalysts. This reaction takes place quite vigorously when a small amount of the catalyst is added to a mixture of the two liquid reagents. FCA enables us to produce new carbon-carbon bonds in these reversible reactions and hence was used to build complex molecules whose boiling points are now high and hence could be separated from the mixture as bottoms.(Larner, 1984,).

The xylenes and ethylbenzene are isomers of C_8 compound and they undergo electrophylic aromatic substitution reactions. . The electron releasing effect of the electrophile, an alkyl group, activates a benzene ring to which it is attached, and directs to ortho and para positions. The side chain is alkane-like and undergoes reaction via free-radical substitution. This is promoted by a catalyst at low temperature because the benzyl radical is more stable It is to form the benzyl radical from toluene than to form the methyl radical from methane (Morrison, *et al.*, 1992)

1.3 Research Objectives

This present study focuses on the development of a computer-assisted procedure for determining the number of independent reactions in a scheme of reactions and a reactive distillation method that will enhance the separation of xylenes and ethylbenzene mixtures. Reactive distillation (RD) is a physico - chemical process which integrates both reaction and separation in one unit operation. Conducting a catalyzed chemical reaction in a distillation process offers many potential advantages over a typical reactor and subsequent distillation. These include reduced capital and operating costs, utilization of the heat of reaction to improve the distillation, reduction of the heat load of condensers and reboilers; further, it drives the reversible chemical reaction to completion, thereby increasing reactant conversion and improving product selectivity. Besides the high purity of the products of RD, all the reactions and separations occur internally within the column and the process is environmentally friendly.

The research shall achieve the following objectives:

- Development of the new transformed composition variables equations which represent the relative system in a lower dimensional composition space.
- Determination of the feasibility of separation of components
- Development of a computer-assisted procedure for determining the number of independent reactions in a scheme
- Determination of column sequencing
- Determination of the reactive mixture solution space of all the components at chemical equilibrium in transformed composition variable
- Determination of the choice of reference components
- Apply the concept and model equations to a simple system of meta- and paraxylenes components of two reactions and six components and to a more complex system of six reactions and ten components

1.4 Scope/limitation of Work

The research work is limited to the conceptual development, modeling and design of a separation method for the mixtures of close boiling substances with emphasis on the xylenes and ethylbenzene mixture.. This work is covered within the scope presented below:

(i) Detailed literature review of reactive distillation systems

(ii) Model development for chemical reaction and separation of system in equilibrium.

(iii) Development and determination of the new transform composition variables.

(iv) Determination of the reaction solution space.

(v) Determination of feasibility and sequencing of columns.

(vi) Application of the derived reactive distillation equations in the separation of metaxylene and paraxylene mixture and a mixture of ortho-, meta- , paraxylenes and ethylbenzene.

1.5 Significance of the Work

The reaearch work has the following significance:

(i) The understanding of the basic principles and fundamentals of reactive distillation;

(ii) The understanding of the basic procedure for the development of reactive distillation equations;

(iii) Understanding of the topology of reactive distillation processes, identification of feasible products and column sequencing;

(iv) Computation experience in the formulation of the basic computational tools of various models of reactive distillation systems and determination of independent sets of reactions;

(v) The applicability of reactive distillation equation models to a simple system; and to a more complex. system.

1.6 OPERATIONAL DEFINITION OF TERMS

1.6.1 ADSORPTION

Adsorption describes the attachment of a specie to the surface(active sites) of a solid. This leads to the formation of a molecular or atomic film of the species on the surface. These species may be liquids or gases. A given catalyst surface has a finite number of active sites at which components may adsorb. When adsorption occurs the dispersion forces it is described as physisorption, when it occurs by formation of a covalent bond, it is described as chemisorption. The amount of material adsorbed by a given mass of adsorbent depends on the physical conditions of the catalyst. The physical adsorption occurring in the separation of the xylenes are the relatively weak attraction due to Van der Waals forces between the catalysts and the xylenes..

1.6.2 CATALYST

Catalysts are substances that increase the rates of a wide variety of chemical reactions. They can be recovered at the end of the reaction, unchanged in mass or chemical composition. Reaction profiles show that the energy required for reaction acts as energy barrier, which the reactants must overcome before they can change into products.. when a reaction mixture includes a suitable catalyst the reaction can occur by an alternative route of lower energy than the uncatalysed reaction. At the same temperature, the greater proportion of the reactant molecules will therefore have sufficient energy to overcome the (lower) energy barrier for the catalysed reaction and so the rate is increased.

1.6.3 RATE OF REACTION

This refers to the speed at which reactants are converted to products. This may be rapid or slow and it depends on factors such as temperature, pressure, concentration or the nature of the components involved.

1.6.4 COMPLEX REACTION

Reactions are said to be complex if products are generated via more than one route and the number of reactants, intermediates and products are many. In this case, the kinetics and modeling as well as the methods of solution required for the total analysis of the system may be cumbersome..

1.6.5 ALKYLATION

This is the transfer of an alkyl group from one molecule to another. The alkyl group may be transferred as an alkyl carbocation, a free radical, a carbanion or a carbene. Alkylating agents are widely used in chemistry because the alkyl group is probably the most common group encountered in organic molecules. Selective alkylation, or adding parts to the chain with the desired functional groups, is used, especially if there is no commonly available precursor. The Friedel & Crafts' alkylation is the attachment of alkyl groups to an aromatic ring using a Lewis base or acid catalyst.

1.6.6 REACTIVE DISTILLATION

This is a unit operation in which chemical reaction and distillation separation are carried out simultaneously within a fractional distillation apparatus.

In this process, fractional distillation is accompanied by a chemical reaction on some or all of the trays in a column. Frequently, this reaction is induced by the deliberate addition of a reactive entrainer. The entrainer selectively reacts with one compound in the mixture to form products which are removed from the column with relative ease. .Reactive distillation columns are often used in place of liquid-phase equilibrium reactors.

1.6.7 CRYSTALLIZATION

This is a process of separating mixtures into the pure components by lowering the temperature of the mixture. As the temperature of the mixture is reduced, it becomes saturated and the component with the highest melting point, will crystallize out as solid crystals and then can be separated. Supersaturation which is the driving force occurs as a reduction in solute solubility when the temperature is reduced.. thus, continuous cooling is required and the conventional way of cooling is by using jacketed crystallizers or similar forms of heat exchange devices.

1.6.8 ALKYL GROUP:

A saturated hydrocarbon chain with one bond available.

1.6.9 AROMATIC HYDROCARBON;

A compound of carbon and hydrogen one or more rings of carbon atoms (often drawn with carbon-carbon single and double bonds in which there is extensive delocalization of pi electrons. Delocalization refers to the process by which electron density is spread over several atoms rather than remaining between two.

1.6.10 FUNCTIONAL GROUP

A specific combination of atoms, typically containing a carbon multiple bond and or heteroatom bond that reacts in a characteristic way no matter in what molecule it occurs.

1.6.11 Le CHATELIER'S PRINCIPLE

This is principle stating that if a system in equilibrium is disturoed, it will undergo a change that shifts its equilibrium position in a direction that reduces the effect of the disturbance In other words a dynamic equilibrium tends to oppose any change in the equilibrium conditions.

1.6.12 DISTILLATION LINES

The adequate form for the presentation of the vapour liquid equiilibrium are the distillation lines. They constitute a sequence of equilibrium stages that rean from a local boiling point maximum to a local boiling point minimum. Starting at any liquid concentration x_{i1}, the equilibrium concentration of the vapour y_{i1} is determined. Condensation of the vapour generates a new liquid with the concentration $x_{i2} = y_{i1}*$. A sequence of such steps

generates the distillation line that describes the maximal enrichment of low boilers in the mixture.

1.6.13 ANHYDRIDE:

A compound which forms an oxoacid when it reacts with water. A formal anhydride is a compound that has the formula of an acid minus the elements of water but does not reacts with water to produce the acid.

1.6.14 PHASE DIAGRAM

A summary in graphical form of the conditions of temperature and pressure at which the liquid and vapour phases of a substance exist.

1.6.15 REFORMING REACTIONS:

These are reactions in which the number of carbon atoms in the reactant hydrocarbons molecule is unchanged but more double bonds and aromatic rings are formed or introduced.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Introduction

Some of the most challenging and time consuming processes involve separating mixtures. Although we need a great deal of pure substances, they almost never occur naturally. In the natural world, matter usually occurs as mixtures. The air is a mixture of gases and the petroleum and coal are complex mixtures of pure substances. In most cases, the reactor effluents are mixtures of substances. Often times, there are needs to separate these mixtures into the pure components. The heterogeneous mixture is less difficult to separate because it has one or more observable boundaries between the components. Thus, its composition is not uniform but the homogeneous mixture has no observable boundaries because the components are mixed as individual atoms, ions and molecules. Thus its composition is uniform. The separation of a homogeneous liquid mixture into its components is an important step in many industrial processes. Of the various methods that might be used for effecting the separation, distillation is the one most used commercially. Distillation separates components through differences in the tendency of substance to become gaseous. The vapour and liquid are brought into intimate contact by countercurrent flow and mass transfer occurs because the two phases are not in thermodynamic equilibrium. As the mixture boils, the vapour is richer in the more volatile component which can be collected separately (Perry and Green, 1997).

Separating compounds with small volatility differences requires many vaporization – condensation steps. The C_8 aromatics, the focus of this study, are important raw materials for petrochemicals. Paraxylene is used for terephthalic ester production, polyester fibres,

plastics and films including dacron, orthoxylene, metaxylene and ethylbenzene are raw materials for phthalic anhydride, isophthalic acid and styrene, respectively. Therefore, there is need to separate the mixture into its pure components. However, the separation is difficult and expensive because their relative volatility is about 1.02. High reflux ratios and large number of plates are required in the column. It is typical to have in excess of 200 theoretical plates and a reflux ratio of 15 or higher are required for its separation (Doherty, *et al.*, 1985). Distillation column can be used advantageously as a reactor for systems in which chemical reactions occur at temperatures and pressures suitable to the distillation of components. This combined unit operation is especially useful for those chemical reactions for which chemical equilibrium limits the conversion. By continuous separation of products from reactants while the reaction is in progress, the reaction can proceed to a much higher level of conversion than without separation.(Alejski, *et al.*, 1996). Some of the possible methods which can be used in the separation of isomeric mixtures include the following:

2.1.1 Extractive Distillation

This is a partial vaporization process in the presence of a miscible high boiling non-volatile mass separation agent. normally called the solvent which is added to a feed mixture to alter the volatilities of the key components. It is used in the petrochemical and chemical processing industries for the close-boiling systems for which simple single-feed distillation is either too expensive or impossible. Extactive distillation works by the exploitation of the selective solvent-induced enhancements or moderations of the liquid-phase nonidealities of the components to be separated. Choosing an effective solvent can

have the most profound effect on the economics of this process. The approach most often adopted is to first generate a short list of potential solvents using simple qualitative screening and selection methods. The solvent selectively alters the activity coefficients of the components being separated. To do this, a high concentration of solvent is necessary.

The most attractive alternative separation method for the xylenes and ethylbenzene mixture is extractive distillation. This method separates closely boiling mixtures by the addition of a third component which increases the relative volatility between the original components. This process is very effective if the components are different in chemical nature. Extractive distillation is favourably applicable to systems in which the components to be separated contain one or more different functional groups. It is usually uneconomical for separating stereoisomers, homologs or structural isomers containing the same functional groups, unless the differences in structure also contribute significantly to different polarity , dipole moment character,(Morrison, *et al.*, 1992).

Therefore, it cannot be successfully applied to the separation of isomers since the entrainer has almost the same effect on each of the components and therefore, does not change their relative volatility. Berg *et al.* (1996) investigated forty entrainers for the separation of metaxylene and paraxylene and found out that their relative volatility of 1.02 could be increased to a mere 1.029. Alternative techniques must therefore be sought or investigated for the separation of isomeric mixtures.

2.1.2 Mixed Extractive Distillation

Mixed extractive entrainers by Berg(1983) who used more than one entrainer for the separation of ethylbenzene from metaxylene and paraxylene mixture. There was no improvement in their relative volatility.

The relative volatility of ethylbenzene and paraxylene is 1.06, ethylbenzene-m-xylene is 1.08. .To separate ethylbenzene from p-xylene 99% purity by convectional rectification requires a minimum of 157 theoretical plates at total reflux. Styrene which is principally produced from ethylbenzene is used in plastics and rubber manufacture. To make high purity styrene it is necessary to use high purity ethylbenzene. Berg et al.(1981) used mixtures of oxygenated organic compounds extractive entrainers but did not increase the relative volatility beyond 1.21.

2.1.3 Extractive Reaction.

Ng *et al.*, (1998) attempted to synthesize extractive reaction processes. His main objective was to develop liquid phase processes involving simultaneous reaction and separation by extraction to achieve improved yield, selectivity to a desired product, and separation of products. The method was based on equilibrium thermodynamic analysis of multicomponent reactive system with multiple liquid phases. A second liquid phase containing a solvent was deliberately imposed on the system to selectively extract an intermediate or a product thereby preventing its further reaction. The removal of morpholine from dilute aqueous waste streams by reaction with benzoyl chloride dissolved in toluene in metal processing was a success (Ng *et al.*, 1998). The epoxide product derived from 6-methylhept-5-en-2-one undergoes facile rearrangement to an

undesirable by-product, 1,3,3-trimethyle-2,7-dioxabicyclo-2.2.1-heptane. The series reaction was carried out in the presence dichloromethane, the product was extracted into the hydrocarbon phase and a higher selectivity to the epoxide product was obtained . This was as a result of the differences in the molecular nature of the species involved. There was phase separation in the liquid phase as a result of partial immiscibility but in the xylenes, the imposed second liquid solvent always affect all the isomeric components in a similar way.

2.1.4 Fractional Crystallization

Fractional crystallization which employs the freezing point differences as demonstrated by Mohameed *et al,* (2006). This method has been used for the separation of paraxylene from the xylene mixture because of its favourable melting temperature compared to those of the rest xylenes. Therefore, by lowering the temperature of the mixture, paraxylene which has the highest melting point, will crystallize firstly (as solid crystals) and then can be separated Table 2 shows some of the thermodynamic properties of the mixed xylene components including the boiling and melting points (Perry and Green., 1997). The first step in cooling crystallization technique is to reach supersaturation – the driving force which occurs as a result of the reduction in solute solubility when the temperature is reduced. Formation of nuclei occurs and finally the subsequent growth of these nuclei to form large crystals. The formation of large crystals is difficult because of the complex kinetics involved and if the obtained crystals have relatively small sizes, the filtration process is expected to be difficult because small crystals will cause filter clogging. Thus, it is of great importance to control the crystallizer conditions to obtain the desired crystal

size distribution (CSD). The CSD depends mainly on the degree of saturation as well as on crystals nucleation and growth rates The crystallization kinetics is complex and quantitatively, each system has its own crystallization kinetics. The scrapping blades of crystallizers also cause crystals damage and thus producing slurries which are difficult to filter. These devices are often costly and require considerable maintenance (Tkrouri, et al., 2006)

2.1.5 Reactive Distillation

Reactive distillation, which exploits chemical reaction differences (selectivity) between the isomers and a third component - the reactive entrainer intentionally introduced. In recent years, a growing number of determined engineers have designed and built commercial distillation systems in which chemical reactions are deliberately introduced in order to achieve the process goals. In fact, a study by Sylvestre *et al.* (1995) shows that for mixtures with a relative volatility less than 1.06, there is a large economic incentive to explore the possibility of using reactive distillation. Some of the requirements of reactive distillation are the liquid phase medium and reversible reactions. The xylenes are liquids at room temperature and this favors reactive distillation as the reactions can be carried out closer to stoichiometric feed conditions thereby eliminating recycle costs. Excess reactant is usually required to suppress side reactions and to overcome limitations imposed by chemical equilibrium. The continual removal of products from reactants causes the reactions to proceed in the forward direction (Le Chartelier's Principle) resulting in increased conversion (Sokhin and Blago, 1996). In some applications, such as in the

synthesis of methyl tertiary butyl ether, chemical reaction has the beneficial effect of reacting away some of the azeotropes in the mixture and greatly simplifying the phase behaviour. A large number of reactions and systems have been successfully designed and performed by using reactive distillation. These include methyl tertiary butyl ether (MTBE) a very effective antiknock additive to gasoline, from methanol and isobutene (Flato, *et al.*, 1992), ethyl tertiary butyl ether (ETBE) from ethanol and isobutene (Thiel, *et al.*, 1997), etheleneglycol from ethelene oxide and water (Ciric, *et al.*, 1992).

Although reactive distillation has many potential applications, it is not appropriate for all situations. Since it is in essence a distillation process, it has the same range of applicability as other distillation operations. Distillation-based equipment is not designed to effectively handle solids, gas phase reactions, or high temperature, or high pressure reactions such as hydrogenation, steam reforming and gasification.

2.2 Current Separation Methods for the Xylenes and Ethyibenzene Mixture

Presently, paraxylene is removed from the C_8 aromatic mixtures and the rest of the stream is recycled to the isomerization unit for re-equilibration. This is because paraxylene is in high demand for conversion to terephthalic acid (TPA) and then to dimethyl-terephthalate (DMT). This in turn is then reacted with ethylene glycol to form polyethelene terephthalate (PET). PET is the raw material for most poly-esters used in the production of fibers, packaging materials and containers. Worldwide production of paraxylene in year 2001 was near 21.4 million metric tons (about 679kg/s). However, in the isomerization process, ethylbenzene conversion to paraxylene is very difficult as it is less selective than ortho and metaxylenes. In fact, paraxylene separation is limited by ethylbenzene

contamination in the convectional separation. Two main methods are currently used for the removal of paraxylene from the C_8 compounds mixture – adsorption and crystallization (Yan, 1989, Mohammed, *et al.*, 2007).

2.2.1. ADSORPTION

This process depends on adsorption of paraxylene molecules by a shape-selective zeolite adsorbent, which is selective only to the para structure. The characteristics of improved adsorbents for the separations are high selectivity for paraxylene over ethylbenzene, high adsorption capacity, and insensitivity to variation in feed composition and impurities. The UOP Parex Process is an example of this method (Halgeri, 2003). Much progress has been made in the industry to improve on the zeolites adsorbent, through modification and preparation procedures. Although the improved zeolitic membrane is now more stable, the high cost of the para-selective makes this separation of hydrocarbon method limited to small scale productions.

2.2.2 CRYSTALLIZATION

This process depends on the variation of melting points of the chemicals in the mixed xylene. Therefore, by lowering the temperature of this mixture, PX, which has the highest melting point, will crystallize firstly (as solid crystals) and then can be separated.

Table 2.1 above shows some of the thermodynamic properties of the mixed xylene components including the boiling and the melting point. Super saturation, the driving force for crystallization, occurs as a result of the reduction in the solute solubility when

the temperature is reduced. The crystal size distribution, (CSD), is very important since the quality and end use properties of the crystals depend on it. The crystallizer conditions are controlled to obtain the desired CSD. Other bottlenecks associated with this method include the knowledge of the cooling profile and crystal behaviour under cooling which is provided from the study of the crystallization kinetics (nucleation and growth rates) (Mohammed, et al., 2007).

2.3 INDEPENDENT CHEMICAL REACTIONS

The relation of stoichiometry to chemical kinetics, both pure and applied is similar to that between kinematics and fluid mechanics. So, stoichiometry could be taken to be the study of possible concentration changes or the kinematics of the change of chemical species in the course of reaction. Mathematical models are reliable tools in the design and construction of chemical reactors (Aries, 1982). They are used for reliable prediction of feedstock utilization and effluent distribution. In modeling, the process system has to be described as completely as possible in the identification of the complete set of chemical species and types of chemical reactions. The changing economics associated with the availability of petroleum-based feedstock have placed premium on incorporating a high degree of flexibility into the design of reaction model. These models could be used for a wide range of feedstock for a long term purpose. The chemical engineering literature is sparse on how the independence of reactions may be established and how the approach illuminates the physical picture of chemically reacting systems. All modern plants now under construction use reactors which may be simulated by a set of ordinary differential equations(Aries, 1982). In catalytic reactive systems, the reactants undergo complex

reaction schemes involving the formation of the diverse products through various mechanistic steps. In particular, in reactions involving hydrocarbon feeds, this complexity increases with increasing molecular mass, conversion and system temperature. The more extensive the postulated steps, the more likely it becomes that they may represent the system. The possible number of alternative paths of elementary steps characterizing a particular reacting system is only limited by the imagination of the kineticist. The two main techniques often used in developing reaction model are:

1. All the reactions compiled from several sources with their rate constants are taken as a set of elementary reactions so that no important reaction is left out.
2. A minimum set of elementary reactions is used and later expanded stepwise by addition of new reations until a satisfactory model is obtained.(Isbarn and Elberrt, 1981, Powers, and Corcoran, *1983, Aries, 1982*).

Just as tensor analysis is proper language of kinematics, so linear algebra is the proper language of stoichiometric study. Its notions of independence and rank express precisely the nature of the chemical reactions and lead to the minimum number of necessary equations in any given situation. With the modern computers, memory allocation and computing time are considered a limitation for a judiciously simplified mechanistic model.. In the Gerald's (1992) review of the design of packed catalytic reactors, he showed clearly the importance of reducing the equations to an independent set. He took the advantage of the compact language of matrix mathematics to reduce chemical and rate equations to an independent set. The set relates the concentrations of the various species

to the concentrations of a minimum number of key reaction species. (Gerald and Wheatly, 1992) used the method of the rank of a non-varnishing matrix to establish the set of independent reactions. This method is cumbersome as the evaluations of the determinants of all possible square matrices must be done until a non-singular determinant has been found.

The number of reactions can be so large that numerical procedure for the reduction of the number of reactions becomes very useful in order to shorten computing time and probably enhance the stability and convergence behaviour of the modelling schemes. One obvious way of achieving this is to use only the independent sets of reactions in the system Billand *et al*(1991) used the Brinkley and Jouguets criteria to determine the number of independent stoichiometric equations for the pyrolysis of cyclohexane..

2.3.1 Brinkley and Jouguet's Criteria

Brinkley criterion says that the number, c. of independent species of a chemical system is equal to the rank of the matrix of the indexes of the elements in the formula of the species. Inert species are considered as independent (Isbarn and Elbert, 1981))

Jouguet's criterion indicates that , s stoichiometric equations are independent if the rank of the matrix of coefficients is equal to s. they are dependent if the rank is less than s.

For a given system, the exact nature of these independent species is not determined in an absolute way, for if several non-inert substances are linked by chemical reactions, any of them can be obtained from the others within the system. Linear combination of stoichiometric equations is also a stoichiometric equation. This emphasizes that the equations thus written in no way represents the mechanisms of the reactions actually

occurring in the reactor. Thus the stoichiometric descriptions of a chemical system requires that n species that are thought to be needed to describe the system be completely fixed.. then a group of s stoichiometric equations are written. For complex systems, it is important to have these criteria above to allow one to fix priory the number s of independent stoichiometries existing between the n considered species. Jouguet concluded that; $s = n - c$

where:

s = number of stoichiometric independent reactions

n = number of chemical species in the system

c = number of independent chemical species in the system

2.3.2 Relationship Between Brinkley and Jouguet's Criteria

In a system of n reactive species and c independent elements, then the number of independent reactions, s , is $s = n - c$. according to Brinkley's criterion.. So, while Brinkley tells the number of independent reactions, Jouguet tells the rank of matrix of the stoichiometric coefficients of the reactions.

They considered a total of eleven stoichiometric equations using this method and found that only eight of them were independent. When one considers the hundreds of elementary reactions used to characterize the pyrolysis of pure hydrocarbons and their mixtures in mechanistic modeling, it becomes quite obvious that a computer-assisted procedure would be valuable in carrying out this determination.

As part of this work, therefore, we present a computer-assisted procedure for determining the number of independent reactions in a scheme consisting of I reactions and J reactive species. In this procedure, redundant reactions are also identified.

CHAPTER THREE

METHODOLOGY

3.1 COMPUTER ALGORITHM FOR DETERMINATION OF INDEPENDENT REACTIONS

Consider a system in which there are J chemical species which participate in I chemical reactions. If these species are denoted by $N_1, N_2 \ldots N_J$, then, the i_{th} reaction may be written in the form

$$\sum_{j=1}^{J} a_{ij} N_j = 0 \qquad (3.1)$$

where a_{ij} is the stoichiometric coefficient of N_j specie in the i_{th} reaction and it is positive for product species and negative for reactants. So, mathematically, if there exist the coefficients $\alpha_1, \alpha_2 \ldots \alpha_i$ such that

$$\sum_{i=1}^{I} \alpha_{i1} a_{ij} = 0 \quad , \qquad j = 1, 2, \ldots, J \qquad (3.2)$$

then, the reactions are dependent, otherwise they are independent. Equation (3.1) may be written in the matrix form

$$\underline{A}\underline{b} = 0 \qquad (3.3)$$

$\underline{A}$ is the matrix of stoichiometric coefficients a_{ij} and $\underline{b}$ represents the components in the system. The condition for the independence of I reactions is that the rank of the matrix $\underline{A}$ should be I. A system of reactions may be written as;

$$\begin{array}{l}
a_{11}N_1 + a_{12}N_2 + \ldots + a_{1J}N_J = 0 \\
a_{21}N_1 + a_{22}N_2 + \ldots + a_{2J}N_J = 0 \\
\ldots + \ldots + \ldots + \ldots = 0 \\
\ldots + \ldots + \ldots + \ldots = 0 \\
\ldots + \ldots + \ldots + \ldots = 0 \\
\ldots + \ldots + \ldots + \ldots = 0 \\
a_{I1}N_1 + a_{I2}N_2 + \ldots + a_{IJ}N_J = 0
\end{array} \qquad (3.4)$$

and the matrix of the coefficients of these reactions is:

$$\begin{bmatrix} a_{11} & a_{12} & \cdots\cdots & a_{1J} \\ a_{21} & a_{22} & \cdots\cdots & a_{2J} \\ & . & \cdots\cdots & . \\ a_{I1} & a_{I2} & \cdots\cdots & a_{IJ} \end{bmatrix} \tag{3.5}$$

Linear independence of reactions means that there is no way of expressing any of the reactions as a linear combination of the others.

The final system after transformation to the echelon matrix (Derald, *et al.*, 1992) has the following form:

$$\begin{bmatrix} C_{11} & C_{12} & \cdots & C_{1r} & \cdots\cdots & C_{1J} \\ O & C_{22} & \cdots & C_{2r} & \cdots\cdots & C_{2J} \\ . & & . & & \cdots\cdots & \cdots \\ O & O & \cdots & C_{Rr} & \cdots\cdots & C_{RJ} \\ . & . & \cdots & . & & \cdots \\ O & O & \cdots & O & \cdots\cdots & O \end{bmatrix} \tag{3.6}$$

Therefore the number of independent reactions for the reduced system is R while the other I-R reactions are dependent (Johnson, *et al.*, 1989).

3.2 Determination of the rank of Matrix

The rank of a matrix is the number of independent equations when the matrix of coefficients is formed from the equations(Chaiho, 1971, Johnson, *et al.*, 1989).

One way of finding the rank is to evaluate the determinants of its square sub-matrices. Given an M x J matrix, where for example M<J and the rank, s, of the matrix is less than M, one may have to evaluate all determinants of M, possibly all determinants of M-1 order or M-2 order and so on, until a non-singular determinant has been found. This is cumbersome. A more convenient way which was employed in this work is to transform the matrix into an echelon matrix(upper triangular) through the elementary row

operations. The algorithm was based on the well known method of reducing the system of equations by re-ordering at each step before elimination. (Ames, 1962) has described the procedure for obtaining an independent set in a system of equations using the echelon matrix containing at least one non-zero element while every element of the remaining I-K rows are reduced to zero. During the re-ordering. the specific serial number of identification of a reaction is carried along with the reaction. We recall that the rank of a matrix is not changed by the interchanges of its rows and columns. Such operations may therefore, be employed to bring the numerically largest element to the top left hand corner of the matrix. This procedure is usually known as the selection of a pivot by row and column interchanges. The top row is then divided through by this pivotal element yielding a leading element of unity. Next, this new top row is multiplied by the leading element of the second row and this is subtracted from the second row, giving a new second row with the leading element of the second row and this is subtracted from the giving a second row with the leading element of zero. This elimination is continued to the last row, so that the first column of the modified matrix is (1, 0, 0 . . .0). Now the pivotal selection and elimination are performed with the (S-1)x(S-1) submatrix which does not contain the first row and the first column. As this process is repeated with the successive submatrices, elements of unity are developed down the diagonal with zeros beneath them. If the rank of the matrix , R, is less than the original number of rows, S, this procedure will yield a new matrix with the last (S-R) rows identically zero(Aries and Mah., 1963)

For example, in the first column, the reduction is thus:

$$a_{ij} \leftarrow a_{ij} - a_{i1} * \frac{a_{ij}}{a_{11}} \quad 2 \le i \le I \,,\; 1 \le j \le J \qquad (3.7)$$

For the second column,

$$a_{ij} \leftarrow a_{ij} - a_{i1} * \frac{a_{2j}}{a_{22}} \qquad 3 \leq I \leq I,\ 2 \leq j \leq J \qquad (3.8)$$

and for k_{th} elimination,

$$a_{ij} \leftarrow a_{ij} - a_{ik} * \frac{a_{kj}}{a_{kk}} \qquad k+1 \leq i \leq I,\ k \leq j \leq J \qquad (3.9)$$

During the process of elimination, elements of unity are developed along the diagonal. It is important to note here that there is some choice in the selection of equations that are most recognizable and significant to the researcher in the elementary operations since:

1. any two equations may be interchanged and chosen arbitrarily;
2. both members of any equation may be multiplied by the same non-zero constant; and
3. the same multiple of the two members of any equation may be added to the corresponding member of a second equation without affecting the fundamental set of independent equations.(Chaiho, 1971)

The system of linear equations represented by the matrix at each step of the reduction has the same solution as the original system.(Johnson, *et al.*, 1989)

3.3 REACTIVE DISTILLATION

Reaction and separation phenomena are closely coupled in a reactive distillation process. Hence, modeling, simulation and design is significantly more complex than that of sequential reaction and separation processes. In spite of this complexity, however, there are large memory capacity computers and reliable flexible routines to handle the complex calculations involved for steady-state reactive distillation systems with either equilibrium or kinetically controlled reaction models.

3.3.1 Fundamentals of Reactive Distillation.

Simplifying assumptions:

(i) The reactions take place in the liquid phase only.

(ii) The reactions are catalyzed either by homogenous or a heterogeneous catalyst.

(iii) With catalyst, the reactions are instantaneous.

(iv) The reactions are reversible, that is both reactants and products exists in the effluent..

These assumptions simplify the conditions. However, these simplifications allow easy descriptions and in turn a good understanding of the fundamental mechanism effective in reactive distillation.

Reactive distillation is usually applied to systems with equilibrium reactions. For the following discussion, it is assumed that the system is in chemical and physical equilibrium. Under this assumption, the degrees of freedom, F, of a system are reduced by the number of independent reactions (Wales, 1985). Knowledge of the equilibrium is the most fundamental prerequisite for a conceptual synthesis of non-reactive as well as reactive distillation processes. The composition of reaction mixture is limited by chemical equilibrium. However, the equilibrium in reactive distillation process is more complex since the chemical equilibrium is superimposed on the vapor-liquid equilibrium (Stichimair and Frey, 1999). This limitation could be over-passed only by product removal from the reaction zone.

3.3.2 Topology of Reactive Distillation Processes

The procedure is, in essence, the same as in the design of non-reactive distillation processes. The most essential steps are:

(a) Determination of the feasible products

(b) Formulation of the material balance around the column

(c) Identification of separation sequence.

3.3.3 Feasible Products

Feasible pure products of distillation columns are either origins or termini of distillation lines. The principle holds also for reactive distillation (Sokhin and Blagov, 1996; Degermo. *et al.,* 1992)

The knowledge of the reactive distillation lines is the basis for the conceptual design of reactive distillation processes. In the formulation of vapor-liquid equilibrium relationships, several methods are available. Equilibrium ratios (K-values) are often used especially for multi-component mixtures. For binary mixtures, the most convenient formulation is the equilibrium curve with temperature independent relative volatility, α. The distillation line is most appropriate for ternary systems.

The equilibrium ratio is defined as

$$K_a = \frac{y_a}{x_a} \tag{3.10}$$

The equilibrium curve is drawn using Dalton's and Raoult's laws:

$$y_a = \frac{p_a}{p_a + p_b} = \frac{x_a p_a^o}{x_a p_a^o + x_b p_b^o} \tag{3.11}$$

The ratio p_a^0 / p_b^o is often preferred because it is often independent of temperature. Therefore, vapor-liquid equilibra are frequently expressed in the form

$$\alpha_{ab} = \frac{p_a^o}{p_b^o} \quad (3.12)$$

$$x_b = 1 - x_a \quad (3.13)$$

Substituting (3.11) and (3.12) in (3.10), gives

$$y_a = \frac{\alpha_{ab}.x_a}{1 + (\alpha_{ab} - 1).x_a} \quad (3.14)$$

For ternary systems, consisting of a, b, and c, analogous relationships exist

$$y_a = \frac{p_a}{p_a + p_b + p_c} = \frac{x_a p_a^o}{x_a p_a^o + x_b p_b^o + x_c p_c^o} \quad (3.15)$$

substituting $\alpha_{ac} = \frac{p^o_a}{p^o_c}$, and $\alpha_{bc} = \frac{p^o_b}{p^o_c}$ $x_c = 1 - x_a - x_b$ into (3.15), we get,

$$y_a = \frac{\alpha_{ac}.x_a}{1 + (\alpha_{ac} - 1).x_a + (\alpha_{bc} - 1).x_b} \quad (3.16)$$

$$y_b = \frac{\alpha_{bc}.x_b}{1 + (\alpha_{bc} - 1).x_a + (\alpha_{bc} - 1).x_b} \quad (3.17)$$

$$y_c = 1 - (y_a + y_b) \quad (3.18)$$

Therefore the general equation for multi-component mixture is:

$$y_i = \frac{\alpha_{ik}.x_i}{1 + \sum_{j=1}^{k-1}(\alpha_{jk} - 1).x_j} \quad \text{for } j = 1, \ldots, k\text{-}1 \text{ components,} \quad (3.19)$$

where k refers to the highest boiling substance. In non-ideal systems, the activity coefficient, γ_i, must be incorporated into the equations. If an initial liquid concentration of component i, x_{io} , is assumed, the equilibrium vapor concentration, y_{io} , is determined. The vapor is then assumed to be totally condensed. Thus a new liquid of composition $x_{i1} = y_{io}$ is obtained and may be located on the triangular diagram. The

vapor state y_{i1} in equilibrium with the liquid state x_{i1} is in turn, determined and so on. Successively, a series of liquid states, x_{i1}, x_{i2}, x_{i3}, ... is finally obtained (see Figure 1). The composition difference in each case represents an equilibrium step. These liquid states can be joined together to give a distillation line. This process leads to a step-by-step enrichment of the more volatile component, which is accompanied by a decrease in boiling point. With this information, a triangular diagram can be sketched with the low boiling component, a, at the top, the intermediate, b, at the bottom right and the high boiling component, c, at the bottom left. The direction of decreasing boiling points are marked by arrows on the sides of the triangle and these arrows point towards decreasing boiling points (see Figure 3.2).

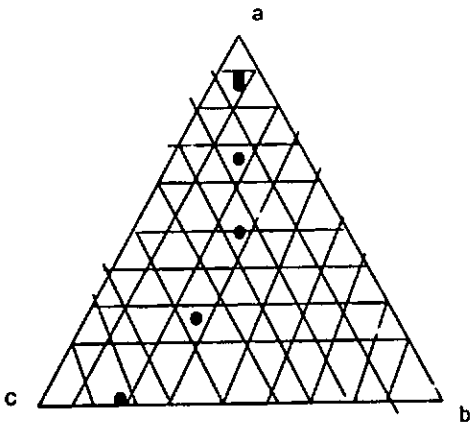


Figure:3.1 · Representation of the phase equilibrium of the ternary mixture

b

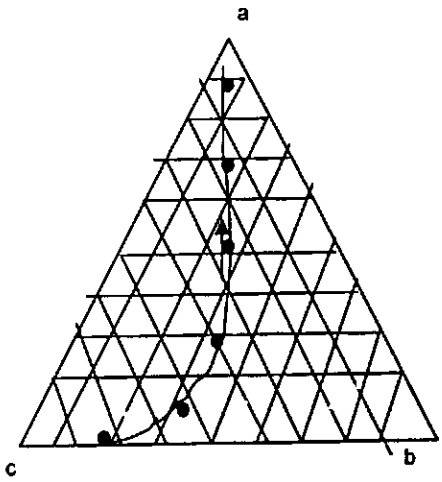


Figure 3. 2: Course of distillation line.

The pure components are at the vertices of the triangular diagram with the most volatile on top and arranged clockwise in increasing order of boiling point.

The distillation lines start at the component with the highest boiling and end at the component with the lowest boiling point. The direction of decreasing temperature is indicated by arrows. Distinct equilibrium states are shown on one line by dots. Distillation lines reveal the presence or absence of azeotropes.

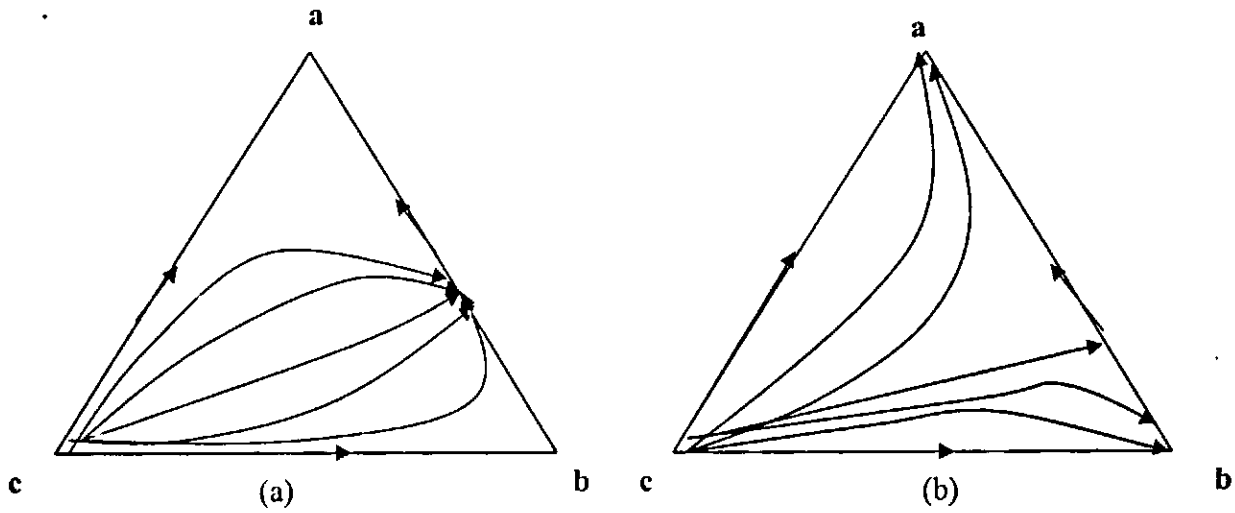


Figure 3.3: (a) Reveals the presence of azeotrope and (b) Reveals border distillation line

In Figure 3.3(a) above, all distillation lines terminate at the ab azeotrope (single origin and terminus). In Figyre 3.3(b), all distillation lines originate at c corner and terminate at either in the b corner or a corner. A border distillation line runs from c to the azeotrope. Border lines are barriers that in most cases cannot be crossed by distillation. They are as important for ternary mixtures as azeotropes are for binary mixtures. The origins or terminus of distillation lines are feasible top or bottom fractions of distillation columns.

3.3.4 Derivation of the Transformed Composition Variables through Formulation of Material Balance around the Column

For the analysis of a non-reactive distillation process, a material balance is utilized to connect the feed, F, the distillate, D and the bottoms, B. These three components are connected in a straight line when lever rule is applied. In reactive distillation, this principle no longer holds since some of the species are converted into other species by

the reaction. Hence, the states, F, D, and B are only co-linear after transformation along the stoichiometric lines. The transformed concentration coordinates can be used to derive the lever rule for a reactive distillation column. When the composition space has dimension greater than three, and since most reactive systems are multi-component, it becomes difficult to visualize the phase diagram in a mole fraction coordinate system. However, because of reaction equilibrium, the phase diagrams are confined to lie on surfaces embedded within the mole fraction coordinate system. These surfaces can be transformed into new lower–dimensional composition coordinate systems that contain all the original information in a simpler way. The new composition variables also have the desirable property of taking the same numerical values before and after reaction. The procedures for assessing separation feasibility and design in non-reactive distillation systems can be applied to reactive systems when they are represented in terms of the transformed composition coordinates.(Ung and Doherty, 1995)

3.3.4.1 Chemical Equilibrium

The main difference between the chemical equilibrium model algorithm and the non-reactive system, is the use of the chemical model in a way that renders the chemical and physical equilibrium phase diagrams look similar to the nonreactive separation systems (Perez, et al.,1997).

The following general reaction mechanism is considered.

$$\nu_a A + \nu_b B \leftrightarrow \nu_p P + \nu_q Q \qquad (3.20)$$

The letter v denotes the stoichiometric coefficient of the substance i, while A, B, P and Q are the species. The reaction is reversible. In ideal mixtures, the following holds for the chemical equilibrium

$$K_R = \frac{x_p^{v_p} x_q^{v_q} \ldots\ldots}{x_a^{v_a} . x_b^{v_b} \ldots\ldots} = \prod_{j=1}^{k} x_i^{v_i} \tag{3.21}$$

In this reactive simple distillation a liquid is vaporized at constant pressure while the vapour is continuously removed and all the equilibrium reactions are proceeding simultaneously. The stoichiometric coefficients are specified by the usual convection, $v_i < 0$, if component i is a reactant in reaction r, $v > 0$, if component i is a product in reaction, and $v = 0$ if component i does not participate in reaction r or if component is an inert. As the liquid is vaporized, the most volatile components generally evaporate first, and the composition of the liquid changes with time. The equilibrium constant of the reaction, K_R, is essentially a function of temperature. Hence, its value can be influenced by the pressure of the reactive distillation column since the mixture is at its boiling point. In non-ideal mixtures, the concentrations need to be corrected by the activity coefficient γ_i.

$$K_R = \frac{x_p^{v_p} . x_q^{v_a} \ldots\ldots \gamma_p^{v_p} . \gamma_q^{v_q}}{x_a^{v_a} . x_b^{v_b} \ldots\ldots \gamma_a^{v_a} . \gamma_b^{v_b}} = \prod_{j=1}^{k} x_i^{v_i} . \gamma_i \tag{3.22}$$

Here, the value of the equilibrium constant K_R is additionally influenced by the concentrations x_i.

The material balance was formulated around the reactive distillation column by considering a multi-component system including inert or non-reactive substance.

Consider a multi-component system of c reacting components and I inert components for a total of C = c + I species undergoing R chemical equilibrium reactions in a column. The inert species do not participate in the reaction but influence the simultaneous chemical reaction and vapor-liquid equilibrium hence the operating conditions. They exhibit non-ideal solution behavior with each other and with the resulting species.

Assumptions:

1. Boiling feed.
2. Heat losses are negligible.
3. The molar heat of phase change for this mixture is constant.
4. The heat of mixing is negligible.
5. The heat capacity of the mixture is constant.
6. The reaction enthalpy change is negligible.
7. On each stage, the equilibrium is attained for the leaving streams.
8. The operating pressure is constant.

The matrix of dimension(C,R) of the stoichiometric coefficients for all the components in all the reactions is given by:

$$\nu = \begin{pmatrix} \nu_{11} & . & . & . & . & \nu_{1C} \\ & \ldots\ldots\ldots\ldots\ldots & & & & \\ \nu_{R1} & . & . & . & & . \nu_{RC} \end{pmatrix} \qquad (3.23)$$

Sometimes, not all the reactions are independent, some are linear combinations of others. Therefore, there wili be C-R remaining reference components. The matrix of the remaining components is given as

$$\nu = \begin{pmatrix} \nu_{(c-R),1} & \cdots & \nu_{(c-R),R} \\ & & \\ \nu_{c,1} & \cdots & \nu_{c,R} \end{pmatrix} \tag{3.24}$$

Consider a reactive column with a feed flow rate, F of composition x_F, a distillate flow rate, D of composition x_D, and bottoms flow rate B of composition x_b .where

$$\begin{aligned} \mathbf{x}_F &= (x_{1F}, x_{2F}, x_{3F}, \ldots\ldots x_{c,F})^T \\ \mathbf{x}_D &= (x_{1D}, x_{2D}, x_{3D}, \ldots\ldots x_{c,D})^T \\ \mathbf{x}_B &= (x_{1B}, x_{2B}, x_{3B}, \ldots\ldots x_{c,R})^T \end{aligned} \tag{3.25}$$

Taking the material balance around the reactive distillation column for each component gives

$$F\mathbf{x}_F = D\mathbf{x}_D + B\mathbf{x}_B - \nu\varepsilon \tag{3.26}$$

ν is defined in equation 3.24 and ε is the column vector of the extents of reaction of the independent reactions. That is

$$\varepsilon = (\varepsilon_1, \varepsilon_2, \varepsilon_3, \ldots\ldots, \varepsilon_R)^T) \tag{3.27}$$

Therefore, equation (3.25) represents C equations, one equation for each component. R reference components were introduced to eliminate the R extents of reaction, and rewrite Equation (3.25) in three blocks, R equations for R reference components

$$F\mathbf{x}_{kF} = D\mathbf{x}_{kD} + B\mathbf{x}_{kB} - \nu_k\varepsilon \tag{3.28}$$

When an equilibrium reaction occurs in a vapour-liquid system, the phase compositions depend not only on the relative volatility of the components in the mixture, but also on the consumption and production of species. Hence the

stoichiometric coefficients of all the species in the system should be considered in the derivation.

The overall material balance is

$$F = D + B - \nu^T_{TOT}\,\varepsilon \tag{3.29}$$

and (C-R-1) equations for the other components

$$Fx_{iF} = Dx_{iD} + Bx_{iB} - \nu_i^T\,\varepsilon \qquad (i = 1,\ldots,C\text{-}R\text{-}1) \tag{3.30}$$

But, ν_i^T and ν^T are row vectors

$$\nu^T_{TOT} = (\nu_{T1},\ldots\ldots\ldots\ldots,\nu_{TR}) \tag{3.31}$$

$$\nu^T_i = (\nu_{i1},\ldots\ldots\ldots\ldots,\nu_{iR}) \tag{3.32}$$

$$x_{kF} = (x_{1F}, x_{2F}, x_{3F},\ldots\ldots x_{c,F})^T \tag{3.33}$$

$$x_{kD} = (x_{1D}, x_{2D}, x_{3D},\ldots\ldots x_{c,D})^T \tag{3.34}$$

$$x_{kB} = (x_{1B}, x_{2B}, x_{3B},\ldots\ldots x_{c,B})^T \tag{3.35}$$

Using equation (3.28) to eliminate ε from Equations (3.29) and (3.30) to give

$$F = D + B + \nu^T_{TOT}(\nu_k)^{-1}(Fx_{kF} - Dx_{kD} - Bx_{kB}) \tag{3.36}$$

and

$$Fx_{iF} = Dx_{iD} + Bx_{iB} + \nu_i^T(\nu_k)^{-1}(Fx_{kF} - Dx_{kD} - Bx_{kB}) \tag{3.37}$$

Rearranging Equations 3.36 and 3.37 we have:

$$F(1-\nu^T_{TOT}(\nu_k)^{-1}x_{k,F}) = D(1-\nu^T_{TOT}(\nu_k)^{-1}x_{k,D}) + B(1-\nu^T_{TOT}(\nu_k)^{-1}x_{k,B}) \tag{3.38}$$

$$F(x_{i,F}-\nu_i^T(\nu_k)^{-1}x_{k,F}) = D(x_{i,D}-\nu_i^T(\nu_k)^{-1}x_{k,D}) + B(x_{i,B}-\nu_i^T(\nu_k)^{-1}x_{k,B}) \tag{3.39}$$

Defining the transformed flow rates in the distillate, bottom and feed, D, B, F respectively as

$$\hat{F} = F(1 - \nu_{TOT}^{T}(\nu_k)^{-1} x_{k,F}) \tag{3.40}$$

$$\hat{D} = D(1 - \nu_{TOT}^{T}(\nu_k)^{-1} x_{k,D}) \tag{3.41}$$

$$\hat{B} = B(1 - \nu_{TOT}^{T}(\nu_k)^{-1} x_{k,B}) \tag{3.42}$$

then Equations (3.38) and (3.39) could be written as

$$\hat{F} = \hat{D} + \hat{B} \tag{3.43}$$

and

$$\frac{\hat{F}(x_{i,F} - \nu_i^T(\nu_k)^{-1} x_{k,F})}{1 - \nu_{TOT}^T(\nu_k)^{-1} x_{k,F}} = \frac{\hat{D}(x_{i,D} - \nu_i^T(\nu_k)^{-1} x_{k,D})}{1 - \nu_{TOT}^T(\nu_k)^{-1} x_{k,D})} + \frac{\hat{B}(x_{i,B} - \nu_i^T(\nu_k)^{-1} x_{k,B})}{1 - \nu_{TOT}^T(\nu_k)^{-1} x_{k,B})} \tag{3.44}$$

repectively, provided the denominators are not zero.

Re-organize equation (3.44) by defining new transformed composition variables as

$$X_{i,F} = \frac{(x_{i,F} - \nu_i^T(\nu_k)^{-1} x_{k,F})}{1 - \nu_{TOT}^T(\nu_k)^{-1} x_{k,F}} \tag{3.45}$$

$$X_{i,D} = \frac{(x_{i,D} - \nu_i^T(\nu_k)^{-1} x_{k,D})}{1 - \nu_{TOT}^T(\nu_k)^{-1} x_{k,D})} \tag{3.46}$$

$$X_{i,B} = \frac{(x_{i,B} - \nu_i^T(\nu_k)^{-1} x_{k,B})}{1 - \nu_{TOT}^T(\nu_k)^{-1} x_{k,B})} \tag{3.47}$$

X_i is known as the transformed composition variable for component i.

$$X_i = \frac{(x_i - \nu_i^T(\nu_{ref})^{-1} x_{ref})}{1 - \nu_{TOT}^T(\nu_{ref})^{-1} x_{ref}} \tag{3.45a}$$

Equation (3.44) could therefore be rewritten in terms of $X_{i,F}$, $X_{i,D}$ and $X_{i,B}$, to give,

$$FX_{iF} = DX_{iD} + BX_{iB} \qquad i = 1,\ldots,C\text{-}R\text{-}1 \tag{3.48}$$

In order to ensure that the new composition variable is satisfied, the denominator in equations (3.45) to (3.47) is not zero. This is guaranteed by a suitable choice of reference component, k.

3.3.5 Rules for Choice of Reference Components

The R reference components can be chosen from among the c components of the reactive mixture according to the following criteria (Ung and Doherty, 1995, Barbosa and Doherty, 2000).

1. If $\nu^{T}_{TOT} > 0$, chose reference component as a reagent.
2. If $\nu^{T}_{TOT} < 0$, chose reference component as product.
3. If $\nu^{T}_{TOT} = 0$, chose reference component as any of the reacting components.

The matrix of reference should be invertible, thus its determinant should not be equal to zero. Since the matrix is the square matrix of stoichiometric coefficients for the R reference components in the R reactions(where the components are ordered by rows and the reaction by columns), a necessary condition for this criterion is that none of the rows or columns of the matrix can be zero. In other words, all the reactions must involve at least one of the reference components chosen.. none of the inerts can be chosen as reference component. Another necessary condition is that none of the rows be the same , which means that no two reference components can have the same stoichiometric coefficients in each reaction(Ung and Doherty, 1995).

3.3.6 Equivalence of Linear Combinations of Stoichiometric Equations

Once a a set of reference components has been chosen, the transformed composition variables take the same expression independently of how the set of independent reactions is written.. the expressions for the transformed composition variables do not depend on which set of stoichiometric equations is chosen to represent the system. Therefore, the shape of the solution space in transformed composition coordinates is the same for all equivalent sets of stoichiometric equations. Therefore, the transform composition variableprovide a canonical representation of the reaction stoichiometry.

3.3.7 Properties of the Transformed Composition Variables.

An important component of these derivations is the calculation and representation of multicomponent reactve liquid-liquid phase diagrams. The phase diagrams are plotted in transformed mole-fraction coordinates in Figures 5 - 8 and 10 - 16. This is one of the methods for projecting high dimensional phase diagrams onto a lower dimensional space. Use of transformed mole fractions eliminates the restriction on visualization of phase behaviour for systems with more than three components. A point on the transformed coordinate phase diagram represents a unique composition that satisfies both phase and reaction equilibrium.

The transformed variables defined in Equations (3.45) to (3.47) show properties similar to that of mole fractions. This means that the sum of the transformed variables weighted with its stoichiometric coefficients is a constant

$$\sum_{i=1}^{C-R-1} X = 1 \qquad (3.49)$$

Describing the reactive distillation using these transformed compositions makes inlet and outlet compositions fall on straight lines, and consequently, the flow rates in the transformed field obey the lever rule. The transformed variables describe the system composition with or without reaction as do mole fractions x_i and y_i. in non-reactive systems. The vapor and liquid transformed compositions at any instant represent a simultaneous phase and chemical reaction equilibrium between any escaping vapor and the liquid remaining in the still (Espinosa, *et al.*, 1995a).

Since the denominators of Equations (3.45) through (3.47) are non-zero, none of the transformed flows F, D, and B is zero and Equations (3.43) and (3.48) could be rearranged to obtain the fractions of the total feed that appears in the distillate and bottom streams.

$$\frac{\hat{D}}{\hat{F}} = \frac{X_{i,F} - X_{i,B}}{X_{i,D} - X_{i,B}} \tag{3.50}$$

$$\frac{\hat{B}}{\hat{F}} = \frac{X_{i,D} - X_{i,F}}{X_{i,D} - X_{i,B}} \tag{3.51}$$

The ratio of the transformed distillate flow rate to the transformed bottoms flow rate is then given as a lever rule in terms of transformed compositions.

$$\frac{\hat{B}}{\hat{D}} = \frac{X_{i,D} - X_{i,F}}{X_{i,F} - X_{i,B}} \tag{3.52}$$

These expressions have the same functional form as the lever rule for non-reactive mixtures (Bessling *et al.*, 1997; King, 1980). This tells us that in an equilibrium reactive distillation column, the overall material balance will be satisfied if the feed, distillate and bottom compositions, in transformed composition coordinates, all lie on a straight line.

Due to this geometrical property of the new composition variables, by using the curves, it is possible to determine the feasibility of a desired separation from the operating onditions

3.4 Meta- and Paraxylene Mixture Separation Through Reactive Distillation Process.

The developed equations of reactive distillation process were employed to separate meta– and para-xylene mixture. A reactive entrainer, di-tertiary butyl benzene (a reactive entrainer) was intentionally introduced to react with m- xylene in the presence of aluminum chloride catalyst to produce tertiary- butyl-m-xylene . The alkylation reaction complex, tertiary- butyl-m-xylene, on reacting with more benzene, liberated the m-xylene in another reaction step after separation from paraxylene. The residue curve maps in the transformed composition variables for the reactive mixture at equilibrium provides information on the feasibility of separation and column sequencing for a desired separation.

The alkylation reactions occurring are the following:

$$\underset{\substack{C(CH_3)_3 \\ (DBB)}}{C_6H_4\text{–}C(CH_3)_3} + \underset{(MX)}{C_6H_4(CH_3)_2} \rightleftharpoons \underset{\substack{C(CH_3)_3 \\ (TBMX)}}{C_6H_3(CH_3)_2} + \underset{(TBB)}{C_6H_5C(CH_3)_3} \qquad (3.53a)$$

$$\underset{(TBB)}{C_6H_5C(CH_3)_3} + \underset{(MX)}{C_6H_4(CH_3)_2} \rightleftharpoons \underset{(TBMX)}{C_6H_3(CH_3)_2} + \underset{(B)}{C_6H_6} \qquad (3.54a)$$

Let

A_1 = di-tert-butyl-benzene

A_2 = m-xylene

A_3 = tert-butyl-m-xylene

A_4 = tert-butyl-benzene

A_5 = benzene

A_6 = p-xylene

Then the two reactions above become:

$$A_1 + A_2 \rightleftharpoons A_3 + A_4 \qquad (3.53b)$$

$$A_4 + A_2 \rightleftharpoons A_3 + A_5 \qquad (3.54b)$$

PX is component A_6 and does not appear in the set of reactions because it acts as an inert. The presence of PX does, however, influence the reactive vapour-liquid phase diagram or the vapour-liquid equilibrium.

Gibbs Phase Rule for the system is given by:

The degrees of freedom for a reactive mixture is

$$F = (c+I) + 2 - \Pi - R \qquad (3.55)$$

where:

c = number of components (reactants and products)

I = number of inert components

Π = number of phases

R = number of independent reactions

For a two-phase ($\Pi = 2$) system, at either constant pressure or temperature, the degrees of freedom become:

$$F = (c+I) - R - 1 \qquad (3.56)$$

So, for this system, $F = 3$ (3.57)

This is in line with a thermodynamic point of view that a reacting quaternary system will be totally specified when the values of any three independent intensive properties have been selected.with a fixed pressure.

The number of degrees of freedom is identical to the dimension of the concentration space in which equilibrium conditions are fulfilled. This part of the concentration space can be defined as reaction space. The geometrical shape of the reaction space depends on the type of reaction, the position of the equilibrium and the presence of inert components. F is the number of compositions that must be specified in the phase equilibrium calculations. This gives rise to a three-dimensional figure. The set of transformed composition variables for this reacting system that have the right dimensionality and have properties similar to those of mole fractions in non-reacting mixtures was determined. The natural variables required to describe reactive mixtures are the reaction-invariant compositions –the transformed composition variables.

The choice of reference components is then made. The reference components are the R components chosen to eliminate the R extents of reaction from the c+I equations. The number of reacting components, c, is greater than the number of independent reactions, R. The criteria for this choice have been given earlier.

For this system, $\nu^T_{Tot} = (0,0)$ hence the reference components are A_i and A_2.

When the number of components in a reacting system exceeds four, the composition space has dimension greater than three, and it becomes difficult to visualize the phase diagram in a mole fraction coordinate system. The phase diagrams are confined to lie on surfaces embedded within the mole fraction coordinate system. These surfaces were then transformed into new lower-dimensional composition coordinate system that contains all the original information in a simpler way. The transformed composition variables are then calculated using the relation below.

$$X_i = \frac{(x_i - v_i^T (v_{ref})^{-1} x_{ref})}{1 - v_{TOT}^T (v_{ref})^{-1} x_{ref}} \qquad i = 3, c+I \tag{3.58}$$

where,:

$$X_3 = x_3 + x_2 \tag{3.59}$$

$$X_4 = x_4 + 2x_1 - x_2 \tag{3.60}$$

$$X_5 = x_5 - x_1 + x_2 \tag{3.61}$$

$$X_6 = x_6 \tag{3.62}$$

And,

$$Y_i = \frac{(y_i - v_i^T (v_{ref})^{-1} y_{ref})}{1 - v_{TOT}^T (v_{ref})^{-1} y_{ref}} \tag{3.63}$$

The calculation is shown in Appendix A.

3.5 Separation of Ortho-, Meta, Paraxylenes and Ethylbenzene Mixture

The separation of the four C_8 close boiling aromatic compounds mixture using reactive distillation was done as a second application of this work. A separation based on alkylation, separation of the alkylated products and their subsequent dealkylation and the final separation produced the high grade pure xylenes and ethylbenzene compounds. Meta, para, ortho – xylenes and ethylbenzene form a close boiling mixture and they are isomers of C_8 compound. A fifth component, di-tertiary butyl benzene, was intentionally introduced into the system (as a reactive entrainer) to react with o-xylene and ethylbenzene with the aid of the highly selective iron III chloride ($FeCl_3$) catalyst in the first column. The separated alkylated complex, tertiary-butyl-o-xylene and tertiary- butyl-ethylbenzene, liberated the o-xylene and ethylbenzene in another reaction step on reacting

with more benzene. $AlCl_3$ catalyst allows the reactive entrainer to react with m- xylene to form a complex : tertiary-butyl-m-xylene. This complex was separated and dealkylated in another step. The residue curve maps in the new transformed composition variables for the reactive mixture at equilibrium provides information on the feasibility of the separation and the column sequencing for the desired separation. The new variables represent the surfaces embedded within the mole fraction coordinate space in a simpler way, thus giving an easier visualization of the diagrams. This made the determination of the feasibility and sequencing of the distillation columns easier.

3.5.1 Fridel-Crafts Alkylation(FCA) and Chemistry of Xylene Alkylation

This is a part of the organic chemist's expertise in the ability to build larger molecules by using substitution reactions to attach groups to aromatic rings. Alkyl groups can be attached to benzene to build a more extensive network of carbon atoms using FCA. The reaction that is named for the French chemist, Charles Friedel and his United States co-worker, James Crafts, used aluminium chloride as a catalyst. In other words, FCA is the attachment of alkyl group to an aromatic ring, using a Lewis base acid or catalyst. (Morrison and Boyd, 1992).

$$C_6H_6 + CH_3Cl \xrightarrow{AlCl_3} C_6H_5CH_3 + HCl \qquad (3.64)$$

This reaction takes place quite vigorously when a small amount of the catalyst is added to a mixture of the two liquid reagents. This is important as it produces a new C-C bond and hence can be used to build up a complex molecule (Larner, *et al.*, 1984).

3.5.2 Alkylation through Dual Mechanism

In FCA, the electrophile is typically through carbocation. It is formed in acid-base equilibrium as suggested in the following reactions:

1. $RCl + AlCl_3 \rightleftharpoons AlCl_4^- + R^+$ (3.65)

2. $R^+ + C_6H_6 \rightleftharpoons C_6H_5(R)(H)$ (slow) (3.66)

3. $C_6H_5(R)(H) + AlCl_4^- \rightleftharpoons C_6H_5(R) + HCl + AlCl_3$ (fast) (3.67)

where R is an akyl halide.

In certain cases, there is no free carbocation involved. Instead, the alkyl group is transferred without a pair of electrons directly to the aromatic ring from the polar complex, I, between $AlCl_3$ and the alkyl halide.

$$\underset{(I)}{Cl\text{-}Al\text{-}Cl\text{-}R} + C_6H_6 \rightarrow C_6H_5(R)(H) + AlCl_4^- \rightarrow C_6H_5R + HCl + AlCl_3 \quad (3.68)$$

The electrophile is thus either R^+ or a molecule like I that can readily transfer R^+ into the aromatic ring. These two mechanisms differ as to the nature of the electrophile. The function of the $AlCl_3$ is to generate this carbocation by abstracting the halogen from the alkyl halide. Other Lewis acids can function the same way and thus take the place of $AlCl_3$. The FCA is also accompanied by the kind of rearrangement that is characteristic of carbocation reactions. Alkybenzenes containing rearranged alkyl groups not only are formed but are sometimes the sole products (Morrison and Boyd, 1992). For example,

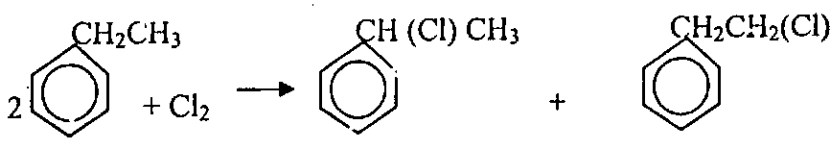
$$C_6H_6 + CH_3CH_2CH_2Cl \rightarrow \underset{(30\text{-}35\%)}{C_6H_5CH_2CH_2CH_3} + \underset{(65\text{-}70\%)}{C_6H_5CH(CH_3)CH_3} \quad (3.69)$$

$$C_6H_6 + CH_2(CH_3)CHCH_2Cl \rightarrow C_6H_5C(CH_3)_3 \quad (3.70)$$

(100%)

3.5.3 Reaction Pathways of the C_8 Compounds.

The xylenes and ethylbenzene are all isomers of C_8 and they undergo electrphylic aromatic substitution (Morrison and Boyd, 1992, Adams, *et al.*, 1996, Harwood and Mordy, 1989).. The electron releasing effect of the electrophile, an alkyl group, activates a benzene ring to which it is attached, and directs to ortho and para positions. Alkyl benzenes clearly offer two sites for attack, the ring and the side chain. The attack to either of these sites could be directed by the choice of reaction conditions. The side chain is alkane-like and undergoes reaction via free-radical substitution. This is promoted by a catalyst at low temperature. This is because the benzyl radical is more stable. For example, bond dissociation energies indicate that 19kcal/mol less energy(104-85)kcal is needed to form the benzyl radical from toluene than to form the methyl radical from methane. The order of ease of abstraction of hydrogen atoms is of the sequence, benzyl $>3^o>2^o>1^o>CH_4$, where 3°, $2^o$and 1° are tertiary, secondary and primary hydrogen atoms respectively. while the ease of formation of free radicals is of the order, benzyl $> 3^o > 2^o > 1^o > CH_3$. Benzylic hydrogen are usually easy to abstract (i.e. easy to form). This also forms the sequence of the relative stability of free radicals. This is why in the reaction,

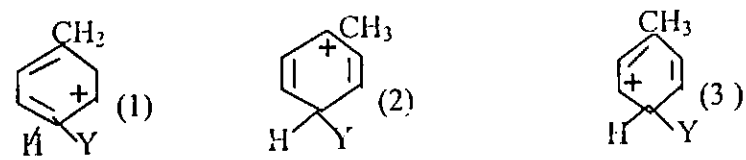


(a) 2° = 91% product (b) 1° =9% product

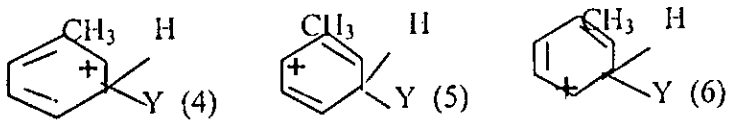
product (a) is preferred. So, the alkylation of ethyl benzene would yield 91% of product (a). The presence of phenyl group in place of H of methyl chloride thus stabilizes the cation by 61 kcal/mol. The stabilization is attributed to the conjugation with the benzene ring and it is the basis of its resonance. The positive charge of the radical is located on the

ortho- and para- carbon atoms. The orbital picture of the benzyl cation is similar to that of the benzyl free radical except that the p orbital that overlaps the π cloud is an empty one. The p orbital contributes no electron but permits further delocalization of the π electrons to include the carbon nucleus of the side chain. Methyl is said to activate the ring because it makes it richer in electrons and react faster than toluene. It causes ortho and para positions or orientation to react faster than at the meta positions. As the positive charge is distributed about the ring, its effect is strongest at the ortho and para position to the carbon atom being attacked (Price, 1984, Hiltegas and Matini., 1985). The second methyl group affects the stability of the carbocations by intensifying or dispersing the positive charge. The methyl group donates more electrons hence tends to neutralise the positive charge of the ring and so become more positive. The dispersal of the charge stabilises the carbocation, hence, leads to faster reaction. This is why tertiary butylbenzene is 16 times as reactive as benzene (Morrison and Boyd, 1992).

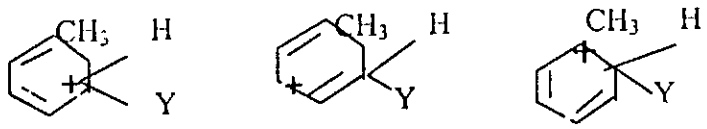
3.5.4 Stability Of Ortho, Meta And Para Positions



Para attack (3.71)



Meta attack (3.72)



Ortho attack (3.73)

(7) (8) (9)

Both ortho, para and meta orientation arise in the same way. The effect of any group whether activating or deactivating is strongest at the ortho and para positions. Strctures 2

and 9 have the most stable carbocations. Thus, the ortho and para substitutions are faster than meta positions because electrons released by activators are more effective during attack at these positions. Each portion of the molecule affects the reactivity of the other portion and determines the orientation of attack.

In this application, we look at the system of the xylene mixture mentioned above.

The separation of OX, MX, PX and EB is made possible using di-tertiary-butyl-benzene (DBB) as a reactive entrainer. It selectively reacts with o-xylene and ethylbenzene using $FeCl_3$ catalyst in the first column. Subsequent alkylation(3.74, 3.76, 33.78) and dealkylation(3.75, 3.77, 3.79) reactions that occur are written below.

$$\underset{\substack{C(CH_3)_3 \\ \text{(DBB)}}}{C_6H_4\text{–}C(CH_3)_3} + \underset{\text{(MX)}}{C_6H_4(CH_3)_2} \rightleftharpoons \underset{\substack{C(CH_3)_3 \\ \text{(TBMX)}}}{C_6H_3(CH_3)_2} + \underset{\text{(TBB)}}{C_6H_5C(CH_3)_3} \qquad (3.74a)$$

$$\underset{\text{(TBB)}}{C_6H_5C(CH_3)_3} + \underset{\text{(MX)}}{C_6H_4(CH_3)_2} \rightleftharpoons \underset{\text{(TBMX)}}{C_6H_3(CH_3)_2} + \underset{\text{(B)}}{C_6H_6} \qquad (3.75)$$

$$\underset{\substack{C(CH_3)_3 \\ \text{(DBB)}}}{C_6H_4\ C(CH_3)_3} + \underset{\text{(OX)}}{C_6H_4(CH_3)_2} \rightleftharpoons \underset{\substack{C(CH_3)_3 \\ \text{(TBOX)}}}{C_6H_3(CH_3)_2} + \underset{\text{(TBB}}{C_6H_5C(CH_3)_3} \qquad (3.76a)$$

$$\underset{\text{(TBB)}}{C_6H_5C(CH_3)_3} + \underset{\text{(OX)}}{C_6H_4(CH_3)_2} \rightleftharpoons \underset{\substack{C(CH_3)_3 \\ \text{(TBOX)}}}{C_6H_3(CH_3)_2} * \underset{\text{(B)}}{C_6H_6} \qquad (3.77)$$

$$\underset{\substack{C(CH_3)_3 \\ \text{(DBB)}}}{C_6H_4\ C(CH_3)_3} + \underset{\text{(EB)}}{C_6H_5C_2H_5} \rightleftharpoons \underset{\substack{C(CH_3)_3 \\ \text{(TBEB)}}}{C_6H_4C_2H_5} * \underset{\text{(TBB)}}{C_6H_5C(CH_3)_3} \qquad (3.78a)$$

$$C_6H_5C(CH_3)_3 + C_6H_5C_2H_5 \rightleftharpoons C_6H_4C_2H_5 + C_6H_6 \qquad (3.79)$$

$$\qquad\qquad\qquad

A_8 = tert-butyl-o-xylene

A_9 = benzene

A_{10} = p-xylene

Then the reactions above become:

$$A_1 + A_2 \rightleftharpoons A_3 + A_4 \quad (100\%)$$

$$A_4 + A_2 \rightleftharpoons A_3 + A_9$$

$$A_1 + A_5 \rightleftharpoons A_6 + A_4 \quad (78\%)$$

$$A_4 + A_5 \rightleftharpoons A_6 + A_9$$

$$A_1 + A_7 \rightleftharpoons A_8 + A_4 \quad (100\%)$$

$$A_4 + A_7 \rightleftharpoons A_8 + A_9$$

Table 3.4: Thermodynamic data of benzene and the alkylated products. (Price, 1984, Morrison, *et al.*,1992)

Component	DBB	TBEB	TBMX	TBB	B	TBOX
Boiling point(°C)	232.8	216	199.5	168.1	78.8	202

PX is component A_{10} and does not appear in the set of reactions because it is the most stable and acts as an inert. It is the most stable of the C_8 compounds. The presence of PX does however, influence the reactive vapour-liquid phase equilibrium. Operating the equilibrium-limited reactions in a distillation column displaces the reaction equilibria as one or more of the products are continuously removed, and this enhances the performance

of the separation process as the reactive entrainer changes the relative volatilities of the compounds. The use of $FeCl_3$ catalyst selectively reacts with EB and OX with DBB in the first reactive column while MX reacts with the entrainer in the third column.. The dealkylation of MX, OX and EB takes place in the fifth, eight and ninth reactive columns respectively.

Using the degrees of freedom for a reactive mixture as stated earlier,

$$F = (c+1) + 2 - \Pi - R \tag{3.80}$$

So for this system, $F = 3$

This is the number of compositions that must be specified in the phase equilibrium calculations. This gives rise to a three-dimensional figure. We then need to find the set of transformed composition variables for this reacting system that have the right dimensionality and have properties similar to those of mole fractions in the non-reacting mixtures. The natural variables required to describe reactive mixtures are the reaction-invariant compositions – the transformed composition variables. The choice of reference components is then made. The reference components are the R components chosen to eliminate the R extents of reaction from the c+1 equations. The number of reacting components, c, is greater than the number of independent reactions, R. The criteria for this choice have been given earlier.

It is always possible to find a set of R reference components in the mixture whose determinant is non-zero. Normally, there will be several feasible sets of reference components for a reaction system. They all lead to equivalent phase diagrams. So, the choice of reference component that satisfies det.v 0 is arbitrary.

For the system under investigation, v^T_{Tot} = (0,0,0,0,0,0), hence, the reference components are A_1 and A_2, A_4, A_5, A_6 and A_9. When the number of components in a reacting system exceeds four, the composition space has dimension greater than three and it becomes difficult to visualize the phase equilibrium diagram in a mole fraction coordinate system. In mole fraction coordinates, this multi-component mixture would be represented in a dimensional composition space greater than three, which cannot be easily visualised. This is a multi-component system and the phase diagram in mole fraction coordinate is complex. However, because of the reaction equilibrium, the phase diagrams are confined to lie on surfaces embedded within the mole fraction coordinate system. This requires the transformation into the new lower-dimensional composition coordinate system that contains all the original information in a similar way. The transformation composition variables are then calculated using equation 3.49. The transformed composition variables are then calculated using the relation below. The derivations of equations (3.81 – 3.84) is given in Appendix I.

$$X_i = \frac{(x_i - v_i^T (v_{ref})^{-1} x_{ref})}{1 - v_{TOT}^T (v_{ref})^{-1} x_{ref}} \qquad i = 7, c+1 \quad (3.45a$$

$$X_3 = x_3 - x_2 + 2x_2 - 2x_5 + 2x_6 + x_9 \qquad (3.81)$$

$$X_7 = x_7 + x_1 - x_2 + 2x_5 - x_6 - x_9 \qquad (3.82)$$

$$X_8 = x_8 - x_1 + x_2 + x_6 - x_9 \qquad (3.83)$$

$$X_{10} = x_{10} \qquad (3.84)$$

$$Y_i = \frac{(y_i - v_i^T (v_{ref})^{-1} y_{ref})}{1 - v_{TOT}^T (v_{ref})^{-1} y_{ref}} \qquad (3.85)$$

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 RESULTS

The results were presented and discussed using two headings namely Independence of Chemical Reactions and reactive distillation system.

4.1.1 Independence of Chemical Reactions

The Brinkley criterion is given by the relationship, s = n - c, where c is the number of elements that are independent in a system consisting of n reactive species participating in s reactions.

The number, c, of independent elements is equal to the rank of the atom-by-species matrix of the elements in the stable compounds and free radicals of the reacting set. If s is the rank of the matrix of stoichiometric coefficients, then the reactions they characterize are deemed to be independent. The last statement is the criterion due to Jouguet. Though the criteria provide the number s of independent reactions, they however do not provide a method for finding unique independent set of reactions in any system of i reactions.

4.1.2 Determination of Independent Reactions of some Hydrocarbon Reactive Systems.

4.1.2.1 n-Butane Pyrolysis

The mechanistic model presented by Powers and Corcoran *(1974)* was used here. It consisted of twenty four steps as shown in Table 4 .1

Table 4.1: Proposed mechanism for the pyrolysis of n-butane.

Reaction No.							
1.	C_4H_{10}			$\rightarrow$	$2C_2H_5^*$		
2.	C_4H_{10}			$\rightarrow$	$C_3H_7^*$	+	CH_3^*
3.	$C_2H_5^*$	+	C_4H_{10}	$\rightarrow$	C_2H_6	+	$C_4H_9^*$
4.	C_2H_5*	+	C_4H_{10}	$\rightarrow$	C_2H_6	+	$1\text{-}C_4H_9^*$
5.	CH_3^*	+	C_4H_{10}	$\rightarrow$	CH_4	+	$C_4H_9^*$
6.	CH_3^*	+	C_4H_{10}	$\rightarrow$	CH_4	+	$1\text{-}C_4H_9^*$
7.	$C_2H_5^*$			$\rightarrow$	C_2H_4	+	H^*
8.	H^*	+	C_4H_{10}	$\rightarrow$	H_2	+	$C_4H_9^*$
9.	H^*	+	C_4H_{10}	$\rightarrow$	H_2	+	$1\text{-}C_4H_9$
10.	$C_3H_7^*$			$\rightarrow$	C_3H_6	+	H^*
11.	$C_3H_7^*$			$\rightarrow$	C_2H_4	+	CH_3^*
12.	$1\text{-}C_4H_9^*$			$\rightarrow$	C_2H_4	+	$C_2H_5^*$
13.	$1\text{-}C_4H_9^*$			$\rightarrow$	H^*	+	$1\text{-}C_4H_8^*$
14.	$C_4H_9^*$			$\rightarrow$	C_3H_6	+	CH_3^*
15.	$C_4H_9^*$			$\rightarrow$	H^*	+	C_4H_8
16.	$2C_2H_5^*$			$\rightarrow$	C_4H_{10}		
17.	$2C_2H_5^*$			$\rightarrow$	C_2H_4	+	C_2H_6
18.	$2CH_{3*}$			$\rightarrow$	C_2H_6		
19.	H^*	+	C_2H_4	$\rightarrow$	$C_2H_5^*$		
20.	$C_2H_5^*$	+	C_2H_4	$\rightarrow$	$1\text{-}C_4H_9^*$		
21.	CH_3^*	+	C_2H_4	$\rightarrow$	$C_3H_7^*$		
22.	CH_3^*	+	C_3H_6	$\rightarrow$	$C_4H_9^*$		
23.	H^*	+	C_3H_6	$\rightarrow$	$C_3H_7^*$		
24.	CH_3^*	+	$C_2H_5^*$	$\rightarrow$	C_3H_8		

There are fifteen chemical species and the rank of the matrix of elements (carbon and hydrogen) is two as shown in Table 4.2.. The notation of identification of the fifteen species is also denoted at the bottom of the table.

Table 4.2 Matrix of elements of the n-butane mechanism species.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
C	4	2	3	0	1	0	4	4	1	2	2	3	3	4	4
H	10	5	7	1	3	2	9	9	4	4	6	6	8	8	8

where:

1 = C_4H_{10}; 2 = $C_2H_5^*$; 3 = $C_3H_7^*$; 4 = H^*; 5 = CH_3^*
6 = H_2; 7 = 1-$C_4H_9^*$; 8 = $C_4H_9^*$; 9 = CH_4; 10 = C_2H_4
11 = C_2H_6; 12 = C_3H_6; 13 = C_3H_8; 14 = 1-C_4H_8; 15 = C_4H_8

In Table 4.3, the stoichiometric coefficients of the reactive species of the mechanism are shown in a matrix. By Brinkley's criterion, S is 13 since N and C are 15 and 2, respectively. The developed algorithm is thus used to determine the matrix of stoichiometric coefficients after reduction to the independent set.

Table 4.3: .Matrix of stoichiometric coefficients of the reactive species of n-butane mechanism before reduction.

Chemical Species

R No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1.	-1	2	0	0	0	0	0	0	0	0	0	0	0	0	0
2.	-1	0	1	0	1	0	0	0	0	0	0	0	0	0	0
3.	-1	-1	0	0	0	0	0	1	0	0	1	0	0	0	0
4.	-1	-1	0	0	0	0	1	0	0	0	1	0	0	0	0
5.	-1	0	0	0	-1	0	0	1	1	0	0	0	0	0	0
6.	-1	0	0	0	-1	0	1	0	1	0	0	0	0	0	0
7.	0	-1	0	1	0	0	0	0	0	1	0	0	0	0	0
8.	-1	0	0	-1	0	1	0	1	0	0	0	0	0	0	0
9.	-1	0	0	-1	0	1	1	0	0	0	0	0	0	0	0
10.	0	0	-1	1	0	0	0	0	0	0	0	1	0	0	0
11.	0	0	-1	0	1	0	0	0	0	1	0	0	0	0	0
12.	0	1	0	0	0	0	-1	0	0	1	0	0	0	0	0
13.	0	0	0	1	0	0	-1	0	0	0	0	0	0	1	0
14.	0	0	0	0	1	0	0	-1	0	0	0	1	0	0	0
15.	0	0	0	1	0	0	0	-1	0	0	0	0	0	0	1
16.	1	-2	0	0	0	0	0	0	0	0	0	0	0	0	0
17.	0	-2	0	0	0	0	0	0	0	1	1	0	0	0	0
18.	0	0	0	0	-2	0	0	0	0	0	1	0	0	0	0
19.	0	1	0	-1	0	0	0	0	0	-1	0	0	0	0	0
20.	0	-1	0	0	0	0	1	0	0	-1	0	0	0	0	0
21.	0	0	1	0	-1	0	0	0	0	-1	0	0	0	0	0
22.	0	0	0	0	-1	0	0	1	0	0	0	-1	0	0	0
23.	0	0	1	-1	0	0	0	0	0	0	0	-1	0	0	0
24.	0	-1	0	0	-1	0	0	0	0	0	0	0	1	0	0

4.1.2.2 Cyclohexane Pyrolysis Reactions.

The pyrolysis of cyclohexane is represented by a molecular mechanism shown in Table 4.4

Table 4.4: Cyclohexane molecular reactions (Aribike *et al.*, 1985)

1.	C_6H_{12}			→	$3C_2H_4$				
2.	C_6H_{12}			→	$2C_3H_6$				
3.	C_6H_{12}			→	C_2H_4	+	C_4H_6	+	H_2
4.	C_2H_4			→	C_2H_2	+	H_2		
5.	C_2H_4	+	H_2	→	C_2H_6				
6.	C_2H_4	+	C_2H_2	→	C_4H_6				
7.	C_2H_4	+	C_2H_6	→	C_3H_6	+	CH_4		
8.	C_3H_6	+	H_2	→	C_2H_4	+	CH_4		
9.	C_3H_6	+	C_2H_6	→	C_4H_8	+	CH_4		
10.	C_3H_6	+	$3H_2$	→	$3CH_4$				
11.	$2C_3H_6$			→	$3C_2H_4$				
12.	C_3H_6			→	C_2H_2	+	CH_4		
13.	H_2	+	$2C_2H_2$	→	C_4H_6				
14.	C_4H_8	+	H_2	→	C_3H_6	+	CH_4		
15.	C_2H_2			→	$2C$	+	H_2		
16.	$2C_2H_6$			→	C_2H_4	+	$2CH_4$		
17.	C_4H_6	+	H_2	→	$2C_2H_4$				
18.	C_2H_4			→	$2C$	+	$2H_2$		

The matrix of stoichiometric coefficients of these reactions are shown in Table 4.5. There are 10 species and 18 reactions. Table 4.6 shows the atom-by species matrix.

Table 4.4:: Matrix of stoichiometric coefficients of cyclohexane reactions before reduction.

Chemical species

Rxn No.	1	2	3	4	5	6	7	8	9	10
1.	-1	3	0	0	0	0	0	0	0	0
2.	-1	0	2	0	0	0	0	0	0	0
3.	-1	1	0	1	1	0	0	0	0	0
4.	0	-1	0	0	1	1	0	0	0	0
5.	0	-1	0	0	-1	0	1	0	0	0
6.	0	-1	0	1	0	-1	0	0	0	0
7.	0	-1	1	0	0	0	-1	1	0	0
8.	0	1	-1	0	-1	0	0	1	0	0
9.	0	0	-1	0	0	0	-1	1	1	0
10.	0	0	-1	0	-3	0	0	3	0	0
11.	0	3	-2	0	0	0	0	0	0	0
12.	0	0	-1	0	0	1	0	1	0	0
13.	0	0	0	1	-1	-2	0	0	0	0
14.	0	0	1	0	-1	0	0	1	-1	0
15.	0	0	0	0	1	-1	0	0	0	2
16.	0	1	0	0	0	0	-2	2	0	0
17.	0	2	0	-1	-1	0	0	0	0	0
18.	0	-1	0	0	2	0	0	0	0	2

Table 4.6 Matrix of the elements of the cyclohexane molecular model species.

	1	2	3	4	5	6	7	8	9	10
C	6	2	3	4	0	2	2	1	4	1
H	12	4	6	6	2	2	6	4	8	0

where the number on top represents:

1	=	C_6H_{12},	2	=	C_2H_4	3	=	C_3H_6
4	=	C_4H_6	5	=	H_2	6	=	C_2H_2
7	=	C_2H_6	8	=	CH_4	9	=	C_4H_8
10	=	C						

The rank of this matrix, C, is 2 and since N is 10, S becomes 8. The algorithm then permits the determination of the matrix of stoichiometric coefficients of the independent set of reactions.

4.1.2.3 n-Heptane Pyrolysis

The number of mechanistic steps in this example is much larger than the two already considered. The relatively larger sequence of steps is shown in Table 4.7.

Table 4.7: Selected reactions of n-heptane pyrolysis (Aribike and Susu, 1988)

Reaction No.							
1.	C_7H_{16}			→	$CH_3^{\bullet}$	+	$1\text{-}C_6H_{13}^{\bullet}$
2.	C_7H_{16}			→	$C_2H_5^{\bullet}$	+	$1\text{-}C_5H_{11}^{\bullet}$
3.	C_7H_{16}			→	$1\text{-}C_3H_7^{\bullet}$	+	$1\text{-}C_4H_9^{\bullet}$
4.	$H^{\bullet}$	+	C_7H_{16}	→	H_2	+	$1\text{-}C_7H_{15}$
5.	$CH_3^{\bullet}$	+	C_7H_{16}	→	CH_4	+	$1\text{-}C_7H_{15}$
6.	$H^{\bullet}$	+	C_4H_{10}	→	H_2	+	$1\text{-}C_4H_9^{\bullet}$
7.	$H^{\bullet}$	+	C_6H_{14}	→	H_2	+	$1\text{-}C_6H_{13}^{\bullet}$
8.	$CH_3^{\bullet}$	+	C_4H_{10}	→	CH_4	+	$1\text{-}C_4H_9^{\bullet}$
9.	$CH_3^{\bullet}$	+	C_6H_{14}	→	CH_4	+	$1\text{-}C_6H_{13}^{\bullet}$
10.	C_2H_4	+	C_4H_{10}	→	C_2H_6	+	$1\text{-}C_4H_9^{\bullet}$
11.	$C_2H_5^{\bullet}$	+	C_6H_{14}	→	C_2H_6	+	$1\text{-}C_6H_{13}^{\bullet}$
12.	C_4H_{10}	+	$1\text{-}C_3H_7^{\bullet}$	→	C_3H_8	+	$1\text{-}C_6H_{13}^{\bullet}$
14.	C_2H_6	+	$1\text{-}C_3H_7^{\bullet}$	→	C_3H_8	+	$C_2H_5^{\bullet}$
15.	$CH_3^{\bullet}$	+	C_3H_8	→	CH_4	+	$1\text{-}C_3H_7^{\bullet}$
16.	$C_2H_5^{\bullet}$	+	H_2	→	C_2H_6	+	$H^{\bullet}$
17.	$H^{\bullet}$	+	C_2H_4	→	$C_2H_5^{\bullet}$		
18.	$H^{\bullet}$	+	C_3H_6	→	$1\text{-}C_3H_7^{\bullet}$		
19.	$H^{\bullet}$	+	$1\text{-}C_4H_9^{\bullet}$	→	$1\text{-}C_4H_9^{\bullet}$		
20.	$CH_3^{\bullet}$	+	C_2H_4	→	$1\text{-}C_3H_7^{\bullet}$		
21.	$CH_3^{\bullet}$	+	C_3H_6	→	$1\text{-}C_4H_9^{\bullet}$		
22.	$C_2H_5^{\bullet}$	+	C_2H_4	→	$1\text{-}C_4H_9^{\bullet}$		
23.	$C_2H_5^{\bullet}$	+	C_3H_6	→	$C_5H_{11}^{\bullet}$		
24.	C_2H_4	+	$1\text{-}C_3H_7^{\bullet}$	→	$1\text{-}C_5H_{11}^{\bullet}$		
25.	$C_2H_5^{\bullet}$	+	$1\text{-}C_5H_{10}$	→	$C_7H_{15}^{\bullet}$		
26.	C_3H_6	+	$1\text{-}C_3H_7^{\bullet}$	→	$C_6H_{13}^{\bullet}$		
27.	$H^{\bullet}$	+	$1\text{-}C_5H_{10}$	→	$1\text{-}C_5H_{11}^{\bullet}$		
28.	$1\text{-}C_5H_{11}^{\bullet}$			→	$C_5H_{11}^{\bullet}$		
29.	$1\text{-}C_6H_{13}^{\bullet}$			→	$C_6H_{13}^{\bullet}$		
30.	$1\text{-}C_6H_{13}^{\bullet}$			→	$C_6H_{13}^{\bullet}$		
31.	$1\text{-}C_7H_{15}^{\bullet}$			→	$C_7H_{15}^{\bullet}$		
32.	$1\text{-}C_7H_{15}^{\bullet}$			→	$C_7H_{15}^{\bullet}$		

33.	$C_7H_{15}^{\bullet}$		→	$-C_7H_{15}^{\bullet}$		
34.	$C_6H_{13}^{\bullet}$		→	$1-C_6H_{13}^{\bullet}$		
35.	$C_2H_5^{\bullet}$		→	$H^{\bullet}$	+	C_2H_4
36.	$1-C_3H_7^{\bullet}$		→	$H^{\bullet}$	+	C_3H_6
37.	$1-C_3H_7^{\bullet}$		→	$CH_3^{\bullet}$	+	C_2H_4
38.	$1-C_4H_9^{\bullet}$		→	$H^{\bullet}$	+	$1-C_4H_8$
39.	$1-C_4H_9^{\bullet}$		→	$C_2H_5^{\bullet}$	+	C_2H_4
40.	$1-C_4H_9^{\bullet}$		→	C_3H_6	+	$CH_3^{\bullet}$
41.	$1-C_5H_{11}^{\bullet}$		→	C_2H_4	+	$1-C_3H_7^{\bullet}$
42.	$1-C_6H_{13}^{\bullet}$		→	C_2H_4	+	$1-C_4H_9^{\bullet}$
43.	$C_5H_{11}^{\bullet}$		→	$C_2H_5^{\bullet}$	+	C_3H_6
44.	$C_6H_{13}^{\bullet}$		→	C_3H_6	+	$1-C_3H_7^{\bullet}$
45.	$C_6H_{13}^{\bullet}$		→	$C_2H_5^{\bullet}$	+	$1-C_4H_8$
46.	$C_6H_{13}^{\bullet}$		→	$CH_3^{\bullet}$	+	$1-C_5H_{10}$
47.	$1-C_7H_{15}^{\bullet}$		→	C_2H_4	+	$1-C_5H_{11}^{\bullet}$
48.	$C_7H_{15}^{\bullet}$		→	C_3H_6	+	$1-C_6H_{12}$
49.	$C_7H_{15}^{\bullet}$		→	$1-C_3H_7^{\bullet}$	+	$1-C_4H_8$
50.	$C_7H_{15}^{\bullet}$		→	$C_2H_5^{\bullet}$	+	$1-C_5H_{10}$
51.	$C_7H_{15}^{\bullet}$		→	$CH_3^{\bullet}$	+	$1-C_6H_{12}$
52.	$1-C_4H_9^{\bullet}$		→	$CH_3^{\bullet}$	+	C_3H_6
53.	$H^{\bullet}$ +	$H^{\bullet}$	→	H_2		
54.	$CH_3^{\bullet}$ +	$CH_3^{\bullet}$	→	C_2H_6		
55.	$CH_3^{\bullet}$ +	$C_2H_5^{\bullet}$	→	C_3H_8		
56.	$C_2H_5^{\bullet}$ +	$C_2H_5^{\bullet}$	→	C_4H_{10}		
57.	$1-C_3H_7^{\bullet}$ +	$1-C_3H_7^{\bullet}$	→	C_6H_{14}		
58.	$CH_3^{\bullet}$ +	$C_2H_5^{\bullet}$	→	CH_4	+	C_2H_4
59.	$C_2H_5^{\bullet}$ +	$C_2H_5^{\bullet}$	→	C_2H_6	+	C_2H_4
60.	C_4H_{10}		→	$CH_3^{\bullet}$	+	$1-C_3H_7^{\bullet}$

These are selected reactions from the sequence of steps developed by Aribike, *et al,* 1988 for the pyrolysis of n-Heptane. The selection of this set was based on the initiation of free radicals, the reasonableness of the activation energy and the order of reactions. There are twenty seven species in the sixty reactions. The matrix of stoichiometric Coefficients of these reactions is available in Evwierhoma, *et al*, 2004 and was obtained in the manner specified above for cyclohexane and n-butane.

The matrix of stoichiometric coefficients of the independent reactions obtained by use of the algorithm is shown in Table 4.8

Table 4.8: Matrix of the elements of the n-heptane.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
C	7	1	1	2	2	2	0	0	3	3	3	4	4	4	4	5	5	5	6	6	6
H	16	3	4	4	5	6	2	1	7	8	6	9	10	9	8	10	11	11	12	13	15

	22	23	24	25	26	27
C	6	6	7	7	7	7
H	13	14	15	15	15	15

Where:

1	=	C_7H_{16}	2	=	CH_3	3	=	CH_4
4	=	C_2H_4	5	=	C_2H_5	6	=	C_2H_6
7	=	H	8	=	H	9	=	1-C_3H_7
10	=	C_3H_8	11	=	C_3H_6	12	=	1-C_4H_9
13	=	C_4H_{10}	14	=	C_4H_9 1	5	=	1-C_4H_8
16	=	1-C_5H_{10}	17	=	1-C_5H_{11}	18	=	2-C_5H_{11}
19	=	1-C_6H_{12}	20	=	1-C_6H_{13}	21	=	C_6H_{13}
22	=	C_6H_{13}	23	=	C_6H_{14}	24	=	1-C_7H_{15}
25	=	C_7H_{15}	26	=	-C_7H_{15}	27	=	C_7H_{15}

In the reactive schemes used as examples in this work, fifteen independent reactions were obtained for the n-butane mechanistic model and ten for the cyclohexane molecular model These are shown in Tables 4.9, 4.10 and and 4.11

Table 4.9: Matrix of stoichiometric coefficients of the reactive species of n-butane mechanism after reduction.

Chemical Species

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	1.0	2.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2		1.0	0.5	0.0	0.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3			1.0	0.0	1.0	0.0	0.0	0.7	0.0	0.0	0.7	0.0	0.0	0.0	0.0
7				1.0	0.0	0.0	0.0	0.3	0.0	1.0	0.3	0.0	0.0	0.0	0.0
5					1.0	0.0	0.0	0.3	1.0	0.0	0.7	0.0	0.0	0.0	0.0
8						1.0	0.0	0.0	1.0	1.0	0.0	0.7	0.0	0.0	0.0
4							1.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
10								1.0	3.3	3.3	3.3	3.3	0.0	0.0	0.0
12									1.0	1.0	1.0	1.0	0.0	0.0	0.0
11										1.0	0.0	0.7	0.0	0.0	0.0
6											1.0	0.0	0.0	0.0	0.0
14												1.0	0.0	0.0	0.0
24													1.0	0.0	0.0
13														1.0	0.0
15															1.0

The following rows appear in the order: 9, 16-23 and they are all zeros.

Table 4.10:Matrix of stoichiometric coefficients of cyclohexane reactions after reduction

	1	2	3	4	5	6	7	8	9	10
1	1.0	-3.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2		1.0	-0.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3			1.0	-0.8	-0.8	0.0	0.0	0.0	0.0	0.0
4				1.0	-1.0	-2.0	0.0	0.0	0.0	0.0
5					1.0	0.5	0.0	0.0	0.0	0.0
7						1.0	-3.0	4.0	0.0	0.0
8							1.0	-1.6	0.0	0.0
9								1.0	-0.4	0.0
10									1.0	0.0
15										1.0

There are 18 rows and rows 11 - 18 contain zeros.

The independent reaction sets were, 1-8,10-15 and 24 for n-butane; 1,2,3,4,5,7,8,9,10 and 15 for cyclohexane. The other reactions were found to be redundant. Considering Brinkley and Jouguet's criteria, thirteen, eight and twenty five independent reactions would be enough to represent the respective reactive schemes.

Table 4.11: Matrix of stoichiometric coefficients of the n-heptane reactions after reduction.

Chemical species

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26
1	1.0	-1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-1.0	0.0	0.0	0.0	0.0	0.0	0.0
2		1.0	0.0	0.0	-1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-1.0	0.0	0.0	0.0	0.0	0.0	0.0
17			1.0	-1.0	0.0	0.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3				1.0	0.0	0.0	0.0	-1.0	0.0	0.0	-1.0	0.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
10					1.0	0.0	0.0	-1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
7						1.0	-1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.0	0.0	0.0	-1.0	0.0	0.0	0.0	0.0
18							1.0	-1.0	0.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
9								1.0	0.0	0.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.0	0.0	-1.0	-1.0	0.0	0.0	0.0
12									1.0	0.0	1.0	-1.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0	1.0	0.0	-1.0	-1.0	0.0	0.0	0.0
19										1.0	2.0	0.0	0.0	-1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-1.0	-1.0	0.0	0.0	0.0
6											1.0	-1.0	0.0	0.0	0.0	0.0	0.0	0.0	-1.0	0.0	0.0	1.0	0.0	0.0	0.0	0.0
13												1.0	-1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	-1.0	0.0	0.0	0.0	0.0
20													1.0	-1.0	0.0	0.0	0.0	0.0	1.0	1.0	0.0	-1.0	-1.0	0.0	0.0	0.0
21														1.0	0.0	-1.0	0.0	0.0	-1.0	-1.0	0.0	1.0	1.0	0.0	0.0	0.0
25															1.0	-1.0	0.0	0.0	0.0	-1.0	0.0	1.0	1.0	0.0	0.0	-1.0
22																1.0	0.0	0.0	-0.3	0.3	0.0	-0.3	-0.3	0.0	0.0	0.0
23																	1.0	0.0	-0.3	0.3	0.0	-0.3	-0.3	0.0	0.0	0.0
48																		1.0	0.7	0.3	0.0	-0.3	-0.3	-1.0	0.0	0.0
15																			1.0	1.0	0.0	-2.0	0.0	0.0	0.0	0.0
4																				1.0	0.0	-1.0	0.0	0.0	0.0	0.0
30																					1.0	-1.0	0.0	0.0	0.0	0.0
24																						1.0	1.0	0.0	0.0	0.0
26																							1.0	0.0	0.0	0.0
33																								1.0	-1.0	0.0
31																									1.0	0.0
27																										1.0

There are several other rows in the following order: 8,14, 16, 28, 29, 32, 34, 57 - 60. They all contain zeros.

This work introduces a good method for the synthesis of mechanisms. The algorithm presented in this research work reduces the volume of mathematical computations significantly especially when it is compared with the determinant rank method of non-

varnishing matrix. Except for systems of only two or three reactions, the determinant method is too inefficient. There are about $\frac{n^3}{2}$ multiplications required to diagonalize a system of n reactions (equations) using the method in Billaud et al., 1991 while only $n^2 n!$ multiplications are required to find the rank using the determinant method (Cramer's rule),(Amundson, 1966). The evaluation of a determinant can perhaps best be done by adopting the technique used in this work. Its utility derives from the fact that the determinant of a triangular matrix (upper or lower) is just the product of its diagonal matrix. In the pyrolysis of hydrocarbons generally, reactions are complex and the number of elementary reactions describing the overall system increases with increase in the molecular weight of hydrocarbons.

The mathematical description of these reactions also becomes complex such that the use of computers becomes inevitable. Application of this algorithm would entail very easy successive elimination of the redundant reactions. The approach maintains and enforces requirements of the directionality of steps during all the reductions and since two equations may be combined to eliminate one of them, the choice of a redundant reaction is a sole task of the researcher. The number of independent reactions (rank) in each system is fundamental although not unique since the elements of the set may be chosen arbitrarily. In all cases the rank of the sets generated are finite and equal. The elementary row operations used here provides a systematic scheme for relating the stoichiometries of various species to the stoichiometries of a minimum number of key reactions. This is possible because the system of linear equations represented by the matrix at each step of the reduction process has the same solution as the original system of equations

Finally, the method presented is general in scope and should facilitate the determination, of independent reactions in any proposed reaction mechanism. Obviously, it would assist in the construction of reaction mechanisms for any kinetic system.

4.2 Reactive Distillation System.

We described and derived the equations for a procedure to determine the feasibility of separating mixtures with multiple equilibrium chemical reactions by reactive distillation. The method involves describing the system in terms of new composition coordinates. In these transformed compositions, the equation for the overall material balance around a reactive distillation column was expressed in form of a lever rule (equations 3.41 -3.43).

$$\frac{\hat{D}}{\hat{F}} = \frac{X_{i,F} - X_{i,B}}{X_{i,D} - X_{i,B}} \tag{3.50}$$

$$\frac{\hat{B}}{\hat{F}} = \frac{X_{i,D} - X_{i,F}}{X_{i,D} - X_{i,B}} \tag{3.51}$$

$$\frac{\hat{B}}{\hat{D}} = \frac{X_{i,D} - X_{i,F}}{X_{i,F} - X_{i,B}} \tag{3.52}$$

These expressions have the same functional form as the lever rule for non reactive mixtures in terms of mole fractions. An implication of this is that in an equilibrium reactive distillation column, the overall material balance will be satisfied if the feed, distillate and bottom compositions, in transformed composition coordinates, all lie on a straight line. These system of linear equations is represented by a straight line on which the feed, F, the top product, D and the bottom product, B have to lie. The concentration

$X_{i,D}$ of the top fraction and $X_{i,B}$ of the bottom fraction are end points of the concentration profile developed within the column.

The transformed variables

$$X_i = \frac{(x_i - \nu_i^T(\nu_{ref})^{-1}x_{ref})}{1-\nu_{TOT}^T(\nu_{ref})^{-1}x_{ref}} \qquad (3.45a)$$

express the conservation of mass at each value of the extent of reaction, and since they describe the composition of the system as if no reaction was occurring, the transformed variables can be thought of as reaction-invariant compositions. Equation (3.40), $\sum_{i=1}^{C-R-1} X_i = 1$, clearly shows that the transformed variables are not independent and reduces the number of independent compositions that must be set by the Gibbs phase rule. This reduction in the number of variables to be used for constructing the composition space (the phase diagram) is an important advantage. This gives a two and three dimensional figures of the separation of meta and paraxylenes mixture(Figures 4.2 and 4.4)

4.2.1 Separation of a Mixture of Meta- and Para-xylenes

For a better understanding of this reacting system, the first case was where para - xylene was absent. This will give useful information for the more interesting case where para-xylene is present as an inert.

4.2.1.1 Reactive System Without P-xylene Present

Since there is no para-xylene, the degrees of freedom is equal to two because c = 5 and the solution space in transformed composition variables is in two dimensions. X_3 and X_5 were chosen as the independent variables from the five components in the mixture while x_1 and

x_2 were chosen as the reference components using the criteria given earlier. The three transformed composition variables are X_3, X_4 and X_5

$$X_3 = x_3 + x_2 \tag{3.50}$$

$$X_4 = x_4 + 2x_1 - x_2 \tag{3.51}$$

$$X_5 = x_5 - x_1 + x_2 \tag{3.52}$$

Since these three transformed variables sum up to unity, only two are independent. The choice is arbitrary as any set of two from among the three can be chosen. The mapping of the pure components into transformed composition coordinates gives the shape of the solution space. In mole fraction coordinates, the five-component mixture would be represented in a four-dimensional composition space, which cannot be easily visualised. The representation of the system in transformed composition variables has the great advantage of reducing the dimensionality from four to two. In the chosen set, X_3 and X_5, the transformed composition space is confined within a trapezoid (Appendix Ib. The pure components, A_1, A_2, A_3, and A_5 are found to be the vertices (corners) of the solution space, Figure 5.

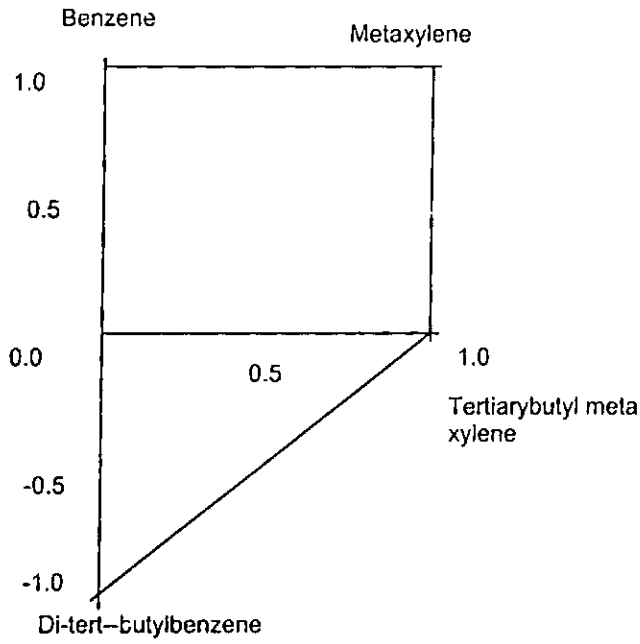


Figure 4.1: The solution space of the reactiove mixture of meta and paraxylene system.

Component A_4 cannot exist as a pure component in the reactive mixture because of the dissociation reaction obtained by the sum and difference of the original two equations.

$$2A_4 \rightleftharpoons A_1 + A_5 \text{ (decomposition of } A_4) \tag{3.55}$$

$$2A_3 + A_5 \rightleftharpoons A_1 + 2A_2 \text{ (no } A_4) \tag{3.56}$$

This second set of equations reveals more of the characteristic features of the system. The mapping of component A_4 from mole fraction space into transformed composition space shows this point to be halfway between the vertices of the pure components A_1 and A_5. This constitutes a reactive edge ($A_1 - A_4 - A_5$) because of the hidden dissociation reaction. There are then three non-reactive edges, ($A_2 - A_3$, $A_1 - A_3$, $A_2 - A_5$, and the reactive edge. The degrees of freedom are equal to two, so we need to specify two

equilibrium mole fractions and calculate the other mole fractions and the equilibrium temperature. The mixture is assumed to obey Raoult's law

$$Py_i = P_i^{sat}x_i \tag{3.57}$$

The plot of the phase diagram was done in transformed composition variables because they reduced the dimensional space. The vertices of the composition space for reacting systems usually consist of all the pure components that are inert species and reacting species that do not dissociate under any non-singular linear combination of the stoichiometries. Clearly, such species are boiled off (as pure components) without any other species being generated. For the purpose of distillation, an easy separation is to take the lightest (low boiler) component as a distillate and obtained a bottom product that is aligned with the feed and the distillate to obey the lever rule. One can also take the heaviest component as a bottom and align the feed and bottoms compositions to obtain a

binary non-reactive mixture. This is n.

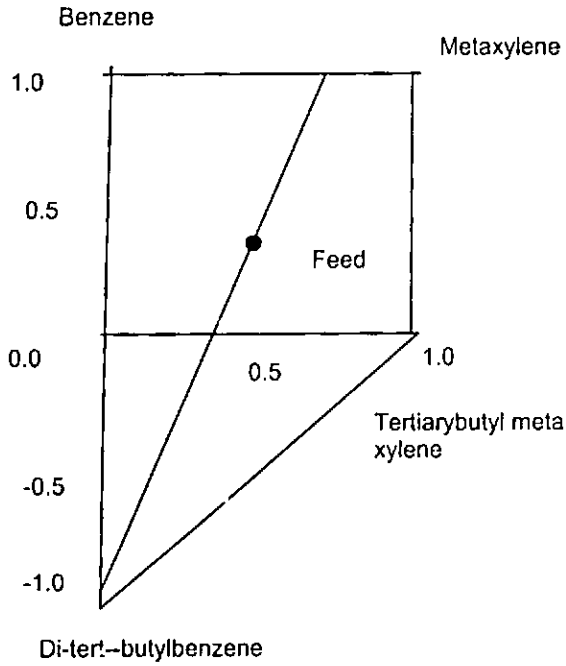


Figure 4.2: Indirect split for the reactive metaxylene system showing the feed,F, bottom,B and a mixture of benzene and metaxylene as distillate, D on a straight line

4.2.1.2 Reactive System With P-xylene Present.

Now that p-xylene is present in the system, the degrees of freedom, F, is equal to three and the solution space in transformed composition is a three-dimensional object shown in Figure 4.3. The base is the same trapezoid shown in Figure 5. The three independent transformed composition variables are X_3 , X_5 , X_6 Pure p-xylene is a vertex that sits above the trapezoid. All the edges linked to p-xylene are non-reactive binary edges. The goal of this separation sequence is to separate m– and p–xylene mixture using di-tert-butylbenzene (DBB) as a reactive entrainer. Originally, we had the binary mixture of meta and para-xylene to separate. As soon as we add DBB, all the other components are instantly created

by reaction and the feed is a reactive mixture represented by a point located somewhere inside the three-dimensional object defining the solution space. Benzene is the lightest component while DBB is the heaviest. Two obvious separations are possible.

1. Take benzene as the distillate and a bottom aligned with the feed and the distillate.
2. Take DBB as the bottom and a distillate aligned with the feed and the bottom.

This again is to satisfy the lever rule. Obtaining pure p-xylene determines the first step in the sequencing of this separation while the recovering of m-xylene from TBMX forms the second step. The easiest separation is to take benzene as the distillate and to

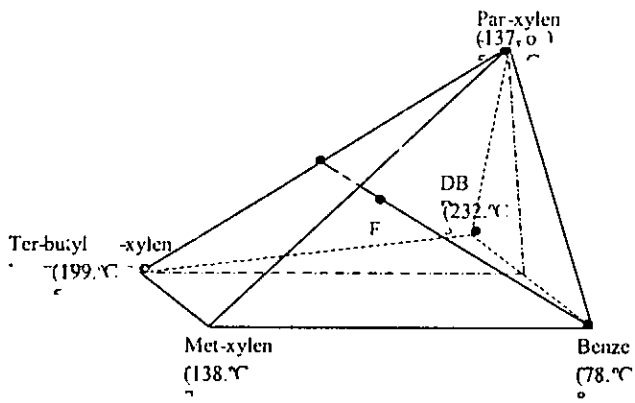


Figure 4.3: Separation feasibility: Step 1 benzene as distillate from fist distillation column.

locate the feed in such alignment that the bottom composition would land on the binary non-reactive edge of TBMX and p-xylene. This binary non-reactive mixture could then easily be separated in a second non-reactive distillation column to obtain p-xylene as distillate. This is shown in Figure 8.

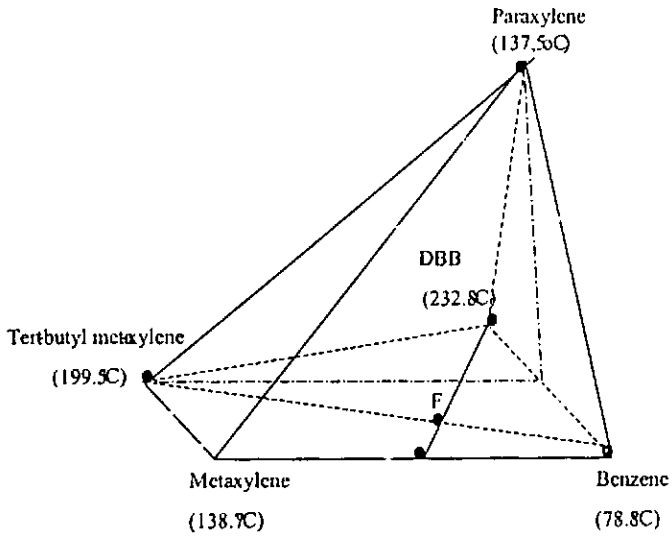


Figure 4.4: Meta-xylene recovery from tert-butyl meta-xylene using benzene distillate from the first distillation column.

Since p-xylene has been eliminated from the system, we are left with a reactive mixture of m-xylene without p-xylene and we fall back to the first case of the trapezoid solution space discussed earlier(Figure 6). It is possible to obtain m-xylene by reacting the TBMX from the second column with the benzene obtained from the first column as distillate (equation 3.13). This creates a reactive feed located in the trapezoid. The bottoms (DBB) could be recycled while the distillate from this reactive column is a non reactive mixture of m-xylene and benzene which could be separated in another column to get pure m-xylene as bottoms and Benzene as the distillate finally. The combined steps which constitute the process of separation is shown in Figure 9.

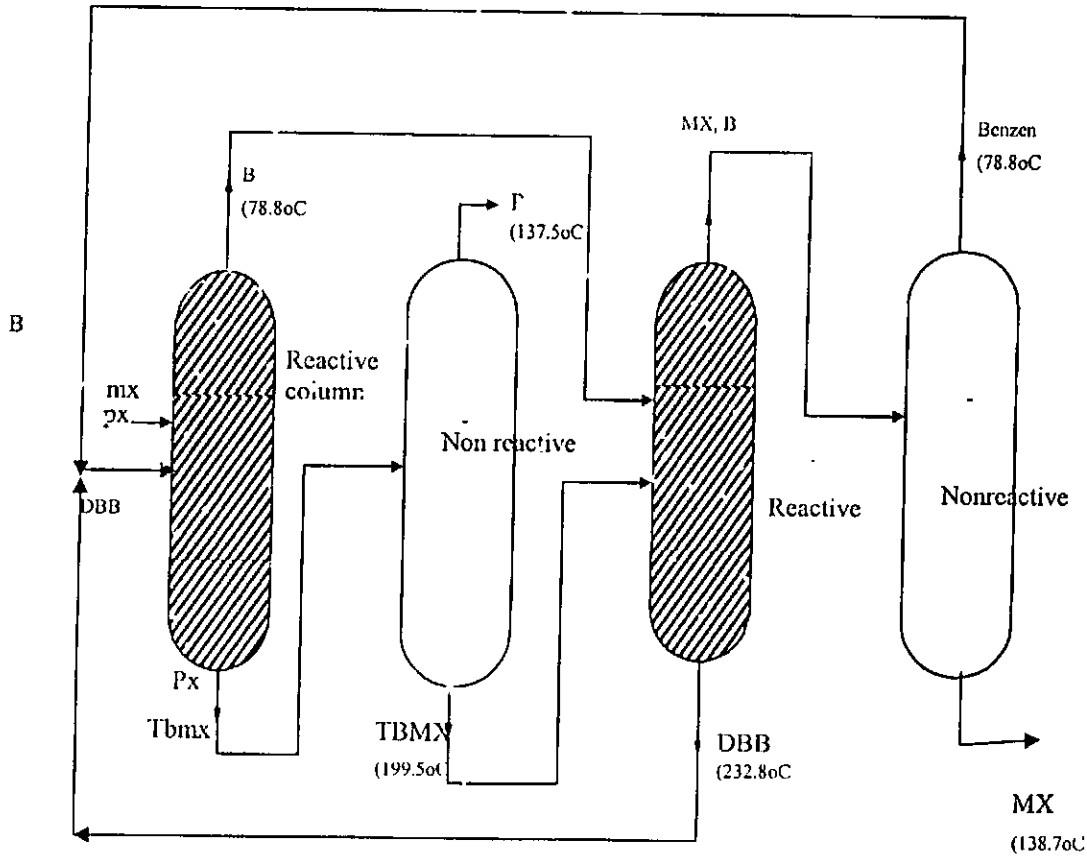


Figure 4.5: The flow sheet for the separation of meta and paraxylene mixture

The summary of this application is that meta and para-xylenes have close boiling points such that the separation of their mixture is uneconomical due to the high cost of investment.. However, by using reactive distillation process, the separation of the mixture is feasible. The combination of reactive and non-reactive distillation columns for the separation was made easy in the transformed composition co-ordinates. The phase diagram would not have been easily visualized in mole fraction coordinates, because the five-component mixture would be represented in a four-dimensional composition space. It

is now clear and possible to combine the components in the reactive mixture for a desired separation. These transformed composition variables reduced the dimensionality of the system from four to two and from five to three for the two steps used in the separation. Therefore using transformed composition variables, we could successfully represent the phase diagram for this five-component mixture with two chemical reactions in three dimensions The plots of the curve maps in transformed composition variables provide information on the feasibility and column sequencing of a desired separation (Figures 10-16).

4.2.2 Separation of a Mixture of Ortho-, Meta-, Para-xylenes and Ethyl benzene

The separation of OX, MX, PX and EB mixture is made possible using DBB as the reactive entrainer which selectively reacts with OX and EB with the aid of the highly selective catalyst $FeCl_3$ in the first column. Again, using the transformed composition variable gives the relationships expressed in equations 3.72 – 3.75.

The same procedure as in the application to a two-component system, was used for a better understanding of this more complex reacting system. The first case was where para - xylene was assumed absent. This gave useful information for the more interesting case where para- xylene was present as an inert.

4.2.2.1 Reactive System Without P-xylene Present ($X_{10} = 0$)

Since there is no para-xylene, the degrees of freedom, F, equals two as c = 9 and the solution space in transformed composition variables is two-dimensional. X_3 and X_7 were chosen as the independent variables from the nine components in the mixture while

x_1, x_2 ,x_4 ,x_5, x_6 and x_9 were chosen as the reference components using the criteria given earlier. The three transformed composition variables are X_3, X_7 and X_8. Since these three transformed variables sum up to unity, only two are independent. The choice is arbitrary as any set of two from amongst the three can be chosen. The mapping of the pure components into transformed composition co-ordinate is shown in Figure 4.10. The representation of the system in transformed composition variables has the great advantage of reducing the dimensionality from eight to two. The calculation is also made in Appendix A. The pure components, A_1, A_3, A_4, A_5 ,A_7 and A_9 , are found to be the vertices (corners) of the solution space shown in Figure 4.10.

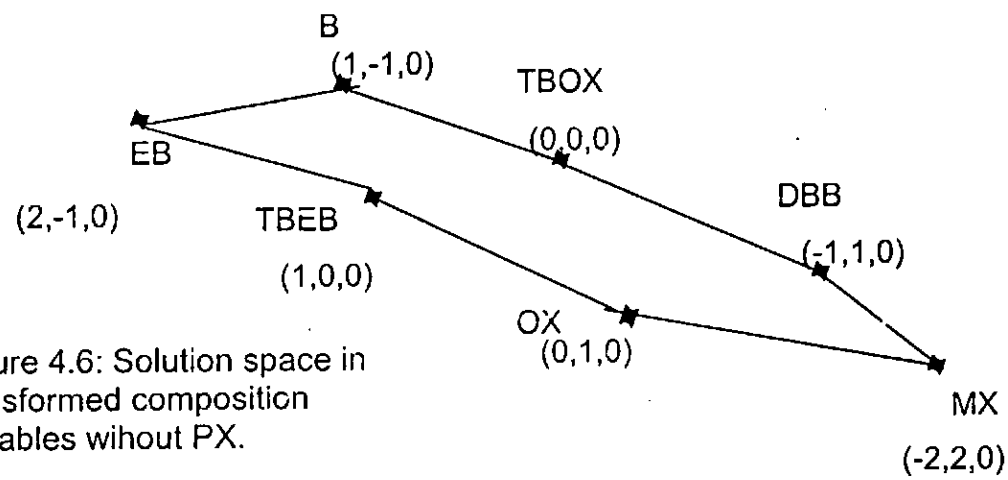


Figure 4.6: Solution space in transformed composition variables wihout PX.

Component TBB cannot exist as a pure component in the reactive mixture because of the dissociation reaction obtained by the sum and difference of the alkylation/dealkylation reactions equations. For example,

$$2TBB \leftrightarrow DBB + B \text{ (decomposition of TBB)} \tag{3.77}$$

$$2TBEB + B \leftrightarrow DBB + 2EB \text{ (no TBB)} \tag{3.78}$$

. The degrees of freedom are equal to two, so we need to specify two equilibrium mole fractions and calculate the other mole fractions and the equilibrium temperature.

The plot of the phase diagram was done in transformed composition variables as they reduced the dimensional space.. The vertices of the composition space for reacting systems usually consist of all the pure components (inert species and reacting species) that do not dissociate under any non-singular linear combination of the stoichiometric coefficients. Clearly, such species can be boiled off, as pure components, without any other species being generated (King, 1980).

For the purpose of distillation, an easy separation is to take the lightest (low boiler) component as a distillate and obtain a bottom product that is aligned with the feed and the distillate to obey the lever rule. One can also take the heaviest component as a bottom and align the feed and bottoms compositions to obtain a binary non-reactive mixture as stated earlier.

4.2.2.2 Reactive System With P-xylene Present.

Now that p-xylene is present in the system, the degrees of freedom, F, is equal to three and the solution space in transformed composition is a three-dimensional object shown in Figure 4.7. The base of this figure is the same solution space of Figure 4.6. The three independent transformed composition variables are X_3, X_7 , X_8.. Pure p-xylene is a vertex that sits above the figure. All the edges linked to p-xylene are non-reactive binary edges.

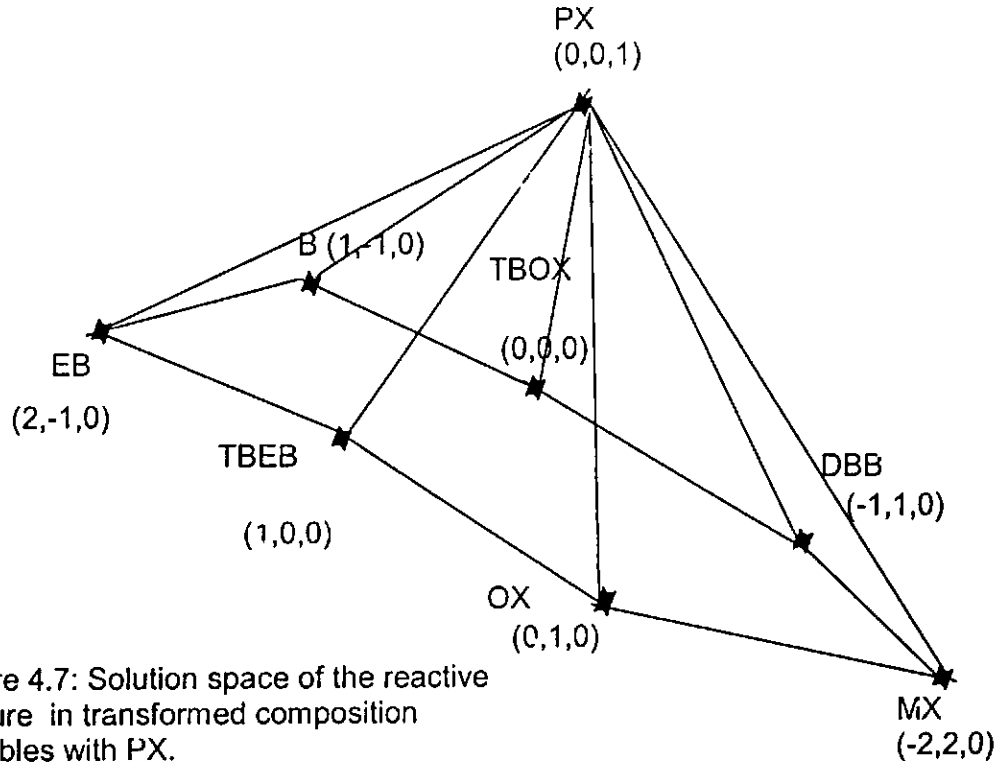


Figure 4.7: Solution space of the reactive mixture in transformed composition variables with PX.

The goal of this separation sequence is to separate meta.- , ortho-, p–xylenes and ethylbenzene mixture using di-tert-butyl benzene (DBB) as a reactive entrainer. Originally, we had a mixture of m–, o- , p–xylenes and ethylbenzene to separate. When DBB was added , all the other components were instantly created by reaction and the feed is a reactive mixture represented by a point located somewhere inside the three-dimensional diagram defining the solution space. Benzene is the lightest component while DBB is the heaviest. Two obvious separations are possible. Benzene can be taken as the distillate and a bottom aligned with the feed and the distillate or we can take DBB as the bottom and a distillate aligned with the feed and the bottom. The nodes of the solution space are the bottoms and distillate products. Here we focus attention on pure component products. The interior of the solution space represents a reactive mixture of all the components at equilibrium. Inside the solution space, reaction is occurring. The transformed composition expression has the same

functional form as the lever rule for non-reactive mixtures in terms of mole fractions. Julka and Doherty, 1985) have shown that in an equilibrium reactive distillation column, the overall balance will be satisfied if the feed, distillate and bottom compositions in transformed composition coordinate, all lie on a straight line.

Obtaining the alkylated products and pure p-xylene determines the first step in the sequencing of this separation, while the recovering of ethylbenzene from TBEB, m-xylene from TBMX and o-xylene from TBOX form the second step. The easiest separation is to take benzene as the distillate and to locate the feed in such alignment that the bottom composition would land on the binary edges of TBOX and TBEB as well as that of MX and PX. This is shown in Figure 4.8.

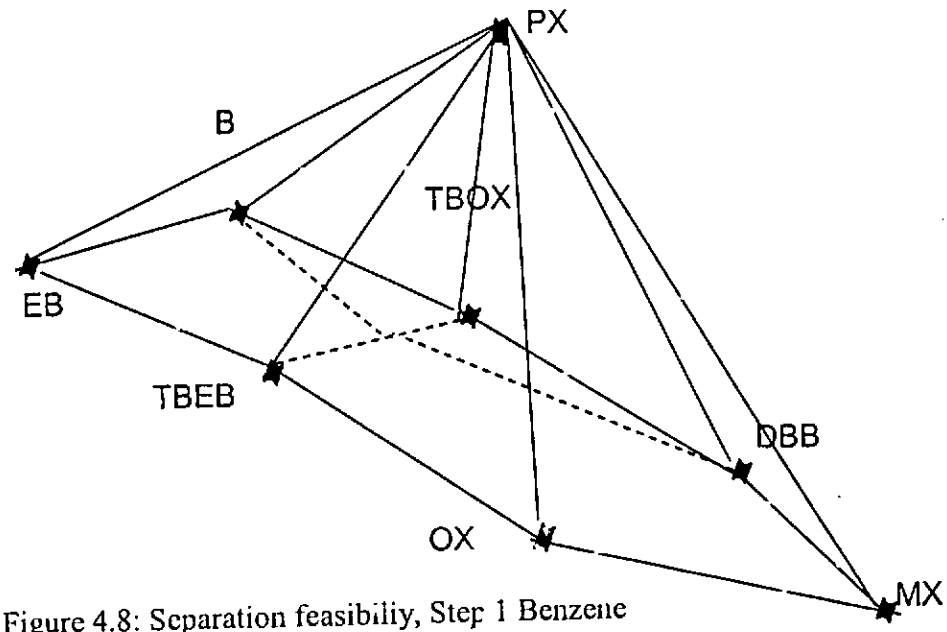


Figure 4.8: Separation feasibiliy, Step 1 Benzene as distillate from first column and a mixture of MX, PX, TBOX and TBEB as bottoms.

The non-reactive mixture was easily separated in a distillation column to obtain MX and PX as distillate and TBOX and TBEB as bottoms. The alkylated products TBOX and TBEB, were separated in the non-reactive column 7 before dealkylating them in the

reactive distillation columns 8 and 9 respectively. In Figure 4.9, it can be seen that DBB could be obtained as bottom while OX and B as distillates. The DBB, produced is recycled to the first column for more reaction with the fresh feeds. The mixture of OX and

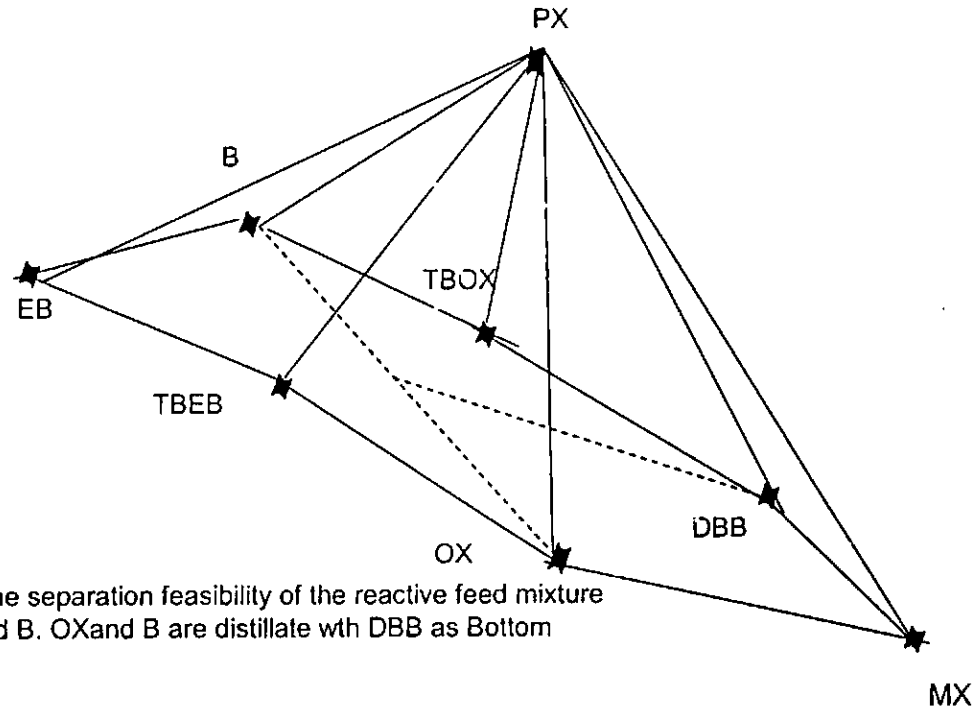


Figure 4.9 he separation feasibility of the reactive feed mixture of TBOX and B. OXand B are distillate wth DBB as Bottom

B are separated in a non-reactive column

This is feasible as a result of the large difference in the boiling points of OX and B. In like manner, TBEB was dealkylated to give EB and B as distillate and DBB as bottoms. This feasibility is shown in Figure 4.10.

The alkylation reaction of MX produces TBMX in column 3.This mixture of TBMX and PX is then separated in a non-reactive reactor to obtain PX as distillate. The feasibility of this separation is shown in Figure 4.11

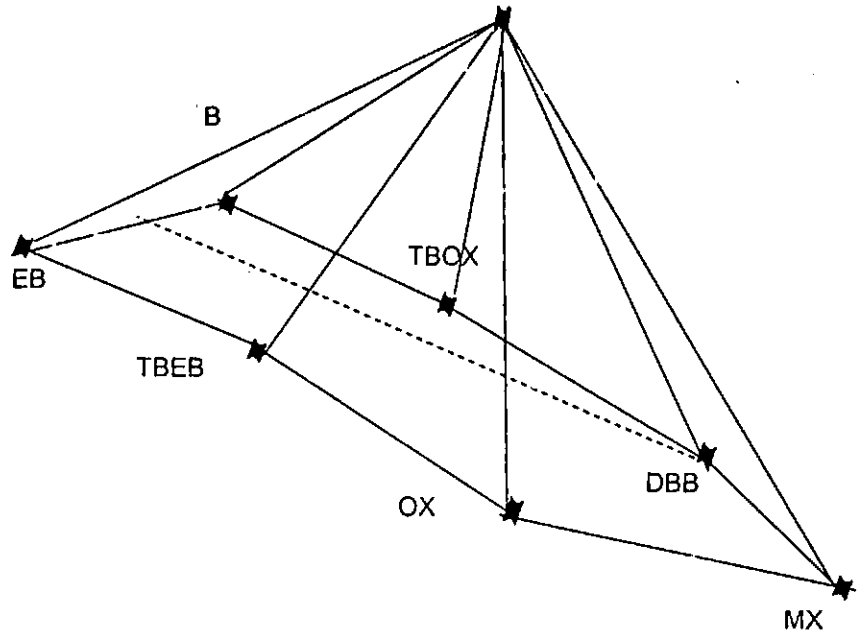


Figure 4.10 : The reactive dealkylation of TBEB.. EB and B are distillates while DBB is the bottom product.

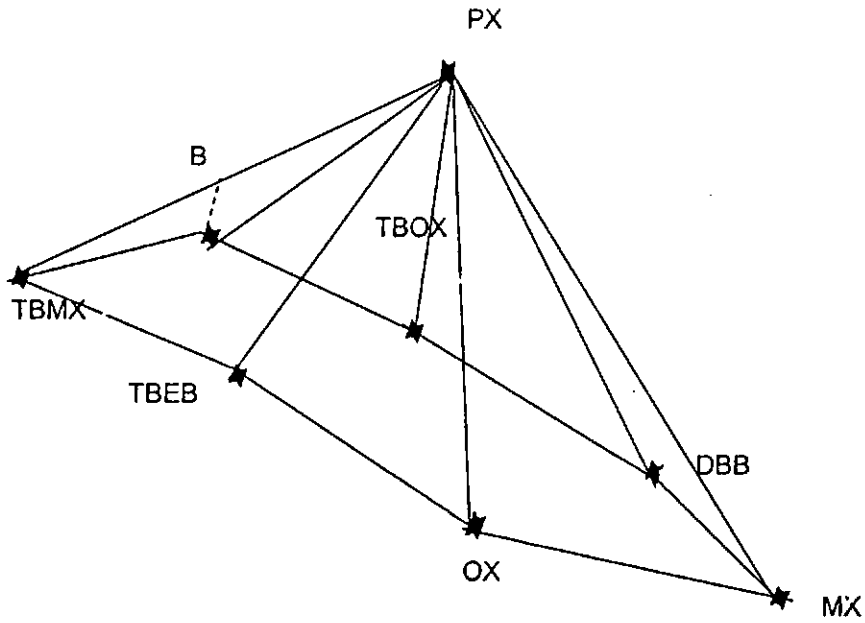


Figure 4.11 Separation feasibility of B as distillate and PX and TBMX as bottoms(RC column 3)

. It is possible to obtain MX by de-alkynating the TBMX from the fourth column with the benzene obtained from the first third columns as distillate (refer to equation (3.45a)). This creates a reactive feed located in the solution space. The bottoms (DBB) is recycled while the distillate from this reactive column is a non reactive mixture of m-xylene and benzene which is separated in a non-reactive column to finally get pure m-xylene as bottoms and benzene as the distillate.

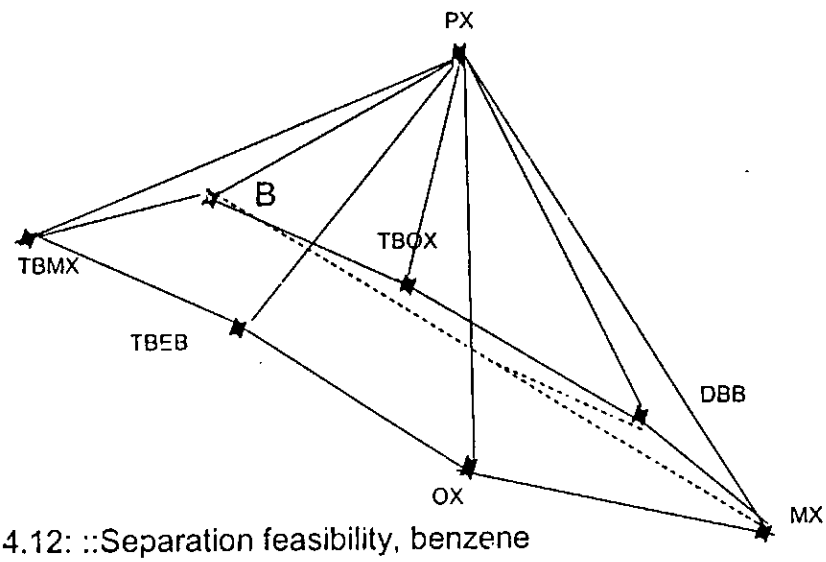


Figure 4.12: ::Separation feasibility, benzene and metaxylene as distillate and DBB as bottoms.

The combined steps, which constitute the entire process of separation, are shown in Figure 4.13

The entire flowsheet which is shown in Figure 4.13 can be summarized thus: (i) alkylation, (ii) dealkylation and (iii) convectional distillation columns.

Alkylation reactions occur in columns 1 and 3 while dealkylation reactions occur in columns 5, 8 and 9. Columns 2, 4, 6, 7, 10 and 11 are convectional non-reactive distillation columns. In the first reactive column, ethylbenzene and orthoxylene were alkylated using ditertiary butyl benzene. This was favoured by the selective iron (III) chloride ($FeCl_3$) catalyst. This catalyst has been recommended for introduction of tertiary butyl group into the orthoxylene and ethylbenzene compounds.(Hiltegang *et al* 1981, Price, 1984). The alkylated products were tertiarybutylorthoxylene and tertiarybutyl ethylbenzene. Benzene is separated in this reactive column as overhead and recycled.. The bottoms from this column- the alkylated products were sent to the second non reactive column where they were separated as a result of their boiling point differences. Metaxylene and paraxylene were separated as overhead. In the third column metaxylene was alkylated to form tertiarybutyl metaxylene. This reaction was favored by using aluminium chloride ($AlCl_3$) catalyst. The tertiarybutyl metaxylene component was separated from paraxylene in the non-reactive column (column 4). This complex (TBMX) was sent to the reactive column (column 5) where the dealkylation was carried out to liberate the metaxylene which was obtained as overhead and DBB the bottom product. Benzene was separated from metaxylene in the non reactive column 6 and recycled. The alkylated products tertiarybutylorthoxylene and tertiarybutyl ethylbenzene were first separated in a non reactive column (column 7) before they were dealkylated respectively in columns 8 and 9. The bottom product, DBB, was recycled into column 1 while the overhead products were separated in the non –reactive columns 10 and 11 to obtain the pure components orthoxylene and ethyl benzene. The overhead product benzene was recycled.

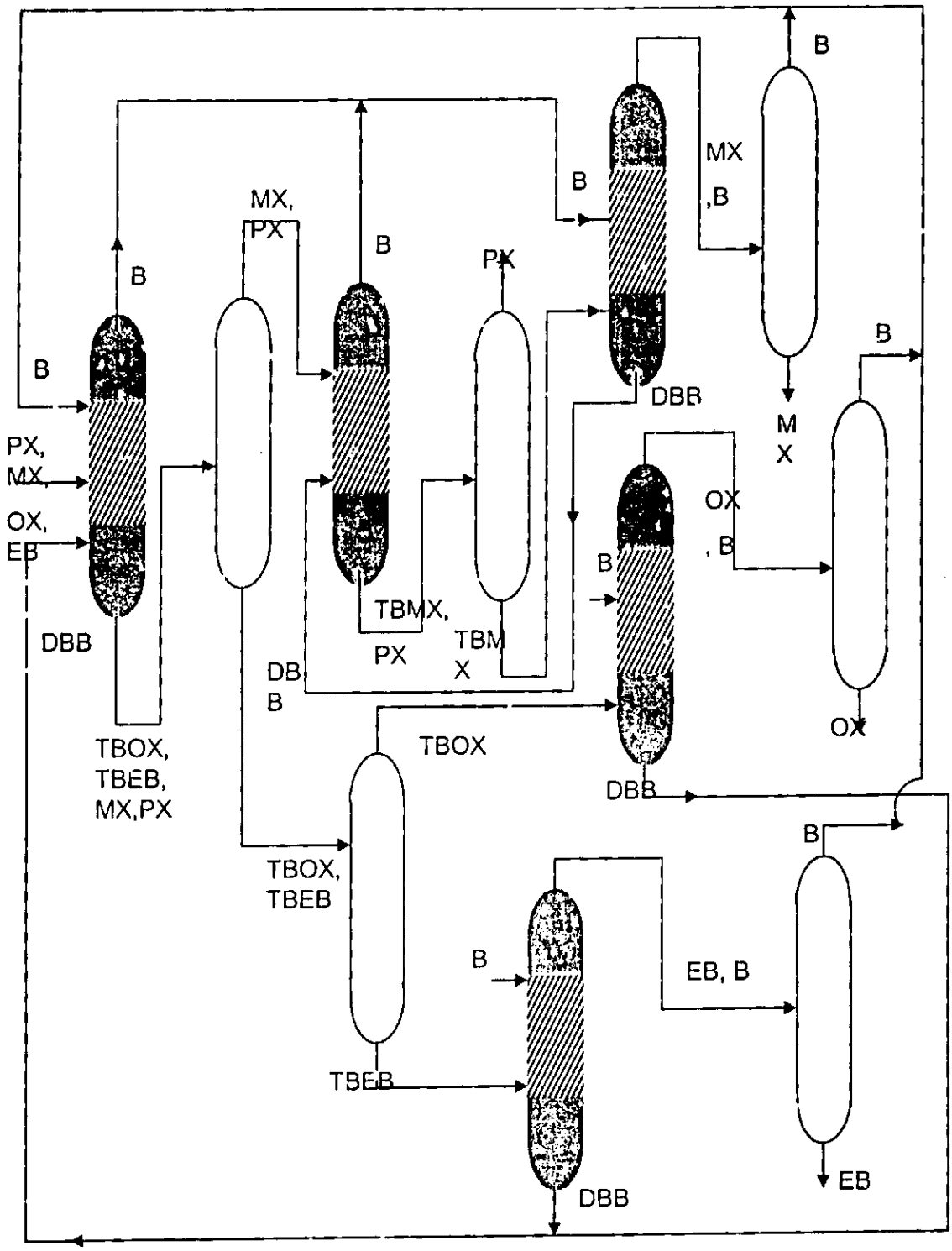


Figure 4.13 : The flowsheet for the separation of meta, ortho , paraxylenes and ethylbenzene mixture.

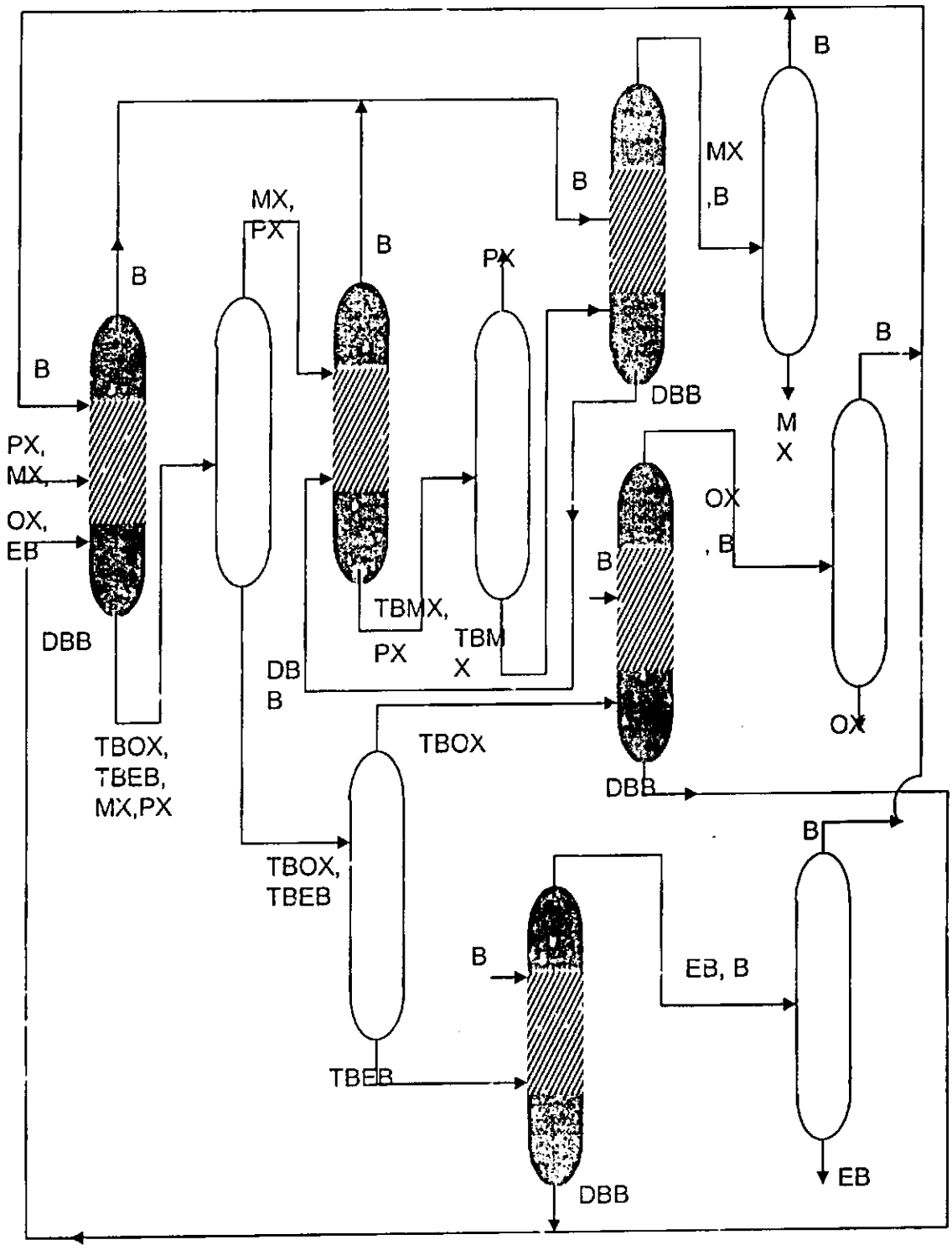


Figure 4.13 : The flowsheet for the separation of meta, ortho , paraxylenes and ethylbenzene mixture.

CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMMEDATIONS

5.1 CONCLUSIONS

The separation of the mixture of xylenes and ethylbenzene compounds with the same molecular formula (C_8H_{10}) and close boiling points is presented. A separation based on simultaneous reaction and distillation produced the high grade xylenes and ethylbenzene compounds. A highly reactive fifth component, di-tertiary butyl benzene was intentionally introduced into the system and with the aid of the highly selective iron III chloride ($FeCl_3$) and aluminina $AlCl_3$ catalysts, alkylated tertiary-butyl-ortho xylene, tertiary-butyl-ethylbezene and tertiary-butyl-metaxylene complexes were produced. These compounds which are high boiling were separated before dealkylation reaction in another step. The residue curve maps in the new transformed composition variables for the reactive mixture at equilibrium provides the information on the feasibility of the separation and the column sequencing for the desired separation. The new variables represent the surfaces embedded within the mole fraction coordinate space in a simpler way, thus giving an easier visualization of the diagrams. As discussed above, we come to the general conclusion that combined reactive-distillation column is more expedient arrangement and method of separation relative to absorption and crystallization. Consequently, the use of reactive distillation allows a large reduction in investments.

To avoid unnecessary complications in the analysis of multiple reactions, we need a method of identifying a set of independent reactions from a larger collection of reactions. A computer-assisted procedure for the determination of independent reactions in a

reactive schemes had been presented. This work introduces a good method for the synthesis of reaction mechanisms. The procedure reduces the volume of mathematical computations significatly and also identifies the redundant reactions. In the reactive schemes used as examples in this work, fifteen independent reactions were obtained for the n-butane mechanistic model containing twenty four, ten for the cyclohexane molecular model containing eighteen and twenty seven for the n-heptane sixty selected reactions, respectively.

5.1.1 CONTRIBUTIONS TO KNOWLEDGE

The formulations and solution approach adopted in this research work differ significantly from other attempts in the study of the separation of mixtures of close boiling compounds such as the xylenes and ethylbenzene mixture.

1. This is the first time that the reactive distillation process has been used for the separation of the close-boiling mixtures of the xylene isomers and ethylbenzene.
2. In carrying out the reactive distillation of these four components (ortho-, meta- and para-xylene) and ethylbenzene, new mathematical developments were made for six equations and ten components. to two existing in the literature.
3. The application of this work in the separation of the xylenes is a departure from the existing methods of adsorption and crystallization.
4. A computer-assisted procedure was developed for the determination of independent elementary steps in pyrolysis reactions. The procedure facilitates the rapid reduction of large mechanistic and molecular pyrolysis reaction schemes into

independent sets of reactions. This algorithm will be very useful on the basis of limited experimental observations

5.2 RECOMMEDATIONS

From this study, it is recommended that further work should be in:

1. Adapting this new method to the separation of other close-boiling compounds such as the alcohols and alkenes(phenols and butane isomers).
2. Organic synthesis where synthesis proceeds through a series of catalytic and non-catalytic equilibrium reaction steps. The screening of potential catalyst and alkylating agents can be done to determine preferred alkylation agent(s) and catalyst or catalyst combination.
3. Development of novel catalyst for the selective alkylation of the component of interest in the mixture of the xylenes and ethylbenzene. This will further lead to the optimization of the preferred catalyst or catalyst combination through kinetic studies.

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APPENDIX A

CALCULATION OF THE TRANSFORMED COMPOSITION VARIABLES FOR

META- AND PARAXYLENE SYSTEM..

1. Calculation of transformed composition variable for the mx and px mixture separation.

The relationship is

$$X_i = \frac{(x_i - \nu_i^T(\nu_{ref})^{-1}x_{ref})}{1-\nu_{TOT}^T(\nu_{ref})^{-1}x_{ref}} \qquad \text{A1}$$

$\nu_{TOT}^T = (\nu_{T1}\nu_{T2}) = (00)$ hence the above equation becomes

$$X_i = x_i - \nu_i^T(\nu_{ref})^{-1}x_{ref} \qquad \text{A2}$$

$$\nu_i^T = (\nu_{i1}\nu_{i2})$$

$$\nu_{ref} = \begin{pmatrix} -1 & 0 \\ -1 & -1 \end{pmatrix} \text{and } (\nu_{ref})^{-1} = \begin{pmatrix} -1 & 0 \\ 1 & -1 \end{pmatrix}$$

$x_{ref} = \begin{pmatrix} x_1 \\ x_2 \end{pmatrix}$ and the equation becomes

$$X_i = x_i - (\nu_{i1}\nu_{i2})\begin{pmatrix} -1 & 0 \\ 1 & -1 \end{pmatrix}\begin{pmatrix} x_1 \\ x_2 \end{pmatrix} \qquad \text{A3}$$

for i = 3 as an example

$$X_3 = x_3 - (\nu_{31}\nu_{32})\begin{pmatrix} -1 & 0 \\ 1 & -1 \end{pmatrix}\begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = x_3 - (11)\begin{pmatrix} -1 & 0 \\ 1 & -1 \end{pmatrix}\begin{pmatrix} x_1 \\ x_2 \end{pmatrix}$$

$$X_3 = x_3 - (0-1)\begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = x_3 + x_2$$

2. Mapping of pure components using X_3 and X_5 for system of para-xylene and metaxylene mixture separation

X_3, X_5 and X_6 are the transformed composition variables.

The equations are

$$X_3 = x_3 + x_2 \tag{3.59}$$

$$X_4 = x_4 + 2x_1 - x_2 \tag{3.60}$$

$$X_5 = x_5 - x_1 + x_2 \tag{3.61}$$

$$X_6 = x_6 \tag{3.62}$$

1. Pure DBB(X_1), $x_1 = 1$, $x_2 = x_3 = x_4 = x_5 = 0$

   $X_3 = 0$, $X_5 = -1$, $X_1(0,-1,0)$

2. Pure m-xylene(X_2), $x_2 = 1$

   $X_3 = 1$, $X_5 = 1$, $X_2(1,1,0)$

3. Pure TBMX(X_3), $x_3 = 1$

   $X_3 = 1$, $X_5 = 0$, $X_3(1,0,0)$

4. Pure TBB(X_4), $x_4 = 1$

   $X_3 = 0$, $X_5 = 0$, $X_4(0,0,0)$

5. Pure Benzene(X_5), $x_5 = 1$

   $X_3 = 0$, $X_5 = 1$, $X_5(0,1,0)$

6. Pure p-xylene(X_6), $x_6 = 1$

   $X_3 = 0$, $X_5 = 0$, $X_6(0,0,1)$ (for the 3-D figure)

APPENDIX B

CALCULATION OF TRANSFORMED COMPOSITION VARIABLES FOR THE ORTHO-, META-, PARAXYLENE AND ETHYLBENZENE MIXTURE SEPARATION.

The relationship is

$$X_i = \frac{(x_i - \nu_i^T(\nu_{ref})^{-1}x_{ref})}{1-\nu_{TOT}^T(\nu_{ref})^{-1}x_{ref}} \qquad \text{A1}$$

$\nu_{TOT}^T = (\nu_{T1}\nu_{T2}\nu_{T4}\nu_{T5}\nu_{T6}\nu_{T9}) = (000000)$ hence the above equation becomes

$$X_i = x_i - \nu_i^T(\nu_{ref})^{-1}x_{ref} \qquad \text{A2}$$

$$\nu_i^T = (\nu_{i1}\nu_{i2}\nu_{i4}\nu_{i5}\nu_{i6}\nu_{i9})$$

$$\nu_{ref} = \begin{pmatrix} -1 & -1 & 1 & 0 & 0 & 1 \\ 0 & -1 & -1 & 0 & 1 & 1 \\ -1 & 0 & 1 & -1 & 1 & 0 \\ 0 & 0 & -1 & -1 & 1 & 1 \\ -1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 1 \end{pmatrix} \text{ and } (\nu_{ref})^{-1} = \begin{pmatrix} 1 & -1 & 0 & 1 & -2 & -1 \\ 0 & -1 & 0 & 1 & 0 & 0 \\ 1 & -1 & 0 & 1 & -1 & -1 \\ 0 & 0 & -1 & 1 & 1 & -1 \\ 0 & 0 & 0 & 1 & 0 & -1 \\ 1 & -1 & 0 & 1 & -1 & 0 \end{pmatrix}$$

$$x_{ref} = \begin{pmatrix} x_1 \\ x_2 \\ x_4 \\ x_5 \\ x_6 \\ x_9 \end{pmatrix}$$ and the equation becomes

$$X_i = x_i - (\nu_{i1}\nu_{i2}\nu_{i4}\nu_{i5}\nu_{i6}\nu_{i9}) \begin{pmatrix} 1 & -1 & 0 & 1 & -2 & -1 \\ 0 & -1 & 0 & 1 & 0 & 0 \\ 1 & -1 & 0 & 1 & -1 & -1 \\ 0 & 0 & -1 & 1 & 1 & -1 \\ 0 & 0 & 0 & 1 & 0 & -1 \\ 1 & -1 & 0 & 1 & -1 & 0 \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ x_4 \\ x_5 \\ x_6 \\ x_9 \end{pmatrix}$$

for i = 7 as an example

$$X_7 = x_7 - (\nu_{71}\nu_{72}\nu_{74}\nu_{75}\nu_{76}\nu_{79}) \begin{pmatrix} 1 & -1 & 0 & 1 & -2 & -1 \\ 0 & -1 & 0 & 1 & 0 & 0 \\ 1 & -1 & 0 & 1 & -1 & -1 \\ 0 & 0 & -1 & 1 & 1 & -1 \\ 0 & 0 & 0 & 1 & 0 & -1 \\ 1 & -1 & 0 & 1 & -1 & 0 \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ x_4 \\ x_5 \\ x_6 \\ x_9 \end{pmatrix}$$

$$= x_7 - (0000\ -1-1) \begin{pmatrix} 1 & -1 & 0 & 1 & -2 & -1 \\ 0 & -1 & 0 & 1 & 0 & 0 \\ 1 & -1 & 0 & 1 & -1 & -1 \\ 0 & 0 & -1 & 1 & 1 & -1 \\ 0 & 0 & 0 & 1 & 0 & -1 \\ 1 & -1 & 0 & 1 & -1 & 0 \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \\ x_4 \\ x_5 \\ x_6 \\ x_9 \end{pmatrix}$$

$$X_7 = x_7 - (-110\ -211) \begin{pmatrix} x_1 \\ x_2 \\ x_4 \\ x_5 \\ x_6 \\ x_9 \end{pmatrix} = x_7 + x_1 - x_2 + 2x_5 - x_6 + x_9$$

Mapping of pure components using X_3 and X_7 for system without para-xylene and X_3, X_7 and X_{10} for system with para-xylene.

The equations are

$$X_3 = x_3 - x_2 + 2x_2 - 2x_5 + 2x_6 + x_9 \quad \text{(C1)}$$

$$X_7 = x_7 + x_1 - x_2 + 2x_5 - x_6 - x_9 \quad \text{(C2)}$$

$$X_8 = x_8 - x_1 + x_2 + x_6 - x_9 \quad \text{(C3)}$$

$$X_{10} = x_{10} \quad \text{(C4)}$$

1. Pure DBB(X_1), $x_1 = 1$, $x_2 = x_3 = x_5 = x_6 = x_9 = 0$

   $X_3 = -1$, $X_7 = 1$, $X_1(-1,1,0)$

2. Pure EB(X_2), $x_2 = 1$

   $X_3 = 2$, $X_7 = -1$, $X_2(2,-1,0)$

3. Pure TBEB(X_3), $x_3 = 1$

   $X_3 = 1$, $X_7 = 0$, $X_3(1,0,0)$

4. Pure TBB(X_4), $x_4 = 1$

   $X_3 = 0$, $X_5 = 0$, $X_4(0,0,0)$

5. Pure MX(X_5), $x_5 = 1$

   $X_3 = -2$, $X_7 = 2$, $X_5(-2,2,0)$

6. Pure TBMX(X_6), $x_6 = 1$

   $X_3 = 2$, $X_7 = -1$, $X_6(2,-1,0)$

7. Pure OX(X_7), $x_7 = 1$

   $X_3 = 0$, $X_7 = 1$, $X_7(0,1,0)$

8. Pure TBOX(X_8), $x_8 = 1$

$X_3 = 0, \quad X_7 = 0, \; X_8\,(0,0,0)$

9. Pure $B(X_9)$, $x_9 = 1$

$X_3 = 1, \quad X_7 = -1, \; X_6\,(1,-1,0)$

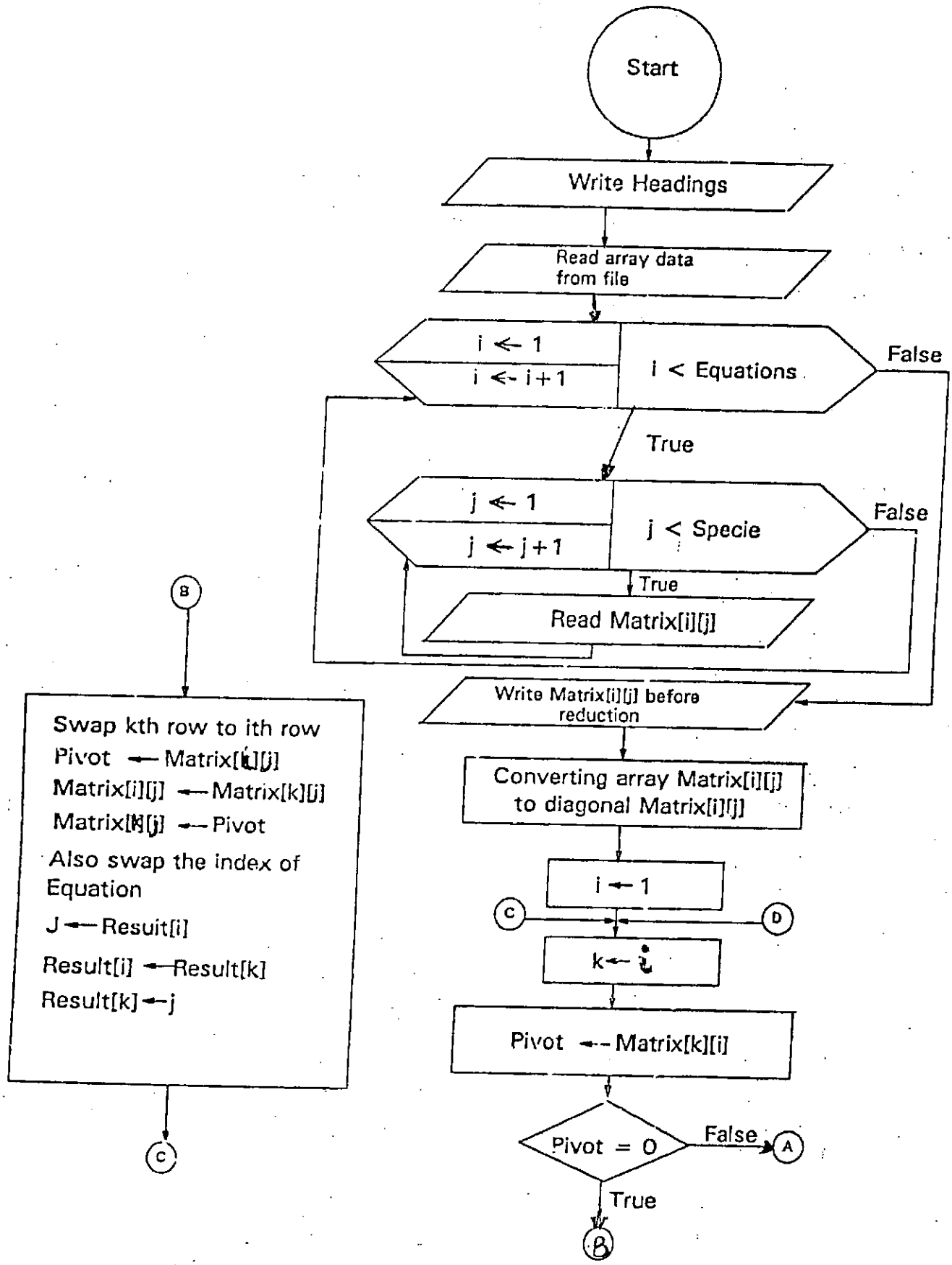
9. Pure $PX(X_{10})$, $x_{10} = 1$

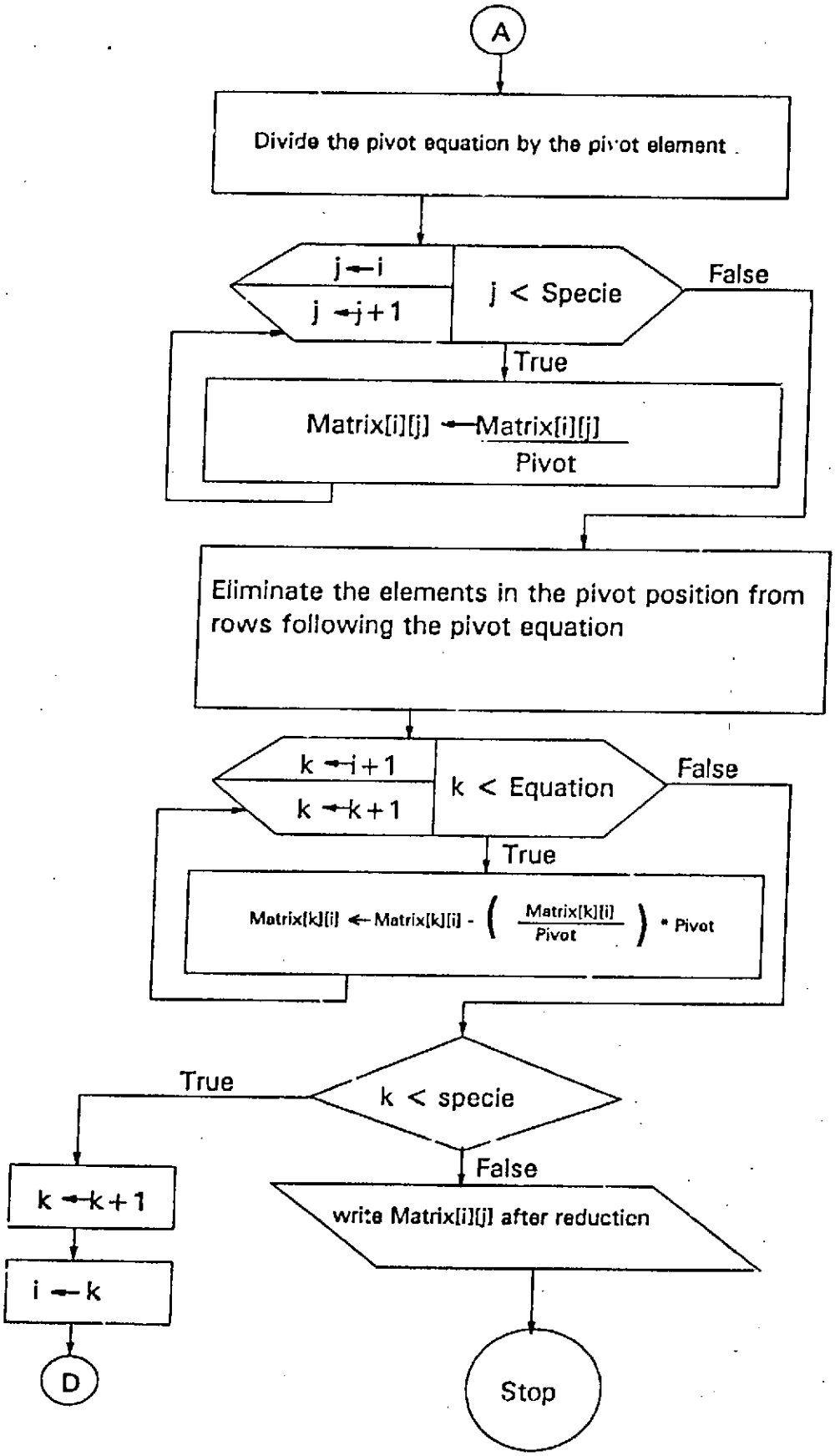
$X_{10} = 1, \quad X_{10}\,(0,0,1)$

APPENDIX D

PROGRAM FLOWCHART FOR THE COMPUTATION OF THE INDEPENDENT SET OF REACTIONS.

PROGRAM FLOW CHART




A
Divide the pivot equation by the pivot element
j ← i
j ← j + 1
j < Specie
False
True
Matrix[i][j] ← Matrix[i][j] / Pivot
Eliminate the elements in the pivot position from rows following the pivot equation
k ← i + 1
k ← k + 1
k < Equation
False
True
Matrix[k][i] ← Matrix[k][i] - (Matrix[k][i] / Pivot) * Pivot
True
k < specie
False
k ← k + 1
i ← k
D
write Matrix[i][j] after reduction
Stop

APPENDIX E

THE COMPUTER PROGRAM FOR THE DETERMINATION OF INDEPENDENT SET OF REACTIONS.

```
/*********************************************************
 * This program uses Gaussian elimination by pivoting     *
 * method to reduce any set of (I,J) matrix of coeffi-    *
 * cients of hydrocarbon pyrolysis reactions to its inde- *
 * pendent reactions. The resultant matrix is in its uppe *
 * triangular (Echelon) form.                             *
 *********************************************************/

#include <stdlib.h>
#include <stdio.h>
#include <conio.h>

void getdata( FILE * );
long filesize(FILE *);
void filescan(FILE *);
void findindpt();
void dispresult(char *,char *,FILE *, int);

/*** public variables ***/
long  equation   =0,
      specie =0;
int   *result;
float huge matrix[100][100];

void main()
{
  long i;
  FILE *fileptr;
  char  str[8], *topic;
  char ch;
  int  top, left, success =0;

  clrscr();
  printf("file to open >> ");
  gets(str);
  printf("\nCompound >> ");
  gets(topic);

  if ((fileptr = fopen(str, "rt")) == NULL)
  {
        fprintf(stderr, "Cannot open input file.\n");
        return;
  };
  filescan(fileptr);

   /* allocate memory to result based on equation */
  if (( result = (int *) calloc(equation,sizeof(int))) == NULL)
  {
        fprintf(stderr, "Not enough memory.\n");
        return;
  };

  /* initialize result */
  for (i=0;i<equation;i++) result[i] = i+1;

  /* get data into the matrix */
  getdata(fileptr);

  /* open file for output */
  strcat(str,".rep");
```

```
    if ((fileptr = fopen(str, "wt")) == NULL)
    fprintf(stderr, "\Error openning report file.\n"); else
    success = 1;

    /* display result before reduction */
    dispresult(topic,"before",fileptr,success);

    /* find independent specie */
    findindpt();

    /* display result after reduction */
    dispresult(topic,"after",fileptr,success);

    /* free allocated memory */
    free (result);

    /* close file */
    fclose(fileptr);
  }

  void getdata( FILE *fileptr )
  {
    int element;
    long i = 0,
         j = 0,
         length;

    length = filesize(fileptr);

    /* seek to the beginning of the file */
         fseek(fileptr, 0, SEEK_SET);
    do
    {
          fscanf(fileptr,"%d",&element);
          if (j == specie)
          {
                ++i; j=0;
          };
          matrix[i][j++] = element;
  } while (ftell(fileptr) < length);
}


long filesize(FILE *fileptr)
{
  long curpos, length;

  curpos = ftell(fileptr);
  fseek(fileptr, 0L, SEEK_END);
  length = ftell(fileptr);
  fseek(fileptr, curpos, SEEK_SET);
  return length;
}

void filescan(FILE *fileptr)
{
  long length;
  char ch = '',
       oldch = '';
```

```
    /* seek to the end of file to determine its length */
    fseek(fileptr, 0, SEEK_END);
    length = ftell(fileptr);

    /* seek to the beginning of the file */
          fseek(fileptr, 0, SEEK_SET);

    /* obtain no. of species and equations */
    do
    {
          /* read a char from the file */
          ch = fgetc(fileptr);

          if (ch == '\n')  // new line
          {
                ++equation;
                ++specie;
          } else if (ch == ' ' && ch != oldch && oldch != '\n') ++specie;
          if ( oldch == ' ' && ch == '\n' ) --specie;
          oldch = ch;
    } while (ftell(fileptr) < length); // until end of file
    if ( ch != '\n' ) {
          ++equation;
          ++specie;
    }
    if ( (specie % equation)  != 0)
    {
          fprintf(stderr, "\n\nData in file not a rectangular matrix.\n");
          exit(1);
    };
    specie = specie / equation;
}

void findindpt()
{
  int i,j,k;
  float pivot;

  /* convert array matrix to a diagonal matrix */
  for(i=0;i<specie;i++) {
    k = i;
    while( (pivot = matrix[k][i]) == 0) ++k;
    if ( k != i )  {
      /* swap data from kth row to ith row */
      for (j=0;j<specie;j++) {
        pivot = matrix[i][j];
        matrix[i][j] = matrix[k][j];
        matrix[k][j] = pivot;
      };
      pivot = matrix[i][i];
      /* also swap the address of result */
      j = result[i];
      result[i] = result[k];
      result[k] = j;
    };

    /* reduce the pivot to 1 along with corresponding row */
    if( pivot != 1.0 ) for( j=0; j<specie; j++ )
    if( matrix[i][j] != 0 ) matrix[i][j] = matrix[i][j] / pivot;
```

```
    /* apply the pivot row on all other rows, reducing the
       pivot column element to zero */
    for( k=i+1; k<equation; k++) if(matrix[k][i] != 0)  {
      pivot = -matrix[k][i];
      for( j=i; j<specie; j++) if( k != i && matrix[i][j] != 0 )
      matrix[k][j] = matrix[i][j] * pivot + matrix[k][j];
    };
  };
}

void dispresult(char *topic,char *when,FILE *fileptr, int success)
{
  long i,j;
  char ch;

  printf("\n\nMatrix of coefficients of");
  printf(" %s pyrolysis %s reduction:\n\n      ",topic,when);
  if (success) {
    fprintf(fileptr,"\n\nMatrix of coefficients of");
    fprintf(fileptr," %s pyrolysis %s reduction:\n\n      ",topic,when);
  }
  for (i=0;i<specie;i++) {
    printf("%-4d  ",i+1);
    if (success) fprintf(fileptr,"%-4d  ",i+1);
  }
  printf("\n"); fprintf(fileptr,"\n");
  for (i=0;i<equation;i++) {
    printf("%3d: ",result[i]);
    if (success) fprintf(fileptr,"%3d: ",result[i]);
    for (j=0;j<specie;j++) {
      printf("%4.1f  ",matrix[i][j]);
      if (success) fprintf(fileptr,"%4.1f  ",matrix[i][j]);
    }
    printf("\n");
    if (success) fprintf(fileptr,"\n");
  };
  ch = getch(); ch =ch;
  close(fileptr);
}
```