

MODELING OF CATALYTIC NAPHTHA REFORMER

PROJECT REPORT SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR

MASTER OF TECHNOLOGY
(REFINING AND PETROCHEMICAL)

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UNDER THE GUIDENCE OF
Dr. D. N. SARAF

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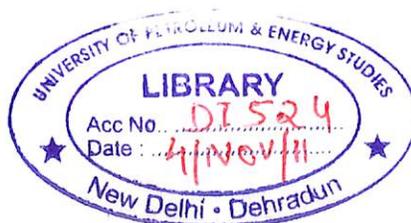
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UNIVERSITY OF PETROLEUM AND ENERGY STUDIES

DEHRADUN

2007



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S.Ramya



चेन्नै पेट्रोलियम कॉर्पोरेशन लिमिटेड
(इंडियनऑयल की ग्रुप कम्पनी)

Chennai Petroleum Corporation Limited
(A group company of IndianOil)

CERTIFICATE

This is to certify that Ms. S. RAMYA, a student of final year M. Tech (Refining and Petrochemical Engineering) from M/s. University of Petroleum & Energy Studies, Dehradun, has completed the Project work on " MODELING OF CATALYIC NAPHTHA REFORMER " in Research & Development Department of our Organisation during the period from 02.04.2007 to 25.04.2007.

During the above training period, her character and conduct were good.

We wish her all success in her future endeavor.

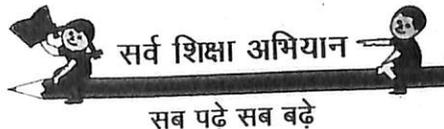
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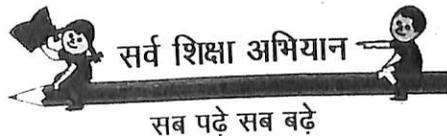
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BONAFIDE CERTIFICATE

This is to certify that project work entitled “**MODELING OF CATALYTIC NAPHTHA REFORMER**” is the bonafide work of Ms. S. RAMYA from **University of Petroleum & Energy Studies, M. Tech (Refining and Petrochemical Engineering)** who carried out the work under joint supervision of Dr M.Bhaskar, CPCL, Chennai and myself. This work has not been submitted anywhere else for a degree.



14-05-07

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ABSTRACT

A detailed kinetic model has been developed for a catalytic reformer unit which simulates how the feed composition and operating conditions affect the reformat composition. The model idealizes the complex naphtha mixture into three hydrocarbons namely, paraffins, naphthenes and aromatics with an average carbon number. The paraffins, naphthenes and aromatics with the same carbon number were treated separately.

The paraffins were further subdivided into three individual components: straight chain, single branched, and multi branched. The five-carbon ring naphthenes were considered differently than six-carbon ring naphthenes.

Out of many reactions they undergo, five major reactions have been considered for naphtha with carbon numbers from C_6 to C_{10} and a total of 35 components were included. The kinetic parameters were estimated from pilot plant experiments. The reactor model will be validated against different sets of plant data which was subsequently used for optimization.

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NOMENCLATURE:

C_5	-	Cracked light gases less than 5 carbon atoms
C_6A	-	Aromatics of six-carbon atom
C_7A	-	Aromatics of seven-carbon atom
C_8A	-	Aromatics of eight-carbon atom
C_9A	-	Aromatics of nine-carbon atom
$C_{10}A$	-	Aromatics of ten-carbon atom
C_p	-	Specific heat capacity
DHCA	-	Detailed Hydrocarbon Analysis
E	-	Activation Energy
K_{eqi}	-	Equilibrium constant for the i^{th} reaction
k_i	-	Forward reaction rate constant, kmol/(h) (kgcat) i^{th} reaction
k_{i-}	-	Backward reaction rate constant, kmol/(h) (kgcat)
k_0	-	Pre-exponential factor
MBP ₆	-	Multi branched hexane
MBP ₇	-	Multi branched heptane
MBP ₈	-	Multi branched octane
MBP ₉	-	Multi branched nonane
MBP ₁₀	-	Multi branched decane
mw	-	Molecular weight
nP ₅	-	n-Pentane
nP ₆	-	n-Hexane
nP ₇	-	n-Heptane
nP ₈	-	n-Octane
nP ₉	-	n-Nonane
nP ₁₀	-	n-Decane
P_j	-	partial pressure of j^{th} component, kpa
r_i	-	rate of i^{th} reaction of j^{th} component
R	-	Universal Gas Constant (kJ/kmol/K)
SBP ₅	-	Single Branched Pentane
SBP ₆	-	Single Branched Hexane
SBP ₇	-	Single Branched Heptane
SBP ₈	-	Single Branched Octane
SBP ₉	-	Single Branched Nonane
SBP ₁₀	-	Single Branched Decane
T	-	Temperature, K
5N ₆	-	Five-carbon ring C ₆ naphthenes
5N ₇	-	Five-carbon ring C ₇ naphthenes
5N ₈	-	Five-carbon ring C ₈ naphthenes
5N ₉	-	Five-carbon ring C ₉ naphthenes
5N ₁₀	-	Five-carbon ring C ₁₀ naphthenes
6N ₇	-	Six-carbon ring C ₇ naphthenes
6N ₈	-	Six-carbon ring C ₈ naphthenes
6N ₉	-	Six-carbon ring C ₉ naphthenes
6N ₁₀	-	Six-carbon ring C ₁₀ naphthenes

CHAPTER I

INTRODUCTION

Catalytic naphtha reforming is practiced extensively in the petroleum refining industry to convert gasoline boiling range low octane hydrocarbons to high-octane gasoline compounds for use as high-performance gasoline fuel. This is accomplished by conversion of n-paraffins into aromatics over bifunctional catalyst such as Pt/Al₂O₃ or Pt-Re/ Al₂O₃.

Recent environmental legislation has banned the use of lead as an additive boosting antiknock property of motor fuel. Coupled with these stricter environmental regulations, there has been a consistent increase in the demand for higher fuel efficiency standards of engines. This requires the use of higher compression ratios in engines, and therefore motor fuel with even greater octane number.

These considerations have continuously forced the refiner toward producing higher-octane-number products from their catalytic naphtha reformers. This can be achieved by reforming the naphtha under more severe conditions, but this will also cause an increase in the rate of coke deposition, reduction of cycle lengths of the catalyst, resulting in significant economic losses. So a proper selection of operating conditions within plant constraints is essential to maximize the profitability of the reformer.

Use of mathematical models as a tool for either off-line or on-line optimization analysis is growing rapidly in the refining and petrochemical industries. A mathematical model requires various amounts of process knowledge and investment of time and effort, depending up on the level of complexity incorporated into these models. The advantage of utilizing rigorous mathematical models as compared to empirical approaches is related to the fact that the prediction accuracy of rigorous models can be significantly superior over wide operating range. Hence detailed mathematical models are frequently employed for optimization studies.

In this work a rigorous mathematical model of a Semi regenerative catalytic reformer, based on fundamental physiochemical concepts, has been developed. The model parameters have been estimated on the basis of data obtained from an industrial unit. The modeling of the chemical reactions occurring on the surface of the bifunctional catalytic naphtha-reforming catalyst during reforming was the most intricate part of the over all modeling effort. Appropriate kinetic modeling of these reactions was imperative in achieving the desired prediction accuracy of the model. A number of different approaches of varying levels of sophistication have been developed in the past to model the reforming chemistry (e.g., Smith, 1959; Krane et al., 1960; Kmak, 1972; Marin et al., 1983; Ramage et al., 1987; Riggs et al., 1997;).

1.1 SCOPE OF PROJECT WORK:

Catalytic naphtha reforming is employed in petroleum refinery to convert low-octane hydrocarbon to high-octane gasoline compounds, which are used as high performance gasoline fuel. This is accomplished by conversion of n-paraffins and naphthenes in naphtha to iso-paraffins and aromatics at relatively high pressure, temperature and high hydrogen to hydrocarbon molar ratio over bifunctional catalyst such as Pt/ Al₂O₃ or Re/ Al₂O₃. The objective of the project is to develop a mathematical model to simulate the performance of industrial catalytic naphtha reformer. The reaction kinetics will be estimated from operating data of the unit. The feed and the product streams will be collected from the reformer, analyzed and used to validate the model.

1.2 CATALYTIC NAPHTHA REFORMING – PROCESS AND CHEMISTRY:

The process flow diagram of the reformer to be modeled in this work is shown in figure. At the core of the reforming process are three or four-fixed bed adiabatically operated reactors in series that conduct the solid catalyzed vapor phase reforming reactions. This is Semi regenerative type of unit, that is, the catalyst is regenerated periodically to compensate for the loss in activity of the catalyst due to coke deposition.

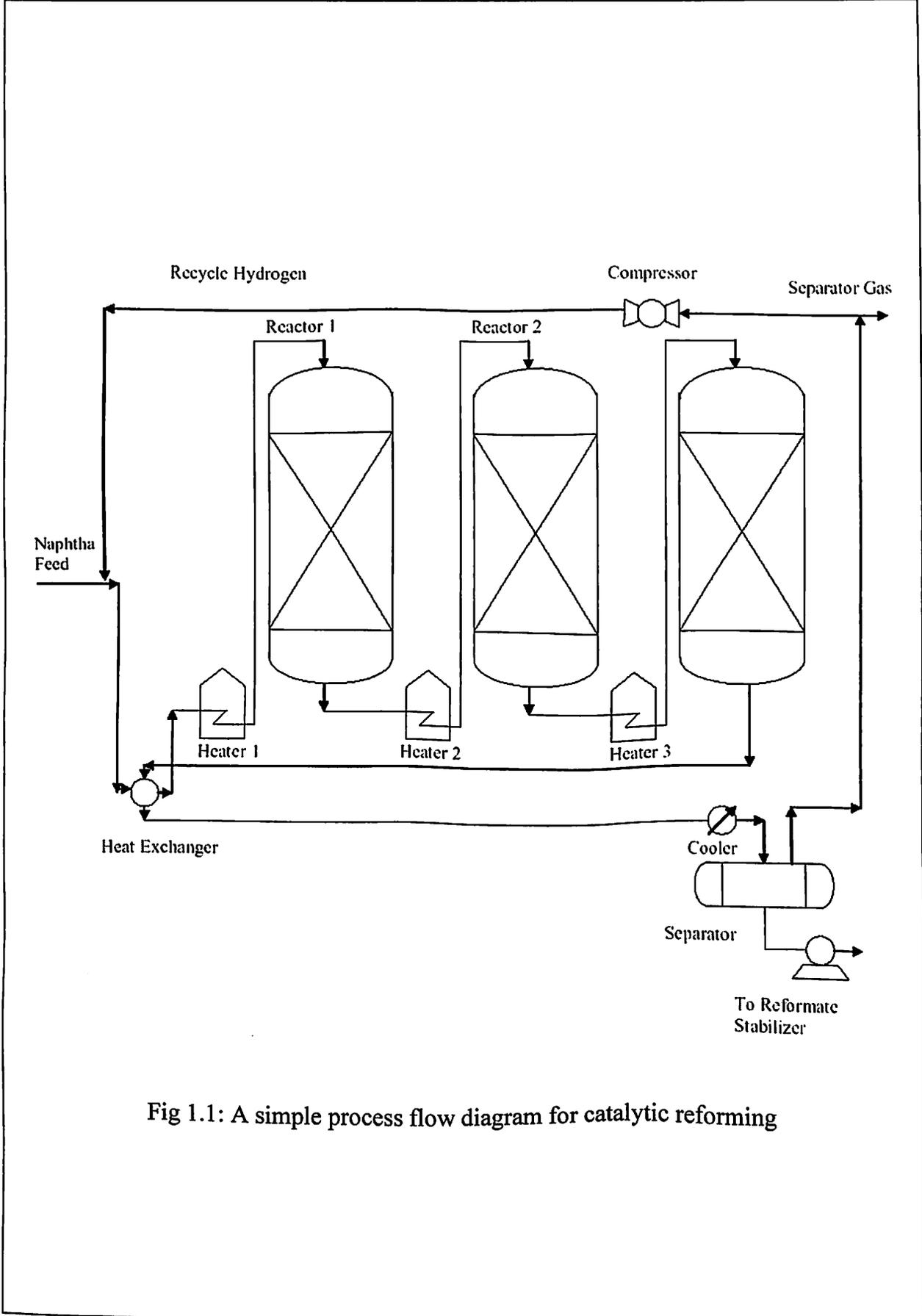


Fig 1.1: A simple process flow diagram for catalytic reforming

The naphtha used as a catalytic reformer feedstock usually contains a mixture of paraffins, naphthenes and aromatics in the range from C₅ to C₁₀ in typical feed the carbon from C₅ to C₁₂. The reformer-reactor charge is combined with a recycle gas stream containing 60 to 90 percent hydrogen. The total reactor charge is heated at first by exchange heat with effluent from the last reactor, and then in the first charge is heater. The inlet temperature of the beds varies between 750 to 780°K, and the reactors are operated at pressures of about 20 to 30 atm. The molar recycle ratio stated in terms of hydrogen to pure hydrocarbon feed varies from 4:1 to 8:1.

The major reactions in the first reactor, such as dehydrogenation of naphthenes are endothermic and very fast, causing a very sharp temperature drop in the first reactor. For this reason, catalytic reformers are designed with multiple reactors and with heater between the reactors to maintain reaction temperature at operable levels. As the total reactor charge passes through the sequence of heating and reacting, the reactions become less and less endothermic and the temperature differential across the reactors decreases. The effluent from the last reactor, at temperature from 750 to 790°K, is cooled to 315 to 320°K, partly by heat exchange with reactor charge. The stream then enters the product separator where flash separation of hydrogen and some of the light hydrocarbons (primarily methane and ethane takes place. The flashed vapor, containing 60 to 90 mol% hydrogen, passes to compressor and then circulates to join the naphtha charge,. Excess hydrogen from the separator is sent to other hydrogen-consuming units in the refinery.

The separator liquid, comprised mostly of the desired reformat product but also containing light gases, is pumped to the reformat stabilizer. Reformat off the bottom of the stabilizer is sent to storage for gasoline blending.

Most of the catalytic reactions in reforming involve rearrangement of the hydrocarbon skeleton, within the same carbon number group, except for the hydrocracking reactions, which crack the high carbon molecules into two lower-molecular weight molecules. The dominant reaction types prevalent in catalytic reforming are dehydrogenation of naphthenes, isomerizations of paraffins and naphthenes, Dehydrocyclization (ring closure) of paraffins, and hydrocracking of paraffins. All the reactions produce an increase in octane number and all the reactions except isomerizations of paraffins, result in a decrease in reformat yield. The fastest reactions are dehydrogenation; isomerization is moderately fast, while Dehydrocyclization and hydrocracking are the slowest. The most rapid reactions (dehydrogenation) reach thermodynamically equilibrium, and the others are kinetically controlled. A high process temperature and a low pressure favor the thermodynamic feasibility as well as the reaction rate in the two important reactions: dehydrogenation and Dehydrocyclization.

Deactivation of catalyst by carbonaceous deposits is primarily caused by the blockage of active sites due to coke generation from the olefinic intermediates formed during the course of the main reforming reactions. Higher hydrogen pressures suppress the diolefin formation, reducing the coke formation. However, higher pressures reduce the selectivity to aromatics in the desired product. Overall, high temperatures and low pressures would seem most desirable for the main reforming reactions. But the same conditions favor deactivation of the catalyst. For this reason the process conditions should be a compromise between attaining a high octane-number product and controlling the rates of catalyst deactivation.

1.3 THEORY OF CATALYTIC REFORMING:

The main objective of the catalytic reforming process is the transformation of low-octane virgin naphthas into high-octane gasoline by increasing concentrations of aromatics and iso-paraffins. The octane of a gasoline increases with increment in aromatic concentration.

An appropriate gasoline for automobiles must have:

A maximum octane number to allow a high compression ratio, which increases the efficiency of the motor.

A minimum capacity to form gums, which are produced by polymerization and oxidation of olefins and which can foul the motor.

A minimum vapor pressure compatible with room temperature in order to avoid loss of vapors.

A minimum capacity to produce smoke or smog, which is produced by heavy olefins and aromatics.

Catalytic reforming produces a product that fulfills these requirements and produces, with good yields, high-octane gasoline (reformate) with research of benzene, toluene, and xylene.

During catalytic reforming, hydrogen and LPG (propane-butane) are produced in addition to reformate. Gaseous products (C_1 - C_4) have a low price; consequently, the selectivity of the catalyst for the production of low amounts of gases and high liquid yields are very important.

The main purpose of this process is to rebuild or reform hydrocarbon molecules, producing molecules with a higher octane number without changing the number of carbon atoms.

By means of paraffins Dehydrocyclization and naphthenes dehydrogenation, aromatics of the same number of carbon atoms are produced. For example, dimethylcyclopentane, ethylcyclopentane, heptanes, and methylcyclohexane should give toluene.

By means of isomerization the molecule is reorganized, increasing the number of branched chains. Paraffins isomerization is also a highly desired reaction because it increases the octane number without producing aromatics, the concentration of which in gasoline is likely to be limited by government regulations in future. But the problem is that, under reforming conditions, limited amounts of isomers are produced because isomerization is a reaction controlled by thermodynamic equilibrium. In addition, some of the isomers produced are subsequently transformed into other products.

A usual feed to a reforming unit contains 45-70% paraffins, 20-50% naphthenes, 4-11% aromatics, and 0-2% olefins. During the process, the content of aromatics increases to 60-70% (depending on the severity of operation), paraffins and naphthenes decrease to 20-45% and 1-8%, respectively, and olefins virtually disappear. Most of the naphthenes are converted into aromatics, but the aromatization of paraffins is more difficult. For this reason, naphthenic naphthas are more easily reformed.

Most of the reforming reactions are highly endothermic, producing a decrease in the temperature of the reaction stream and catalyst along the bed; therefore, a corresponding decrease in the rate of reactions is produced. To avoid this problem, the total mass of catalyst is distributed in three or four adiabatic reactors with heating before each reactor.

Reforming units are operated under severe conditions (high temperature and low hydrogen partial pressure) to achieve the greatest production of aromatics. However, catalyst stability is a limiting factor for the severity of the operation. Although hydrogen is harmful to the thermodynamics and kinetics of the desired reactions, the process is carried out in the presence of hydrogen to decrease the catalyst deactivation produced by coverage of the active surface with carbonaceous deposits.

1.4 TYPES OF REFORMING PROCESS:

Concurrent with the commercialization of bimetallic catalyst systems, process licensors for reforming process have directed considerable research and developments effort to the application of operating concepts and techniques to improve the basic engineering design of the reforming units.

Process licensors like UOP, IFP decided that the entire design concept would need rethinking if such aims were to be attainable, which led to the commercial realization of continuous reforming process.

1.4.1 Semi regenerative process:

Semiregenerative units generally operate for six months or more and then are shut down for catalyst regeneration. The hydrocarbon process lines are utilized for in place regeneration of the catalyst using nitrogen and or inert gas and air.

Some of the available Semiregenerative processes are: Houdriforming Institute Francaise du Petrole, Platforming (UOP), Rheniforming and Magnaforming. Usually three or four reactors with inert-heaters are employed and the down stream reactors are larger than the first.

1.4.2 Regenerative process:

Two types of regenerative processes have been developed; one in which catalyst regeneration takes place in the reactor itself and the other regeneration is carried out outside the reaction zone.

To the first type, belong processes such as:

Power forming (Esso Research & Engineering Co.)

Ultoforming (American Oil Co.)

Swing reactor is used which is put on stream whenever any reactor is under regeneration. Reactor after regeneration is put back on stream without affecting plant feed or octane and continuous supply of hydrogen for downstream units.

The second type of process includes:

UOP continuous regenerative platforming.

IFP continuous regenerative reforming.

1.5 REFORMING REACTIONS:

Typical naphtha may contain 200 or more identifiable compounds and have an octane number that is below 60. The purpose of the reformer is to selectively convert many of the compounds in the feed to higher-octane compounds so that the reformate octane number will meet specification. Reformer naphtha is composed of normal and branched paraffins, five and six membered ring naphthenes and single ring aromatics. Each of these general feed constituents can undergo several competing reactions.

1.5.1 Reactions of paraffins

Isomerization: Branched paraffins have higher-octane value than linear paraffins, so the isomerization reaction is of important in gasoline reforming. As total conversion of normal paraffins increases with an increase in temperature, the selective yields to the iso-paraffins increase to a maximum limit and then decrease rapidly because of iso-paraffin cyclization and hydrocracking reactions. The selectivity of the paraffin isomerization reactions at typical reforming operating conditions is relatively insensitive to total reaction pressure, hydrogen partial pressure and space velocity.

The reactivity of the paraffin isomerization reactions increases as paraffin carbon number increases. Isomerization reaction rates increase with an increase in temperature and/or total pressure. These reactions are mildly exothermic. The approximate heat of reaction is $-3,700$ Btu per mole of n-paraffin converted.

Dehydrocyclization: This is the most critical reaction in reforming, is favored by high temperatures and low pressures. Space velocity has very little effect on the conversion at low pressures, but at high pressures low space velocities can hinder the overall conversion. The conversion of paraffins to naphthenes increases with an increase in paraffin carbon number. The Dehydrocyclization reactions are endothermic. The approximate heat reaction is 21,000 Btu per mole of paraffin converted to naphthenes.

Hydrocracking: Hydrocracking of paraffins typically forms less valuable products than the other reactions. Conversion of normal, iso-paraffins, and cycloparaffins to lower molecular weight paraffins increase with an increase in temperature and pressure. Also, the conversion increases as space velocity decreases. The reactivity of the hydrocracking reactions increases with an increase in carbon number. Unlike the other reforming reactions, these reactions are irreversible and only the forward rate constant, i.e., from paraffin to cracked products, is used in the model. The distribution of the cracked products of each individual cracked component has been predetermined from literature sources. To a certain extent, the cracked product distribution is dependent on feed stock properties, catalyst acid activity and catalyst type.

Hydrocracking reaction rates are slow compared with dehydrogenation and isomerization reactions and proceed at about the same rate as Dehydrocyclization reactions. Actually, hydrocracking and Dehydrocyclization reactions compete with each other and the incremental economics of the reforming process can well depend on the extent to which these two important reactions occur. The paraffin hydrocracking reactions are exothermic. The average heat of reaction is approximately $-20,000$ Btu per mole of the component cracked.

1.5.2 Reactions of naphthenes

Dehydrogenation: The conversion naphthenes to aromatics are the primary naphthene reaction and the most rapid of all general reactions. The overall conversion is a measure of reformer severity, but in typical units, 90 to 98 percent of most naphthenes are dehydrogenated.

Conversions of cyclohexanes and cyclopentanes to aromatics increase with an increase in temperature and a decrease in pressure. At typical reforming operating conditions, these reactions essentially attain complete equilibrium conversion to the aromatics. However, the higher the operating pressure, the higher the temperature required to attain this conversion. This especially applies to the cyclopentane dehydrogenation reactions.

Normally, the effect of space velocity on the dehydrogenation reaction is minimal since these reactions are so rapid. The only exception is the dehydrogenation of methylcyclopentane to benzene; high space velocities will decrease the methyl cyclopentane conversion assuming all other conditions are equal. The reactivity of the dehydrogenation reaction increases with an increase in naphthene carbon number. These reactions are highly endothermic. The average heat of reaction is approximately 82,000 Btu per mole of naphthenes converted.

Isomerization: The isomerization of cyclohexanes to cyclopentanes is similar to paraffin isomerization. The cyclopentanes are favored thermodynamically in these reactions. These are mildly endothermic. The average heat of reaction is 8,900Btu per mole of naphthenes converted.

Hydrocracking: Like paraffins, cracking of cycloparaffins increase with temperature and residence time in the reactors. The extent of naphthene cracking is considerably less than paraffins since naphthenes are rapidly converted to aromatics. The reaction is irreversible and exothermic with an average heat of reaction of approximately -40,800 Btu per mole of cracked component.

1.5.3 Reactions of Aromatics:

Hydrodealkylation: Hydrodealkylation of both naphthenes and aromatics to respective homologous of lower carbon number occurs in the reforming process but to considerably less extent than the other primary reactions. High temperatures, pressures and low space velocity aid Hydrodealkylation reactions. The reactivity of these reactions increases sharply with an increase in carbon number. However the reaction rates are slowest of all the major reforming reactions. Hydrodealkylation reactions are exothermic. The average approximate heat of reaction is $-20,500$ But per mole of component dealkylated.

Other aromatic reaction: Although all of the aromatic forming reactions are reversible, the equilibrium lies far to the right side. Once produced, aromatics do not crack, reopen or dehydrogenate to any appreciable extent. Isomerization between meta-, para-, and ortho-xylene occurs rapidly and equilibrium compositions are obtained. On the other hand, isomerization between the xylene and ethyl benzene at the reformer temperatures occurs so slowly that this reaction is ignored. The equilibrium concentration of the xylene is relatively insensitive to temperature.

1.5.4 Desulphurization

All types of sulphur compounds are hydrogenated, yielding sulphide and saturated hydrocarbons. Sulphur compounds are converted to the extent to over 95%.

1.5.5 Conversion of Nitrogen compounds

Nitrogen compounds are hydrogenated, yielding ammonia and saturated hydrocarbons. Although nitrogen compounds are more difficult to hydrogenate than sulphur compounds, they are converted to a reasonable extent.

1.5.6 Conversion of Oxygen compounds

Oxygen compounds are converted into water and hydrocarbons.

1.6 REACTOR OPERATING CONDITIONS:

There are four operating variables which can within limits be chosen at will to obtain the required conversion and the desired life of catalyst. These variables are

Reactor pressure

Hydrogen to naphtha mole ratio

Space velocity

Reactor temperature

1.6.1 Reactor pressure:

A change in pressure, which will result in a change in hydrogen partial pressure will affect the dehydrogenation, dehydroisomerization and Dehydrocyclization reactions. A decrease in hydrogen partial pressure, for instance, will promote the production of aromatics, which will result in improved yield – octane number relationship. Caution would be exercised, however, in lowering the partial pressure of the hydrogen since this may result in excessive coke formation on the catalyst.

1.6.2 Hydrogen to naphtha mole ratio:

Coke is formed by the cumulative addition of conjugated diolefin to condensed aromatics. A diolefin may also be hydrogenated to harmless paraffins provided sufficient hydrogen is available in the vicinity of the diolefin at the moment of its formation. In order to promote the latter reaction, a high concentration of hydrogen is maintained by recycling hydrogen rich gas. This measure can be considered complementary to increasing the hydrogen partial pressure, which is essential for preventing excessive coke lay down on the catalyst.

Therefore, in those operations where a low hydrogen partial pressure is essential example for the manufacture of benzene and toluene and the production of super octane number motor gasoline components, a high hydrogen/naphtha mole ratio has to be maintained in order to safeguard the catalyst.

1.6.3 Space velocity:

Relatively slow reactions, e.g., hydrocracking and hydrocyclisation are more sensitive to changes in contact time than fast reactions, such as dehydrogenation and dehydroisomerization. It will therefore, be clear that when platforming a highly naphthenic feed whereby dehydrogenation is the principal reaction contributing to octane number improvement, satisfactory results will be obtained at a shorter contact time.

1.6.4 Reactor Temperature:

A change in reactor temperature has a pronounced effect upon the various reaction rates. An increase in reactor temperature will increase the rate of all reactions taking place. Since under normal operating conditions the dehydrogenation and dehydroisomerization reactions and the isomerization of normal to single branched paraffins will have proceeded almost completely to equilibrium, the temperature influence will be most perceptible for those reactions which even at the end of the last catalyst bed have not yet reached equilibrium, this will be the case with the hydrocracking and dehydrogenation reactions.

The combined effect of a temperature rise will therefore be a smaller yield of platformate owing the greater extent of hydrocracking taking place; the octane number on the other hand will increase owing to the concentration effect and the increase in absolute quantity of aromatics formed.

CHAPTER II

LITERATURE REVIEW

An effective kinetic reforming model must properly represent all the major types of reactions, recognize the fact this is a solid catalyzed gas phase reaction system, and account at least for the most important classes of chemical species present in the reaction mixture. The large number of reactions and hundreds of components taking part in the actual reaction system make this a rather complex problem.

To reduce the complexity of the model to a manageable level, the large numbers of chemical components are assigned to a smaller set of kinetic lumps, each composed of chemical species grouped together according to some criteria.

As a first significant attempt at delumping naphtha into different constituents, Smith (1959) considered naphtha consisting of three basic components: paraffins, naphthenes and aromatics. In a more extensive attempt to model reforming reactions of whole naphtha, Krane et al (1960) recognized the presence of various carbon numbers from C6 to C10 as well as the difference between paraffins, naphthenes and aromatics within each carbon number group.

Kmak (1970), presented the first endeavor to incorporate the catalytic nature of the reaction by deriving a reaction scheme with Hougen-Watson Langmuir-Hinshelwood type of kinetics. In another notable effort, Ramage et al. (1987) Developed a detailed kinetic model based on extensive studies of an industrial pilot-plant reactor.

The Kmak (1972) model was later refined by Marin and coworkers (1983), who presented the reaction network for whole naphtha, containing hydrocarbons in the carbon-number fraction from C₅ to C₁₀. The reaction networks include 23 pseudo components and used Hougen-Watson type rate reaction.

Marin and Forment (1982) and Van Trimpom et al. (1988) also conducted separate studies on C₆ to C₇ carbon-number fractions, respectively, and developed the corresponding Hougen-Watson type rate equations.

Taskar and Riggs (1997) developed a detailed kinetic scheme involving 35 pseudocomponents connected by a network of 36 reactions in the C₅ –C₁₀ range was modeled using Hougen-Watson Langmuir-Hinshelwood-type reaction rate expressions.

Garimella and Chaudhuri (1997) also developed a detailed kinetic scheme involving 26 lumps in the carbon range C₆-C₉. The naphtha feed has been characterized by naphthenes (alkyl cyclohexanes and alkyl cyclopentanes), paraffins (normal paraffins and isoparaffins) and Aromatics.

But in the absence of published data on kinetics of the reactions of the lump undergo, it was not possible to use either the Mobil or the Kmak model in the present study.

On the other hand, Riggs et al model is probably the detailed one which considers the larger number of lumps viz. Paraffins, naphthenes and aromatics. This means that within a class of hydrocarbons distinction is made on the basis of number of carbon atoms.

Another implication, that five and six ring naphthenes are also lumped separately, is open to criticism in view of the fact the latter is known to be much more reactive than the formation of aromatics Kuo and Wei (1969). However its simplicity and elegance turn out to be extremely advantageous in the wake of paucity of data if one is ready to give up a little bit of exactitude in predicating plant performance.

In the present study, Modified Taskar and Riggs(1997) model has been used successfully to predict plant performance for different cases.

CHAPTER III

THE MODEL

3.1 LUMPING OF NAPHTHA FEED:

Naphtha being a complex mixture of hydrocarbons, under goes variety of reactions. So it is not practical to identify all the constituent components of naphtha and account for the reactions they may undergo, so the complete, the detailed reaction model symbolizing the main reforming reactions of the components of naphtha with carbon numbers from C_5 to C_{10} connected of a total of 33 components connected together by a network of 37 reactions. As an example the figure 3.1, shows the reaction path for C_8 . The components are listed in the table 3.1, the paraffins, naphthenes and aromatics within each carbon number fraction were treated separately. The paraffins in each carbon group were considered into there individual components; straight chain, single branched, and multi branched. The five-carbon ring naphthenes were considered differently than the six-carbon ring naphthenes.

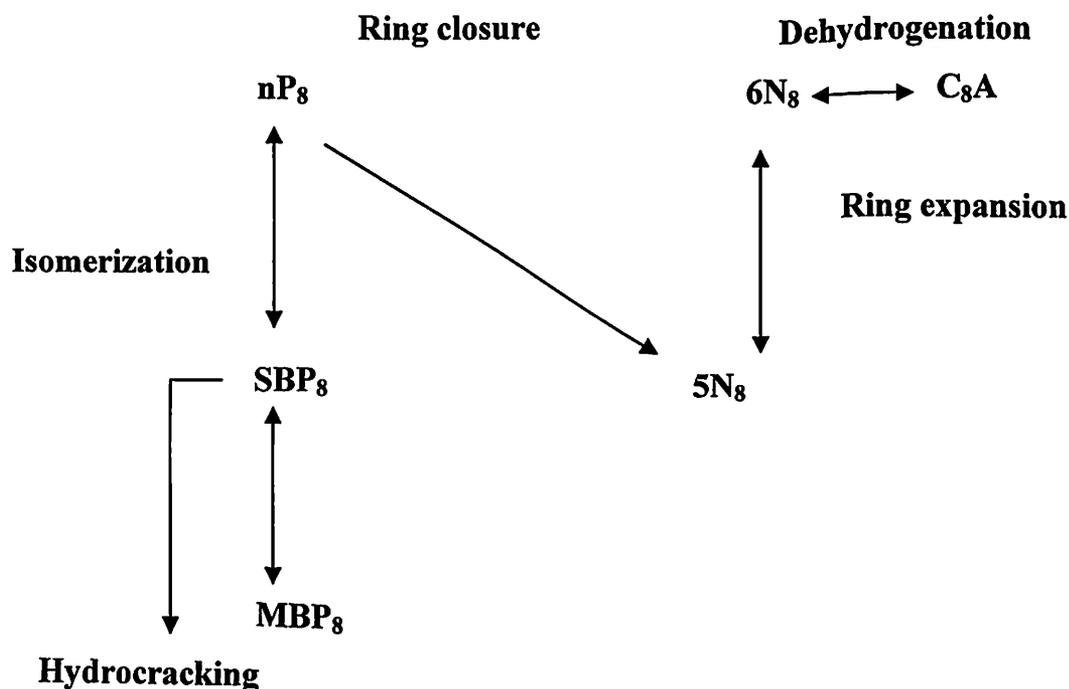


Fig 3.1 Reaction path for C_8 fraction

Chemical components
<i>C₅ fraction</i>
n-Pentane Single branched Pentane
<i>C₆ fraction</i>
n-Hexane Single branched Hexanes Multi branched Hexanes Five carbon ring C ₆ naphthenes C ₆ Aromatics
<i>C₇ fraction</i>
n-Heptane Single branched Heptanes Multi branched Heptanes Five carbon ring C ₇ naphthenes Six carbon ring C ₇ naphthenes C ₇ Aromatics
<i>C₈ fraction</i>
n-Octane Single branched Octane Multi branched Octane Five carbon ring C ₈ naphthenes Six carbon ring C ₈ naphthenes C ₈ Aromatics
<i>C₉ fraction</i>
n-Nonane Single branched Nonane Multi branched Nonane Five carbon ring C ₉ naphthenes Six carbon ring C ₉ naphthenes C ₉ Aromatics

<i>C₁₀ fraction</i>
n-Decane
Single branched Decane
Multi branched Decane
Five carbon ring C ₁₀ naphthenes
Six carbon ring C ₁₀ naphthenes
C ₁₀ Aromatics
<i>Cracked light gases</i>

Table 3.1 Chemical components

3.2 REACTIONS AND THEIR KINETICS

The reactions accounted in the model are

Dehydrogenation of naphthenes

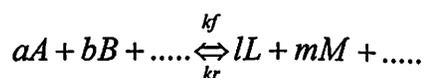
Isomerization of paraffins

Isomerization of naphthenes (ring expansion)

Dehydrocyclization of paraffins (ring closure) and

Hydrocracking of paraffins and naphthenes

Though the reactions are heterogeneously catalyzed, they are assumed to follow homogeneous kinetics. For a reversible reaction such as



Assuming the ideal gas law to hold, the general rate expression can be written as

$$-\left(\frac{dN_A}{dV_R}\right) = k_f P_A^a P_B^b \dots - k_r P_L^l P_M^m \dots$$

For the rate constant, a modified Arrhenius type rate expression is assumed to apply, i.e.,

$$k_f = k_{of} \exp\left(\frac{-E}{RT}\right) A_c$$

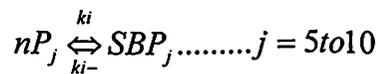
The pre-exponential factor is a function of molarity of the reaction but it is independent of the catalyst used. The values of these factors reported by Garimella and Chaudhuri (1997), Taskar and Riggs (1997) have been used in this model. The A_c in the expression for the rate constant accounts for the catalyst activity, which declines with catalyst age.

Ideally, the model should have provision for individually accounting for the activity declines of Pt.- Al_2O_3 . But since the plant data available were for the fresh catalyst and were not over the extended period, both the declines were lumped together as a parameter varying between 1 and 0. It has been assumed that the cycle last for six months, at the end of which the catalyst is regenerated.

At the end of each cycle the catalyst activity declines to 93% of the value at the start of the cycle and after regeneration, retains 98% of the start of the cycle value. These values are chosen on the basis of the plant experience.

3.2.1 Isomerization reaction

Normal paraffins



The rate of disappearance of normal paraffins is given by

$$-\left(\frac{dN_{nP_j}}{dV_R}\right) = k_i \left(P_{nP_i} - \frac{P_{SBP_j}}{K_{eqi}} \right) = r_i \dots \dots \dots i = 1, 2, 4, 6, 8, 10$$

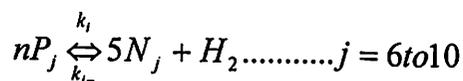
Isoparaffins



The rate of disappearance of Isoparaffins is given by

$$-\left(\frac{dN_{SBP_j}}{dV_R}\right) = k_i \left(P_{SBP_j} - \frac{P_{MBP_j}}{K_{eqi}} \right) = r_i \dots \dots \dots i = 3, 5, 7, 9, 11$$

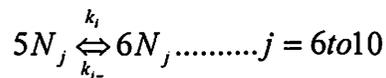
3.2.2 Dehydro cyclization (ring closure)



The rate of disappearance of normal paraffins is given by

$$-\left(\frac{dN_{nP_j}}{dV_R}\right) = k_i \left(P_{nP_j} - \frac{P_{5N_j} P_{H_2}}{K_{eqi}} \right) = r_i \dots \dots \dots i = 12 \text{ to } 16$$

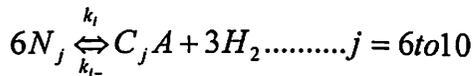
3.2.3 Ring expansion



The rate of disappearance of 5N_j is given by

$$-\left(\frac{dN_{5N_j}}{dV_R}\right) = k_i \left(P_{5N_j} - \frac{P_{6N_j}}{K_{eqi}} \right) = r_i \dots \dots \dots i = 17 \text{ to } 21$$

3.2.4 Dehydrogenation

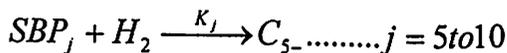


The rate of disappearance of 6N_j is given by

$$-\left(\frac{dN_{6N_j}}{dV_R}\right) = k_i \left(P_{6N_j} - \frac{P_{C_j A} P_{H_2}^3}{K_{eqi}} \right) = r_i \dots \dots \dots i = 22 \text{ to } 26$$

3.2.5 HYDROCRACKING

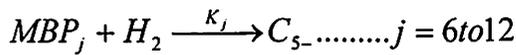
Single branched paraffins



The rate of disappearance of Single branched paraffins is given by

$$-\left(\frac{dN_{SBP_j}}{dV_R}\right) = k_i \left(\frac{P_{SBP_j}}{P_T} \right) = r_i \dots \dots \dots i = 27, 28, 30, 32, 34, 36$$

Multi branched paraffins



The rate of disappearance of Multi branched paraffins is given by

$$-\left(\frac{dN_{MBP_j}}{dV_R}\right) = k_j \left(\frac{P_{MBP_j}}{P_T}\right) = r_i \dots \dots \dots i = 29, 31, 33, 35, 37$$

3.3 MATERIAL BALANCE EQUATIONS:

$$\left(\frac{dN_{nPS}}{dV_R}\right) = -r_1 \dots \dots \dots (1)$$

$$\left(\frac{dN_{IP}}{dV_R}\right) = +r_1 - r_{27} \dots \dots \dots (2)$$

$$\left(\frac{dN_{nPS6}}{dV_R}\right) = -r_2 - r_{12} \dots \dots \dots (3)$$

$$\left(\frac{dN_{SBP_6}}{dV_R}\right) = -r_2 - r_3 - r_{28} \dots \dots \dots (4)$$

$$\left(\frac{dN_{MBP_6}}{dV_R}\right) = +r_3 - r_{29} \dots \dots \dots (5)$$

$$\left(\frac{dN_{nPS7}}{dV_R}\right) = -r_4 - r_{13} \dots \dots \dots (6)$$

$$\left(\frac{dN_{SBP_7}}{dV_R}\right) = +r_4 - r_5 - r_{30} \dots \dots \dots (7)$$

$$\left(\frac{dN_{MBP_7}}{dV_R}\right) = +r_5 - r_{31} \dots \dots \dots (8)$$

$$\left(\frac{dN_{nP8}}{dV_R}\right) = -r_6 - r_{14} \dots\dots\dots(9)$$

$$\left(\frac{dN_{SBP_8}}{dV_R}\right) = +r_6 - r_7 - r_{32} \dots\dots\dots(10)$$

$$\left(\frac{dN_{MBR_8}}{dV_R}\right) = +r_7 - r_{33} \dots\dots\dots(11)$$

$$\left(\frac{dN_{nP9}}{dV_R}\right) = -r_8 - r_{15} \dots\dots\dots(12)$$

$$\left(\frac{dN_{SBP_9}}{dV_R}\right) = +r_8 - r_9 - r_{34} \dots\dots\dots(13)$$

$$\left(\frac{dN_{MBR_9}}{dV_R}\right) = +r_9 - r_{35} \dots\dots\dots(14)$$

$$\left(\frac{dN_{nP10}}{dV_R}\right) = -r_{10} - r_{16} \dots\dots\dots(15)$$

$$\left(\frac{dN_{SBP_{10}}}{dV_R}\right) = +r_{10} - r_{11} - r_{36} \dots\dots\dots(16)$$

$$\left(\frac{dN_{MBR_{10}}}{dV_R}\right) = +r_{11} - r_{37} \dots\dots\dots(17)$$

$$\left(\frac{dN_{5N_6}}{dV_R}\right) = +r_{12} - r_{17} \dots\dots\dots(18)$$

$$\left(\frac{dN_{5N_7}}{dV_R}\right) = +r_{13} - r_{18} \dots\dots\dots(19)$$

$$\left(\frac{dN_{5N_8}}{dV_R}\right) = +r_{14} - r_{19} \dots\dots\dots(20)$$

$$\left(\frac{dN_{5N_9}}{dV_R}\right) = +r_{15} - r_{20} \dots\dots\dots(21)$$

$$\left(\frac{dN_{5N_{10}}}{dV_R}\right) = +r_{16} - r_{21} \dots\dots\dots(22)$$

$$\left(\frac{dN_{6N_6}}{dV_R}\right) = +r_{17} - r_{22} \dots\dots\dots(23)$$

$$\left(\frac{dN_{6N_7}}{dV_R}\right) = +r_{18} - r_{23} \dots\dots\dots(24)$$

$$\left(\frac{dN_{6N_8}}{dV_R}\right) = +r_{19} - r_{24} \dots\dots\dots(25)$$

$$\left(\frac{dN_{6N_9}}{dV_R}\right) = +r_{20} - r_{25} \dots\dots\dots(26)$$

$$\left(\frac{dN_{6N_{10}}}{dV_R}\right) = +r_{21} - r_{26} \dots\dots\dots(27)$$

$$\left(\frac{dN_{C_6A}}{dV_R}\right) = +r_{22} \dots\dots\dots(28)$$

$$\left(\frac{dN_{C_7A}}{dV_R}\right) = +r_{23} \dots\dots\dots(29)$$

$$\left(\frac{dN_{C_8A}}{dV_R}\right) = +r_{24} \dots \dots \dots (30)$$

$$\left(\frac{dN_{C_9A}}{dV_R}\right) = +r_{25} \dots \dots \dots (31)$$

$$\left(\frac{dN_{C_{10}A}}{dV_R}\right) = +r_{26} \dots \dots \dots (32)$$

$$\left(\frac{dN_{H_2}}{dV_R}\right) = +r_{12} + r_{13} + r_{14} + r_{15} + r_{16} + 3r_{22} + 3r_{23} + 3r_{24} + 3r_{25} + 3r_{26} - \left(\frac{r}{3}\right) \cdot (r_{27} + r_{28} + r_{29} + r_{30} + r_{31} + r_{32} + r_{33} + r_{34} + r_{35} + r_{36} + r_{37}) \dots \dots \dots (33)$$

3.4 HEAT BALANCE EQUATION

$$\left(\frac{dT}{dV_R}\right) = \sum_{i=1}^{37} \frac{\Delta H_i}{N_T(mw)_R c_p} (r_i) \dots \dots \dots (34)$$

3.5 MODEL PARAMETER ESTIMATION

The objective of this study was to use the model, it was therefore essential to benchmark the model against data obtained from the industrial unit. The choice of kinetic-rate parameters are adjustable parameters in the model was quite obvious since the values are seldom known exactly for the given system. The base-case operating conditions chosen for model parameter estimation are listed in table 3.2

	Units	Feed	Reformat
ASTM D-86 DISTILLATION			
IBP	°C	91.0	47.4
10%	°C	97.4	84.1
30%	°C	101.6	117.8
50%	°C	107.0	133.6
70%	°C	113.6	146.3
90%	°C	125.9	164.3
FBP	°C	140.6	211.9
API Gravity		63.9	53.5
PNA Analysis			
Paraffins (P)	mol%	68.354	49.24
Naphthenes (N)	mol%	21.038	3.11
Aromatics (A)	mol%	10.592	48.62

Table 3.2

Since we have only limited amount of data available for benchmarking, the number of unknown coefficients was more than the number of independent measurements available. Therefore, the number of unknown kinetic parameters in the model had to be reduced. This was accomplished by following certain guidelines or heuristic rules that were developed from the large amount of information published in the past on the chemistry and relative rates of various reforming reactions (Hettinger et al., 1955; Riggs et al., 1997). These guidelines are, within a given carbon number fraction, Rate constants for all paraffin isomerization reactions were assumed to be equal. Similarly, rate constants for all the hydrocracking reactions with in a carbon number fraction were considered to be equal.

The activation energies of the paraffin isomerization reactions were considered to be equal irrespective of the carbon number. Similar arguments were also extended for all other reactions.

The Heat of formation, Gibbs free energy of formation is taken from the book "Thermodynamics of chemical process" Zhorov (1987). The equilibrium constants are calculated from thermodynamic relation $\Delta G^\circ = -RT \ln K$. The rate constants follow an

Arrhenius relation, $k = k_0 \exp(-E/RT)$.

The kinetic parameters, k_0 and E , are taken from the literature Garimella and chaudhuri (1997); Taskar and Riggs (1997) and from literature data as an initial basis and these are fine-tuned to the commercial plant data. The operating and performance data of present commercial reformer are used to estimate the kinetic parameters by fine-tuning. The fine-tuning is done by minimization of the sum of the squares of the deviations between the plant and calculated values of aromatics conversion and temperature drops across each reactor for the given set of operating conditions corresponding to start of cycle.

The values of heat of reaction, activation energy and pre-exponential factor to calculate rate constants of various reforming reactions used in the model are presented in the Table. Table gives constants used to calculate equilibrium constants of reversible reactions. The equations 1 to 34 are integrated using 4th order Runge-Kutta method to obtain the calculated values of aromatics, naphthenes and paraffins at any point of the reactor volume.

TABLE 3.3: HEAT OF REACTION, E/R AND LN A VALUES

		ΔH KJ/mol	$(E/R)*10^{-3}$ K	ln A kmol/h.kg cat.kpa
Isomerization	nP ₅	-6.732	26.0	24.18
	nP ₆	-6.699	26.0	22.18
	SBP ₆	-6.699	26.0	19.87
	nP ₇	-6.364	26.0	23.38
	SBP ₇	-6.364	26.0	21.08
	nP ₈	-5.945	26.0	22.58
	SBP ₈	-5.945	26.0	20.27
	nP ₉	-5.623	26.0	22.58
	SBP ₉	-5.623	26.0	20.27
	nP ₁₀	-5.319	26.0	25.18
SBP ₁₀	-5.319	26.0	25.18	
Dehydrocyclization	nP ₆	60.19	33.11	31.76
	nP ₇	60.38	33.11	30.32
	nP ₈	60.17	33.11	32.47
	nP ₉	60.38	33.11	32.42
	nP ₁₀	60.97	33.11	30.66
Ring expansion	5N ₆	-14.6	23.81	20.92
	5N ₇	-23	23.81	20.92
	5N ₈	-18.4	23.81	20.92
	5N ₉	-18.8	23.81	19.84
	5N ₁₀	-16.5	23.81	19.84
Dehydrogenation	6N ₆	73.52	19.5	17.06
	6N ₇	71.89	19.5	16.85
	6N ₈	67.24	19.5	16.85
	6N ₉	65.23	19.5	16.86
	6N ₁₀	63.17	19.5	17.89
Hydrocracking	SBP ₅	-48.43	34.61	30.29
	SBP ₆	-49.66	34.61	28.99
	MBP ₆	-49.66	34.61	31.29
	SBP ₇	-50.91	34.61	26.78

Hydrocracking	MBP ₇	-50.91	34.61	29.09
	SBP ₈	-51.67	34.61	26.88
	MBP ₈	-51.67	34.61	26.88
	SBP ₉	-52.17	34.61	28.68
	MBP ₉	-52.17	34.61	28.68
	SBP ₁₀	-53.28	34.61	28.68
	MBP ₁₀	-53.28	34.61	28.68

TABLE 3.4: EQUILIBRIUM CONSTANTS

$K_{eq}=\exp(A^1/B^1/T)$	Units	A ¹	B ¹
Dehydrogenation			
$6N_6 \leftrightarrow C_6A$	kpa ³	69.4706	25240.93
$6N_7 \leftrightarrow C_7A$	kpa ³	71.5908	25430.21
$6N_8 \leftrightarrow C_8A$	kpa ³	71.1909	23973.97
$6N_9 \leftrightarrow C_9A$	kpa ³	69.7522	23911.64
$6N_{10} \leftrightarrow C_{10}A$	kpa ³	69.7522	23911.64
Dehydrocyclization			
$nP_6 \leftrightarrow 5N_6 + H_2$	kpa ⁻¹	20.0041	5869.89
$nP_7 \leftrightarrow 5N_7 + H_2$	kpa ⁻¹	15.4514	5869.89
$nP_8 \leftrightarrow 5N_8 + H_2$	kpa ⁻¹	14.3439	5869.89
$nP_9 \leftrightarrow 5N_9 + H_2$	kpa ⁻¹	14.1796	5869.89
$nP_{10} \leftrightarrow 5N_{10} + H_2$	kpa ⁻¹	14.1796	5869.89
$K_{eq}=\exp(A^1/B^1/T)$			
Isomerization			
$nP_5 \leftrightarrow SBP_5$	-	-0.9654	1034.22
$nP_6 \leftrightarrow SBP_6$	-	-3.7185	1034.22
$SBP_6 \leftrightarrow MBP_6$	-	-2.1403	1034.22
$nP_7 \leftrightarrow SBP_7$	-	-1.6603	1034.22
$SBP_7 \leftrightarrow MBP_7$	-	-1.8025	1034.22

$nP_8 \leftrightarrow SBP_8$	-	0.4601	1034.22
$SBP_8 \leftrightarrow MBP_8$	-	0.2552	1034.22
$nP_9 \leftrightarrow SBP_9$	-	0.3648	1034.22
$SBP_9 \leftrightarrow MBP_9$	-	-1.3298	1034.22
$nP_{10} \leftrightarrow SBP_{10}$	-	-0.3879	1034.22
$SBP_{10} \leftrightarrow MBP_{60}$	-	0.4515	1034.22
Ring expansion			
$5N_6 \leftrightarrow 6N_6$	-	9.8679	2487.71
$5N_7 \leftrightarrow 6N_7$	-	13.9325	2487.71
$5N_8 \leftrightarrow 6N_8$	-	15.0063	2487.71
$5N_9 \leftrightarrow 6N_9$	-	16.6837	2487.71
$5N_{10} \leftrightarrow 6N_{10}$	-	13.6086	2487.71

3.6 VALIDATION OF THE MODEL:

The model is validated against different cases of plant data which make use of varying naphtha composition as feed.

CASE-I

Feed : straight run naphtha
Catalyst : Pt-Re/Al₂O₃
Feed rate : 3 m³/hr
H₂/HC : 5.3-6.3
H₂ Recycled : 17.5 kN m³/hr
H₂ purity : 72.0%

TABLE 3.5: REFINERY OPERATING CONDITIONS DATA FOR CASE-I

Reactor	Temperature, °K	Catalyst, kg	Pressure, kg/cm ²
R-I	783	1160	27.5
R-II	772	2460	27.5
R-III	772	2460	27.5

TABLE 3.6: DHA DATA OF FEED AND REFORMATE FOR CASE I

Components	Feed, mol%	Reformate, mol%
nP ₅	0.026	0.014
SBP ₅	0.003	0.022
nP ₆	6.54	3.89
SBP ₆	3.46	5.67
MBP ₆	0.302	1.78
nP ₇	13.02	5.17
SBP ₇	7.25	8.67
MBP ₇	1.37	2.79
nP ₈	12.08	2.25
SBP ₈	9.02	4.83
MBP ₈	3.02	1.68
nP ₉	2.61	0.99
SBP ₉	4.06	5.23
MBP ₉	3.71	4.23
nP ₁₀	0.056	0.09
SBP ₁₀	1.09	1.25
MBP ₁₀	0.471	0.69

5N ₆	1.48	0.04
5N ₇	3.65	0.012
5N ₈	4.04	0.59
5N ₉	0.42	0.12
5N ₁₀	0.008	0.003
6N ₆	1.43	0.64
6N ₇	3.86	0.41
6N ₈	3.61	0.72
6N ₉	2.62	0.57
6N ₁₀	0.011	0.005
C ₆ A	0.61	3.51
C ₇ A	4.02	15.97
C ₈ A	5.46	25.74
C ₉ A	0.303	3.37
C ₁₀ A	0.005	0.03
RON	51.104	84.373
Mol wt	106.55	95.142

TABLE 3.7: CONCENTRATION VARIATION OF C₃ FRACTION CASE I

Volume, m ³	nP ₅ , kmol/hr	IP, kmol/hr
0	0.02421	0.002748
1	0.01785	0.009052
2	0.01441	0.01248
2.72	0.01293	0.01394
4	0.01156	0.0153
5.5	0.01085	0.016
7	0.01055	0.01629
80.	0.01042	0.01641
10	0.0104	0.01642
11.5	0.01039	0.01643
13	0.01037	0.01645
14.3	0.01035	0.01651

**TABLE 3.8: COMPARISON OF CALCULATED VALUES AND PLANT
DATA OF C₅ FRACTION FOR CASE I**

Reformat	Predicted by model, %	Actual plant, %	Error, %
nP ₅	.014	.013	4.39
IP	.021	.022	2.94

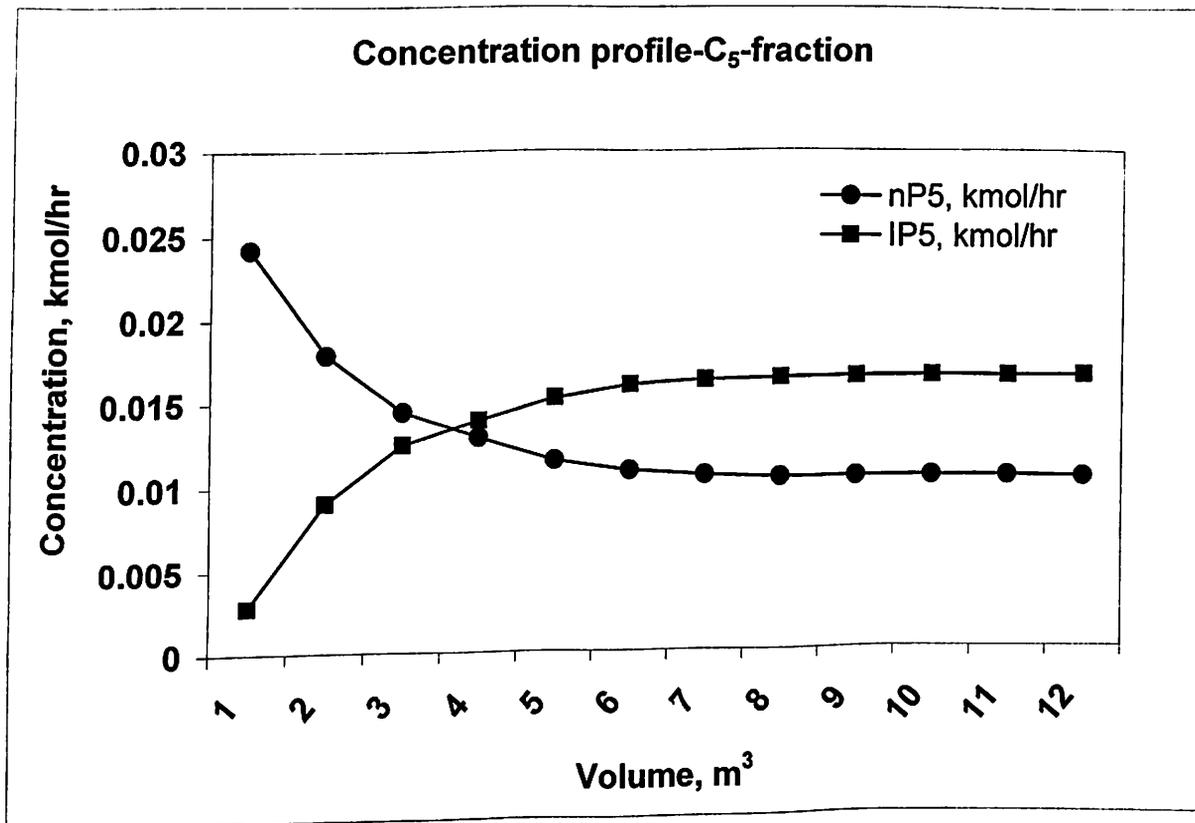


FIG 3.2: CONCENTRATION PROFILE OF C₅ FRACTION IN THE REACTOR FOR CASE-I

TABLE 3.9: CONCENTRATION VARIATION OF C₆FRACTION CASE I

Volume, m ³	nP ₆ , kmol/hr	SBP ₆ , kmol/hr	MBP ₆ , kmol/hr	5N ₆ , kmol/hr	6N ₆ , kmol/hr	C ₆ A, kmol/hr
0	5.8740	3.1075	0.2717	1.3374	1.2932	0.5521
1	5.7692	3.1961	0.2842	1.0017	0.6739	1.5071
2	5.6530	3.2833	0.3132	0.7504	0.6127	1.8196
2.72	5.5329	3.3734	0.3432	0.6095	0.57299	2.0003
4	5.2387	3.6328	0.3729	0.4212	0.5629	2.1987
5.5	4.8326	3.7831	0.4539	0.2732	0.5513	2.213
7	4.5321	3.8561	0.5353	0.1773	0.5327	2.252
8.5	4.3520	3.9326	0.5937	0.1152	0.4983	2.3777
10	3.7580	4.1597	0.6327	0.0749	0.4901	2.4972
11.5	3.4516	4.2381	0.7135	0.04878	0.4835	2.5348
13	3.2134	4.3297	0.9133	0.06159	0.4792	2.5513
14.3	2.8230	4.5326	1.324	0.0295	0.4719	2.5619

TABLE 3.10: COMPARISON OF CALCULATED VALUES AND PLANT DATA OF C₆FRACTION FOR CASE I

Reformate	Predicted by Model, %	Actual Plant, %	Error, %
nP ₆	3.65	3.89	6.14
SBP ₆	5.86	5.67	3.38
MBP ₆	1.71	1.78	3.80
5N ₆	0.038	0.04	4.62
6N ₆	0.61	0.064	4.64
C ₆ A	3.31	3.51	5.60

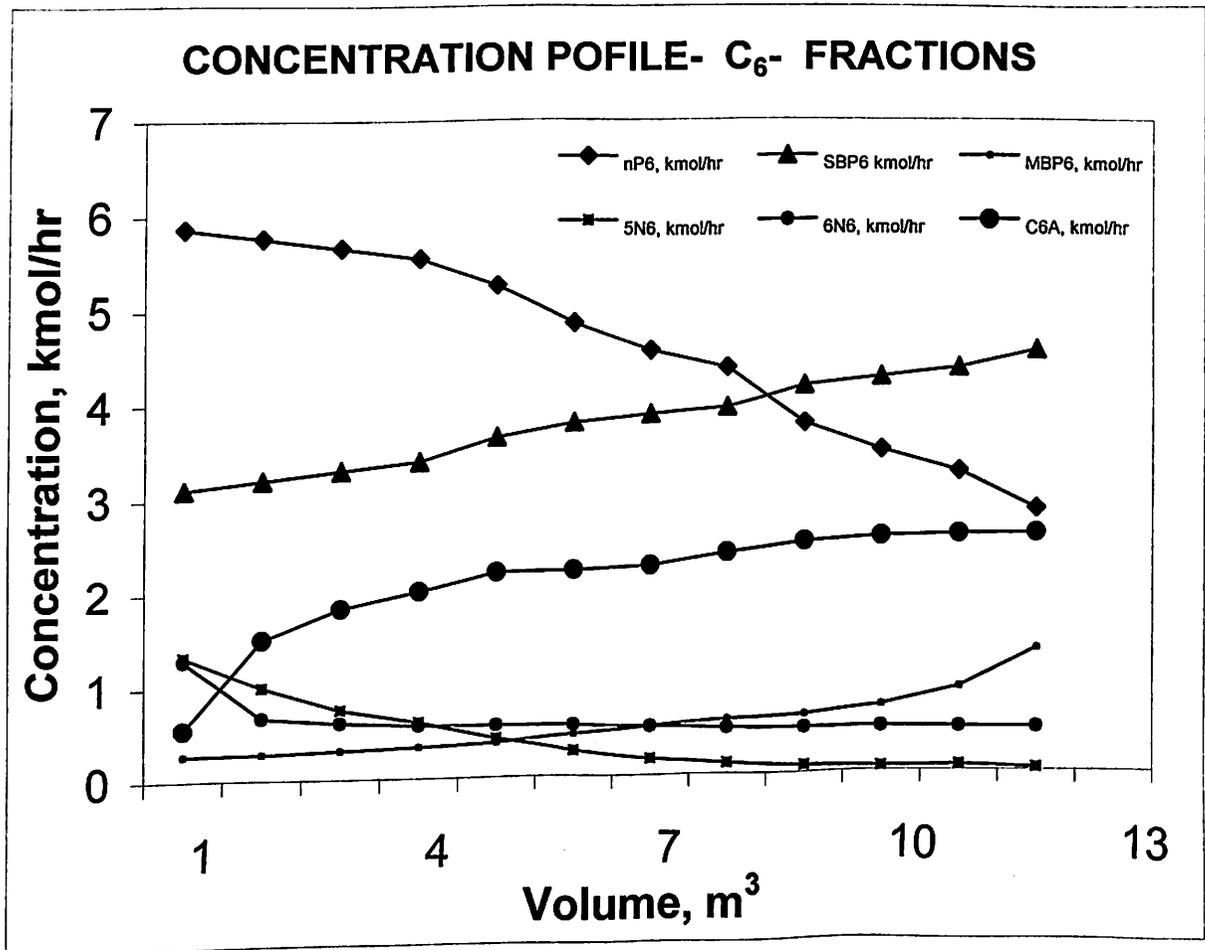


Fig 3.3: CONCENTRATION PROFILE OF C₆ FRACTION IN THE REACTOR FOR CASE I

TABLE 3.11: CONCENTRATION VARIATION OF C₇ FRACTION CASE I

Volume, m ³	nP ₇ , Kmole/hr	SBP ₇ , Kmole/hr	MBP ₇ , Kmole/hr	5N ₇ , Kmole/hr	6N ₇ , Kmole/hr	C ₇ A, Kmole/hr
0	11.704	6.5195	1.2318	3.2851	3.4695	3.6129
1	10.1619	6.5863	1.3072	2.2597	1.0155	7.9921
2	8.6177	6.6169	1.3805	1.84177	0.7765	9.84911
2.72	8.1849	6.6381	1.4321	1.4855	0.7157	10.5961
4	7.5311	6.6944	1.5195	1.0326	0.6411	11.6136
5.5	6.9671	6.7302	1.6177	0.6691	0.6023	12.2159
7	6.4021	6.7341	1.7115	0.4335	0.5695	12.5343
8.5	5.7376	6.67558	1.801	0.2809	0.4793	12.7159
10	5.2761	6.7925	1.8856	0.182	0.3295	12.8054
11.5	4.6469	6.8229	1.9665	0.1179	0.3239	12.8352
13	4.1563	6.8519	2.0103	0.0981	0.3187	12.8537
14.3	3.7325	6.9312	2.3125	0.0893	0.3015	12.8821

TABLE 3.12: COMPARISON OF CALCULATED VALUES AND PLANT DATA OF C₇ FRACTION FOR CASE I

Reformate	Predicted by Model, %	Actual Plant, %	Error, %
nP ₇	4.82	5.17	6.63
SBP ₇	8.96	8.67	3.38
MBP ₇	2.99	2.79	7.19
5N ₇	0.115	0.12	3.76
6N ₇	0.389	0.41	4.89
C ₇ A	16.66	15.97	4.32

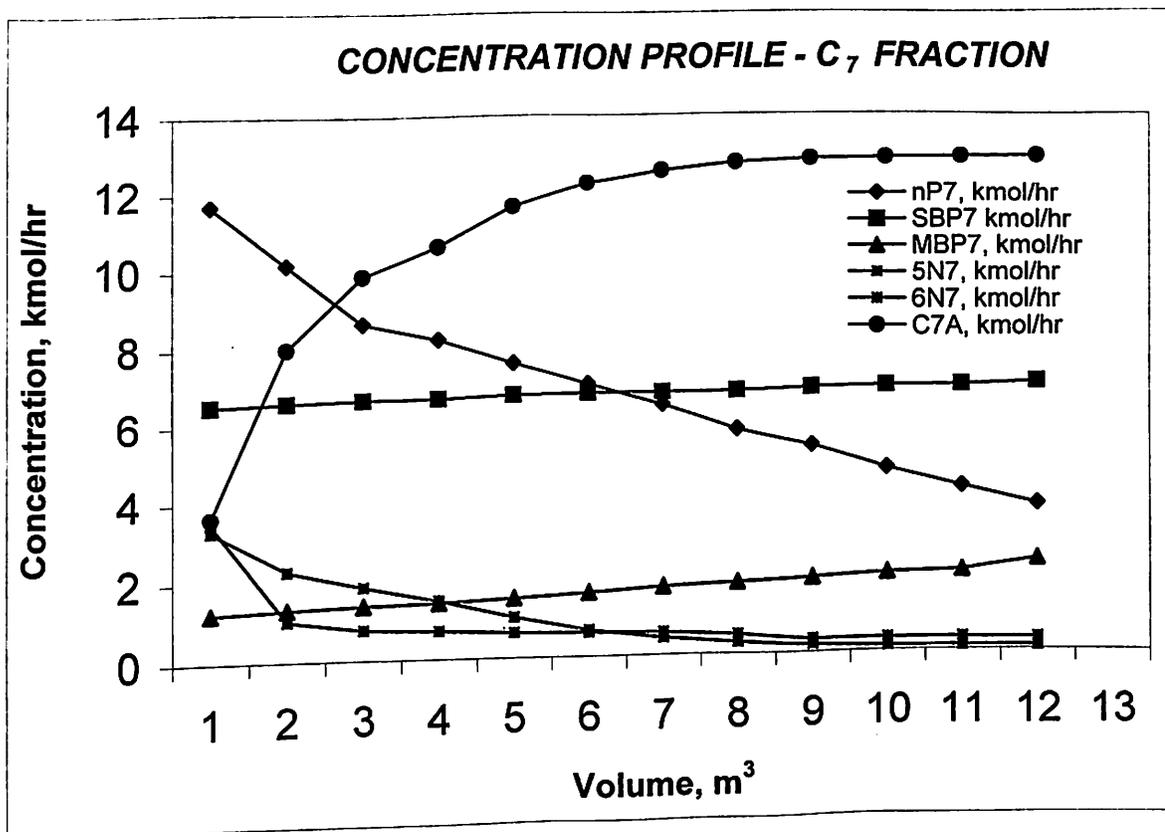


FIG 3.4: CONCENTRATION PROFILE OF C₇ FRACTION IN THE REACTOR FOR CASE-I

TABLE 3.13: CONCENTRATION VARIATION OF C₈ FRACTION CASE I

Volume, m ³	nP ₈ , kmol/hr	SBP ₈ , kmol/hr	MBP ₈ , kmol/hr	5N ₈ , kmol/hr	6N ₈ , kmol/hr	C ₈ A, kmol/hr
0	10.8587	8.1108	2.7172	3.6348	3.2411	4.9132
1	9.8765	7.9854	2.6751	1.3546	0.9185	10.616
2	9.1532	7.4529	2.1342	1.0107	0.8763	12.3988
2.72	8.5637	7.2691	1.9775	0.7324	0.7938	13.3093
4	7.6598	6.7656	1.9558	0.6953	0.7654	14.4039
5.5	6.8327	6.1818	1.8497	0.5877	0.7323	15.3616
7	5.7681	5.483	1.7458	0.4783	0.6987	16.4719
8.5	4.9325	4.8707	1.6439	0.4652	0.6105	17.0123
10	3.7567	4.544	1.5438	0.4519	0.5136	17.7251
11.5	2.9539	4.3053	1.4454	0.4437	0.5138	18.3267
13	2.4853	3.9165	1.4173	0.4412	0.5131	18.4873
14.3	1.6357	3.5319	1.3194	0.4387	0.5017	18.6234

TABLE 3.14: COMPARISON OF CALCULATED VALUES AND PLANT DATA OF C₈ FRACTION FOR CASE I

Reformate	Predicted by Model, %	Actual Plant, %	Error, %
nP ₈	2.11	2.25	5.98
SBP ₈	4.56	4.83	5.43
MBP ₈	1.71	1.68	1.56
5N ₈	0.567	0.59	3.83
6N ₈	0.648	0.71	8.61
C ₈ A	24.08	25.74	6.42

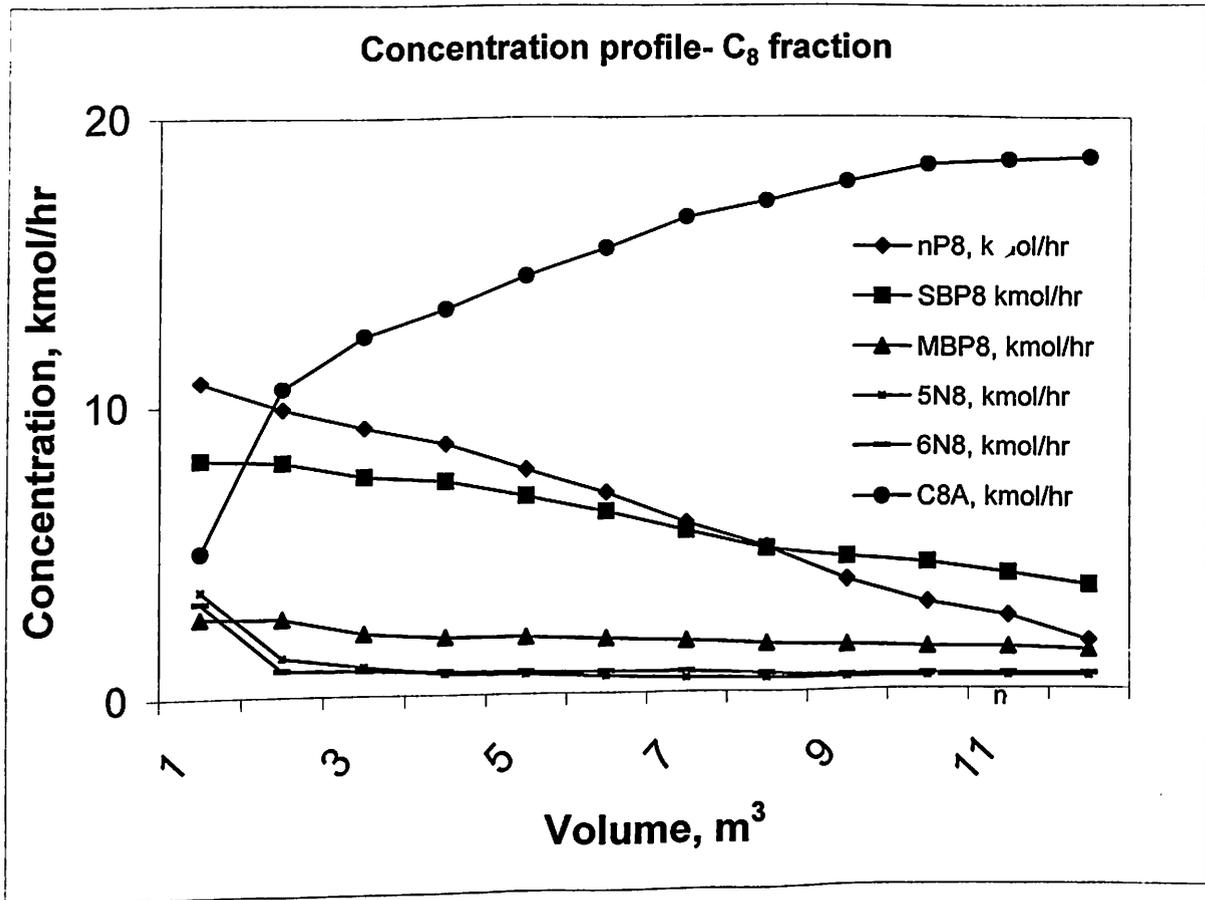


FIG 3.5: CONCENTRATION PROFILE OF C₈ FRACTION IN THE REACTOR FOR CASE-I

TABLE 3.15: CONCENTRATION VARIATION OF C₉ FRACTION CASE I

Volume, m ³	nP ₉ , kmol/hr	SBP ₉ , kmol/hr	MBP ₉ , kmol/hr	5N ₉ , kmol/hr	6N ₉ , kmol/hr	C ₉ A, kmol/hr
0	2.3475	3.6482	3.3373	0.3776	2.6263	0.273
1	2.3063	3.6868	3.3395	0.3424	1.0808	1.8326
2	2.1661	3.7238	3.3423	0.3104	0.90315	2.0301
2.72	2.0378	3.7495	3.3446	0.2892	0.8392	2.1248
4	1.8938	3.7938	3.3484	0.2551	0.7433	2.2542
5.5	1.7349	3.8429	3.3585	0.2202	0.5694	2.462
7	1.5826	3.8892	3.3593	0.1901	0.5575	2.464
8.5	1.3325	3.9328	3.3656	0.1641	0.5497	2.5378
10	1.1848	3.974	3.3719	0.1416	0.4826	2.6271
11.5	0.9939	4.0127	3.3787	0.1179	0.475	2.6541
13	0.8794	4.1293	3.4351	0.1007	0.457	2.6813
14.3	0.7319	4.3147	3.4519	0.0857	0.433	2.7389

TABLE 3.16: COMPARISON OF CALCULATED VALUES AND PLANT DATA OF C₉ FRACTION FOR CASE I

Reformat	Predicted by Model, %	Actual Plant, %	Error, %
nP ₉	2.11	2.25	5.98
SBP ₉	4.56	4.83	5.43
MBP ₉	1.71	1.68	1.56
5N ₉	0.567	0.59	3.83
6N ₉	0.648	0.71	8.61
C ₉ A	24.08	25.74	6.42

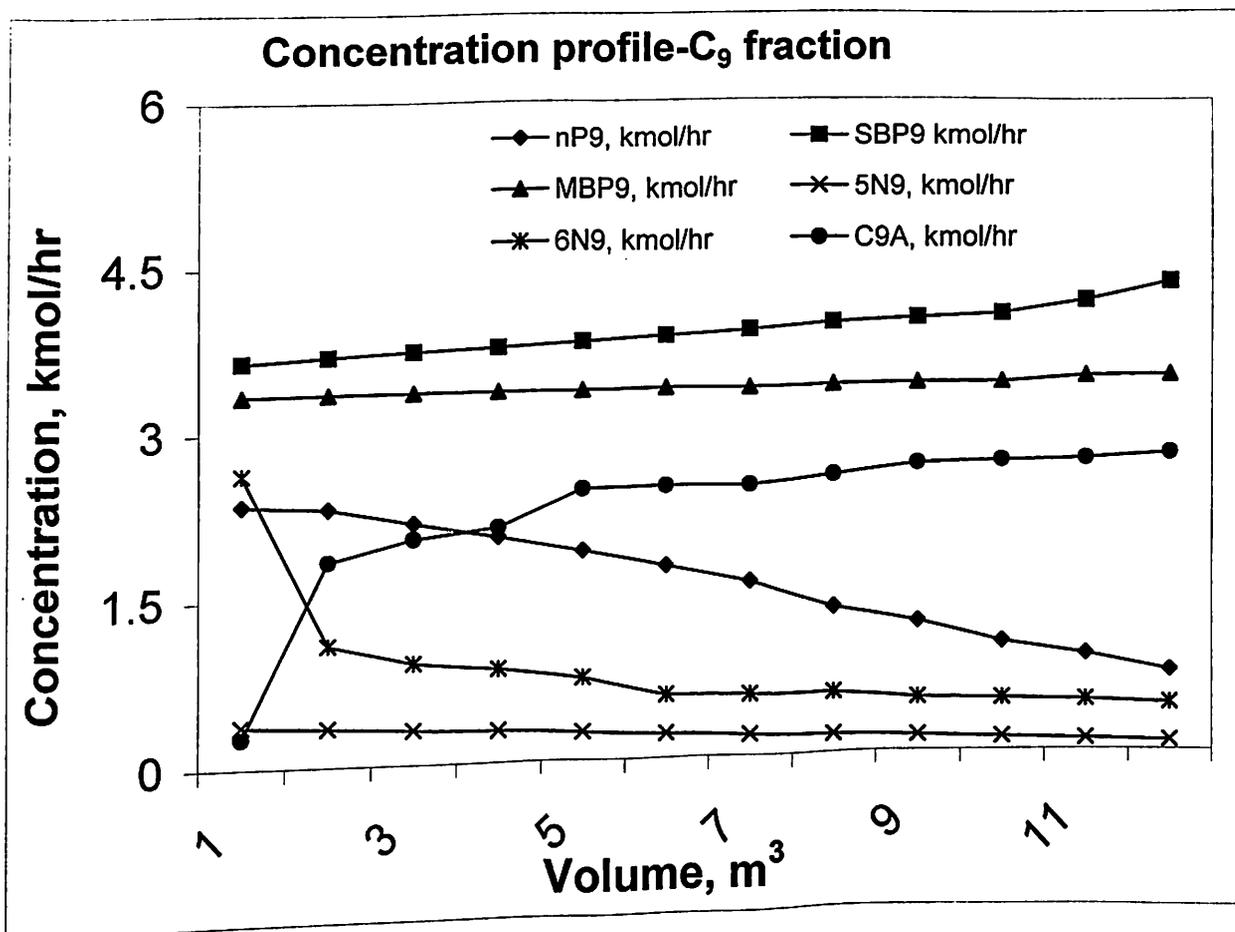


FIG 3.6: CONCENTRATION PROFILE OF C₉ FRACTION IN THE REACTOR FOR CASE-I

TABLE 3.17: CONCENTRATION VARIATION OF C₁₀ FRACTION CASE I

Volume, m ³	nP ₁₀ , kmol/hr	SBP ₁₀ , kmol/hr	MBP ₁₀ , kmol/hr	5N ₁₀ , kmol/hr	6N ₁₀ , kmol/hr	C _{10A} , kmol/hr
0	0.05097	0.9858	0.4229	0.007852	0.009815	0.0053
1	0.05218	0.9812	0.4264	0.007121	0.005745	0.01007
2	0.05336	0.9767	0.4299	0.00645	0.005729	0.01751
2.72	0.0542	0.9734	0.4324	0.00601	0.005571	0.01503
4	0.05571	0.9677	0.4369	0.005302	0.005456	0.01609
5.5	0.05745	0.9611	0.4422	0.004578	0.004836	0.01842
7	0.05916	0.9545	0.4474	0.003953	0.004561	0.01853
8.5	0.06084	0.948	0.4525	0.003413	0.004130	0.01951
10	0.0625	0.9415	0.4576	0.002946	0.003763	0.02036
11.5	0.06415	0.9351	0.4627	0.00254	0.037050	0.02082
13	0.06697	0.9263	0.4731	0.00237	0.036850	0.02097
14.3	0.06785	0.9175	0.4857	0.00228	0.003613	0.02118

TABLE 3.18: COMPARISON OF CALCULATED VALUES AND PLANT DATA OF C₁₀ FRACTION FOR CASE I

Reformat	Predicted by Model, %	Actual Plant, %	Error, %
nP ₁₀	0.087	0.09	2.50
SBP ₁₀	1.18	1.25	5.07
MBP ₁₀	0.628	0.69	8.96
5N ₁₀	0.0029	0.003	1.71
6N ₁₀	0.0046	0.005	6.54
C _{10A}	0.027	0.03	8.69

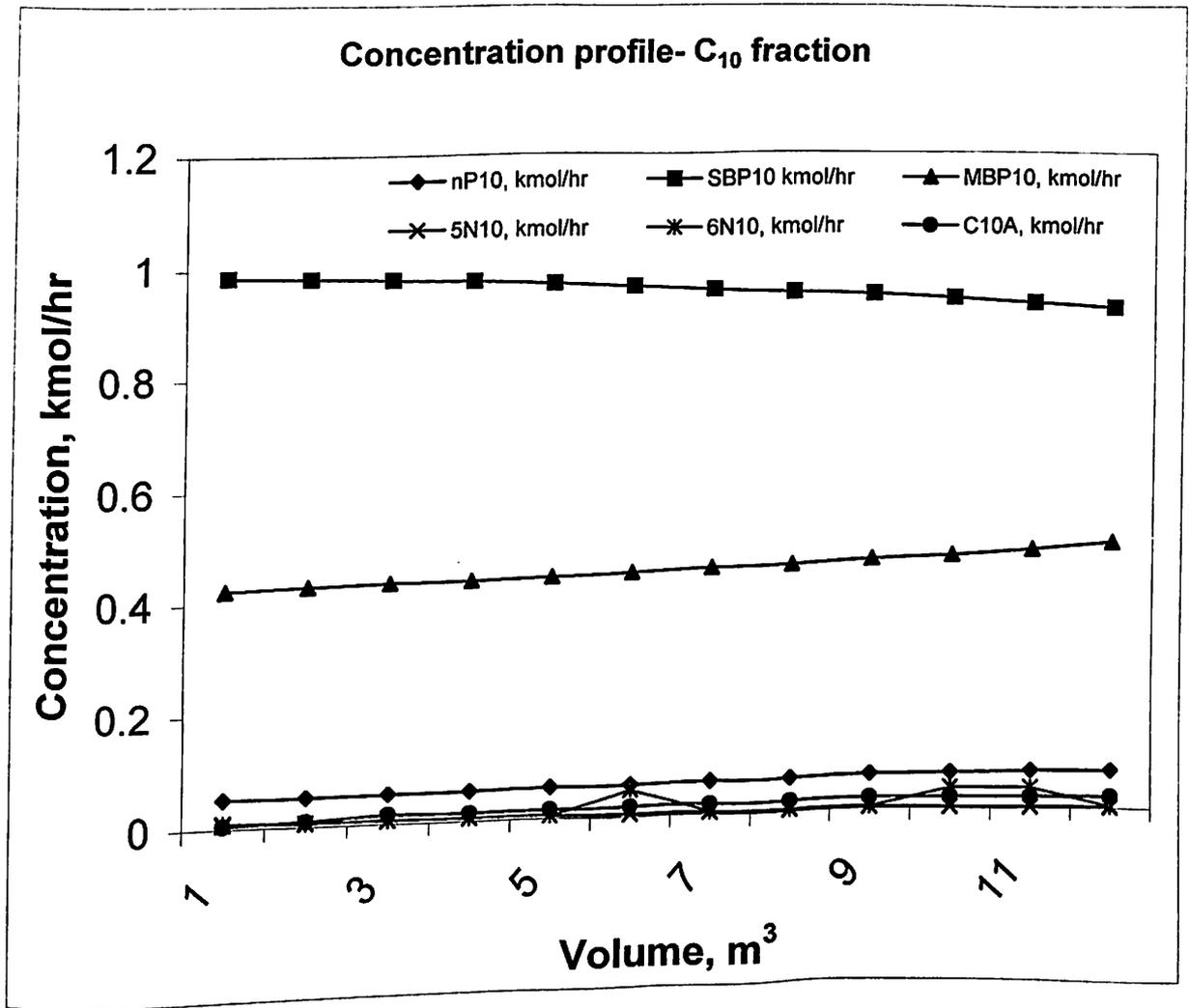


FIG 3.7: CONCENTRATION PROFILE OF C₁₀ FRACTION IN THE REACTOR FOR CASE-I

TABLE 3.19: TEMPERATURE DATA FOR CASE I

Volume, m³	Reactor 1	Reactor 2	Reactor 3
0	783		
1	771.23		
2	768.59		
2.72	763.19	772	
4		765.13	
5.5		763.59	
7		761.71	
8.5		759.76	772
10			767.93
11.5			765.18
13			764.91
14.3			763.57

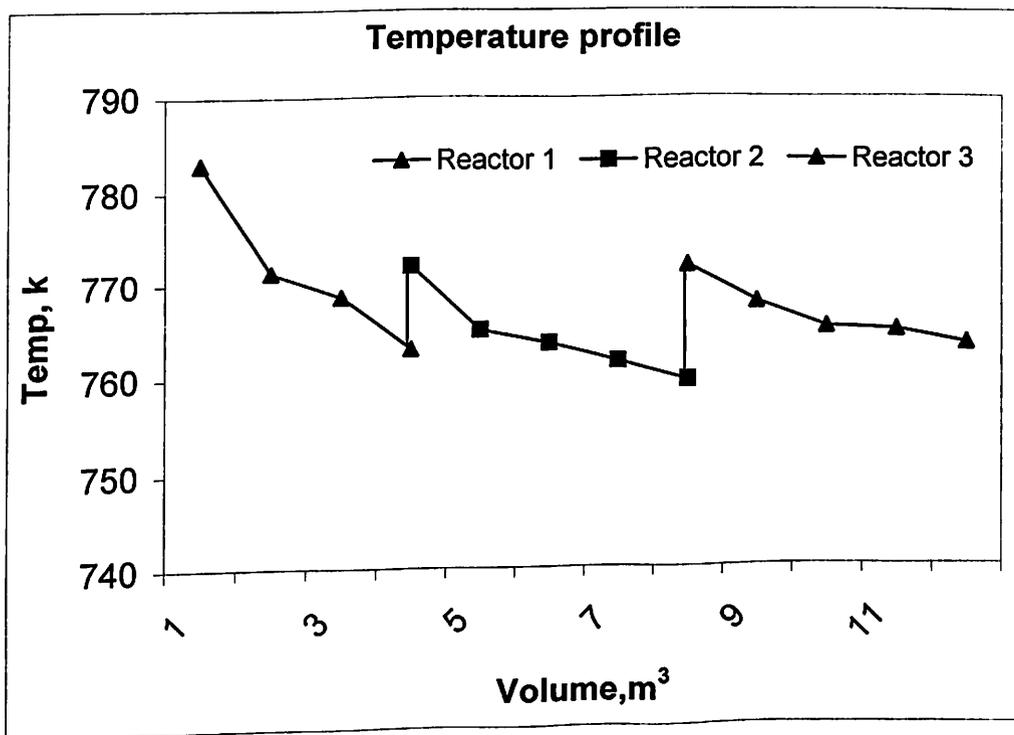


FIG 3.8: TEMPERATURE PROFILE IN THE REACTOR FOR CASE I

CASE II

Feed	:	SR Light run Naphtha
Catalyst	:	Pt-Re/Al ₂ O ₃
Feed rate	:	12.5 m ³ /hr
H ₂ /HC	:	5.3 – 6.3
H ₂ Recycled	:	17.2 kN m ₃ /hr
H ₂ Purity	:	72.0%

TABLE 3.19 : REFINERY OPERATING CONDITIONS DATA FOR CASE-II

Reactor	Temperature, °K	Catalyst, kg	Pressure, kg/cm ²
R-I	783	1160	27.5
R-II	772	2460	27.5
R-III	772	2460	27.5

TABLE 3.20 : DHA DATA OF FEED AND REFORMATE FOR CASE II

Components	Feed, mol%	Reformate, mol%
nP ₅	0	0
IP	0	0
nP ₆	5.5296	5.4618
SBP ₆	1.5454	3.1257
MBP ₆	0.0748	0.5598
nP ₇	16.2483	11.0953
SBP ₇	9.2046	14.6732
MBP ₇	1.7611	3.1590
nP ₈	9.1783	4.7185
SBP ₈	8.6659	2.6107
MBP ₈	3.1798	4.8748
nP ₉	1.2119	0.6981

SBP ₉	1.4001	2.1019
MBP ₉	1.8855	2.4127
nP ₁₀	0.0216	0.0110
SBP ₁₀	0.2822	0.0330
MBP ₁₀	0.1069	0.3500
5N ₆	1.4650	5.7200
5N ₇	3.2677	0.3700
5N ₈	3.5500	0.4118
5N ₉	0.2032	0.1241
5N ₁₀	0.1069	0.0650
6N ₆	1.6447	3.8000
6N ₇	4.1777	0.5200
6N ₈	2.4446	0.2801
6N ₉	0.3949	0.0422
6N ₁₀	0.1161	0.0310
C ₆ A	0.5454	4.5800
C ₇ A	4.3540	18.4561
C ₈ A	3.9123	18.2301
C ₉ A	0.2230	1.0246
C ₁₀ A	0	0.1500
RON	50.443	82.976
Mol wt	104.117	93.57

TABLE 3.21: CONCENTRATION VARIATION OF C₆ FRACTION CASE II

Volume, m ³	nP ₆ , Kmol/hr	SBP ₆ , Kmol/hr	MBP ₆ , Kmol/hr	5N ₆ , Kmol/hr	6N ₆ , Kmol/hr	C ₆ A, Kmol/hr
0	5.5296	1.5454	0.0748	1.465	1.6447	0.5454
1	5.4376	1.5803	0.0917	0.6973	0.932	2.0258
2	5.3557	1.6213	0.1122	0.6221	0.8598	2.1732
2.72	5.3243	1.6417	0.1204	0.5516	0.8273	2.2862
4	5.1219	1.7455	0.1597	0.5165	0.7813	2.3693
5.5	4.9192	1.8522	0.2104	0.4542	0.6888	2.5241
7	4.8065	1.9115	0.2385	0.3918	0.5388	2.7365
8.5	4.6155	2.0120	0.2863	0.3491	0.4643	2.8537
10	4.5378	2.0529	0.3057	0.2621	0.4036	3.0014
11.5	4.3128	2.1713	0.3619	0.2123	0.3613	3.0935
13	4.2251	2.2175	0.3839	0.1697	0.3367	3.1607
14.3	4.1279	2.2686	0.4082	0.1365	0.3124	3.2182

TABLE 3.22: COMPARISON OF CALCULATED VALUES AND PLANT DATA OF C₆ FRACTION FOR CASE II

Reformate	Predicted by Model, %	Actual Plant, %	Error, %
nP ₆	5.3491	5.4618	2.17
SBP ₆	2.9398	3.1257	5.94
MBP ₆	0.5289	0.5598	5.51
5N ₆	0.1768	0.1673	5.72
6N ₆	0.4048	0.39	3.80
C ₆ A	4.1703	3.9876	4.58

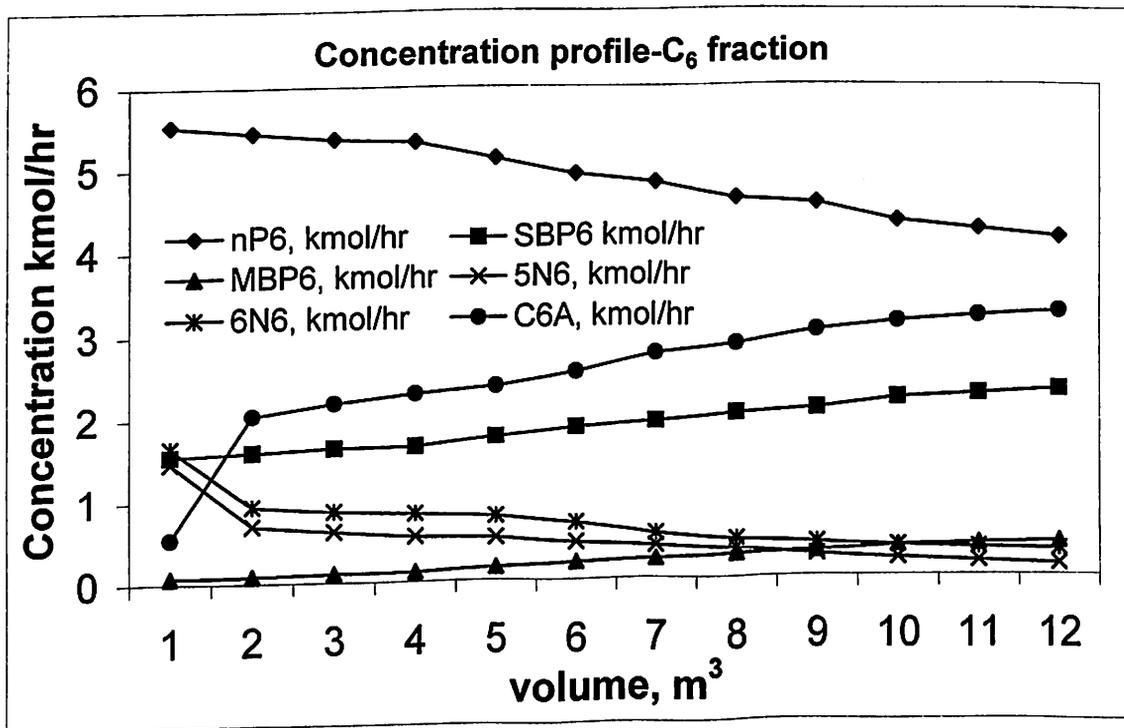


Fig 3.9: CONCENTRATION PROFILE OF C₆ FRACTION IN THE REACTOR FOR CASE II

TABLE 3.23: CONCENTRATION VARIATION OF C₇ FRACTION CASE II

Volume, m ³	nP ₇ , kmol/hr	SBP ₇ , kmol/hr	MBP ₇ , kmol/hr	5N ₇ , kmol/hr	6N ₇ , kmol/hr	C ₇ A, kmol/hr
0	16.2483	9.2046	1.7611	3.2677	4.1777	4.354
1	15.8933	9.3111	1.80015	2.4467	1.3239	8.15305
2	15.4352	9.44853	1.850541	1.8319	1.2566	8.995485
2.72	14.9914	9.58167	1.899359	1.6967	1.1783	9.364315
4	14.2171	9.81396	1.984532	1.1715	1.0353	10.30352
5.5	12.9271	10.20096	2.126432	0.7591	0.9208	11.28192
7	11.8312	10.52973	2.246981	0.6471	0.8884	11.80989
8.5	10.7962	10.84023	2.360831	0.5516	0.7219	12.43414
10	9.7113	11.1657	2.48017	0.4574	0.6103	13.01965
11.5	9.4187	11.25348	2.512356	0.3893	0.5376	13.26286
13	8.9323	11.39928	2.565816	0.3641	0.4593	13.53646
14.3	8.7593	11.4513	2.58489	0.2783	0.3987	13.74355

TABLE 3.24: COMPARISON OF CALCULATED VALUES AND PLANT DATA OF C₇ FRACTION FOR CASE II

Reformate	Predicted by Model, %	Actual Plant, %	Error, %
nP ₇	11.3507	11.0953	2.30
SBP ₇	14.8391	14.6732	1.13
MBP ₇	3.3496	3.1590	6.08
5N ₇	0.3606	0.3700	2.53
6N ₇	0.5166	0.5200	0.64
C ₇ A	17.8095	18.4561	3.50

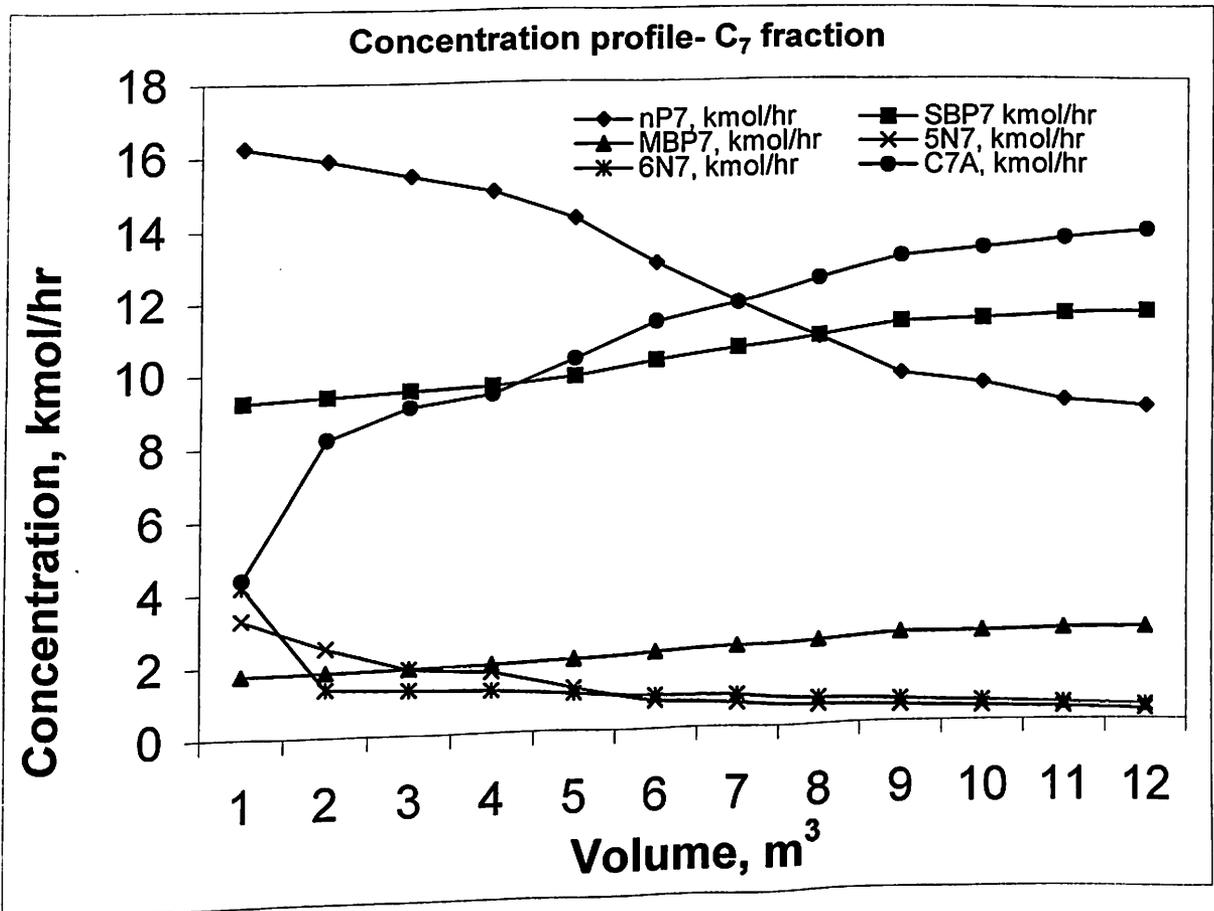


FIG 3.10: CONCENTRATION PROFILE OF C₇ FRACTION IN THE REACTOR FOR CASE-II

TABLE 3.25: CONCENTRATION VARIATION OF C₈ FRACTION CASE II

Volume, m ³	nP ₈ , kmol/hr	SBP ₈ , kmol/hr	MBP ₈ , kmol/hr	5N ₈ , kmol/hr	6N ₈ , kmol/hr	C ₈ A, kmol/hr
0	9.1783	8.6659	3.1798	3.55	2.4446	3.9123
1	8.991	8.4938	3.241	2.6567	1.1838	8.0699
2	8.8081	8.0161	3.3031	1.8679	0.7588	9.7637
2.72	8.6784	7.7008	3.3483	1.1409	0.5735	10.496
4	7.455	7.4438	3.4297	0.9271	0.3902	10.8735
5.5	6.9017	6.6005	3.5206	0.8226	0.3526	11.1122
7	6.4582	5.9457	3.6251	0.7009	0.3469	11.8379
8.5	5.871	5.1496	3.6617	0.5972	0.34116	12.3856
10	4.9416	4.6625	3.7619	0.3866	0.3284	13.0258
11.5	4.6329	3.7321	3.7619	0.3513	0.2917	13.336
13	4.1961	2.8125	3.7619	0.3394	0.2814	13.7155
14.3	3.6413	2.0147	3.7619	0.3178	0.2239	13.0681

TABLE 3.26: COMPARISON OF CALCULATED VALUES AND PLANT DATA OF C₈ FRACTION FOR CASE II

Reformate	Predicted by Model, %	Actual Plant, %	Error, %
nP ₈	4.7185	4.7315	0.27
SBP ₈	2.6101	2.6378	1.02
MBP ₈	4.8748	5.1346	5.05
5N ₈	0.4118	0.3959	4.02
6N ₈	0.2801	0.3100	6.40
C ₈ A	18.2301	18.789	2.97

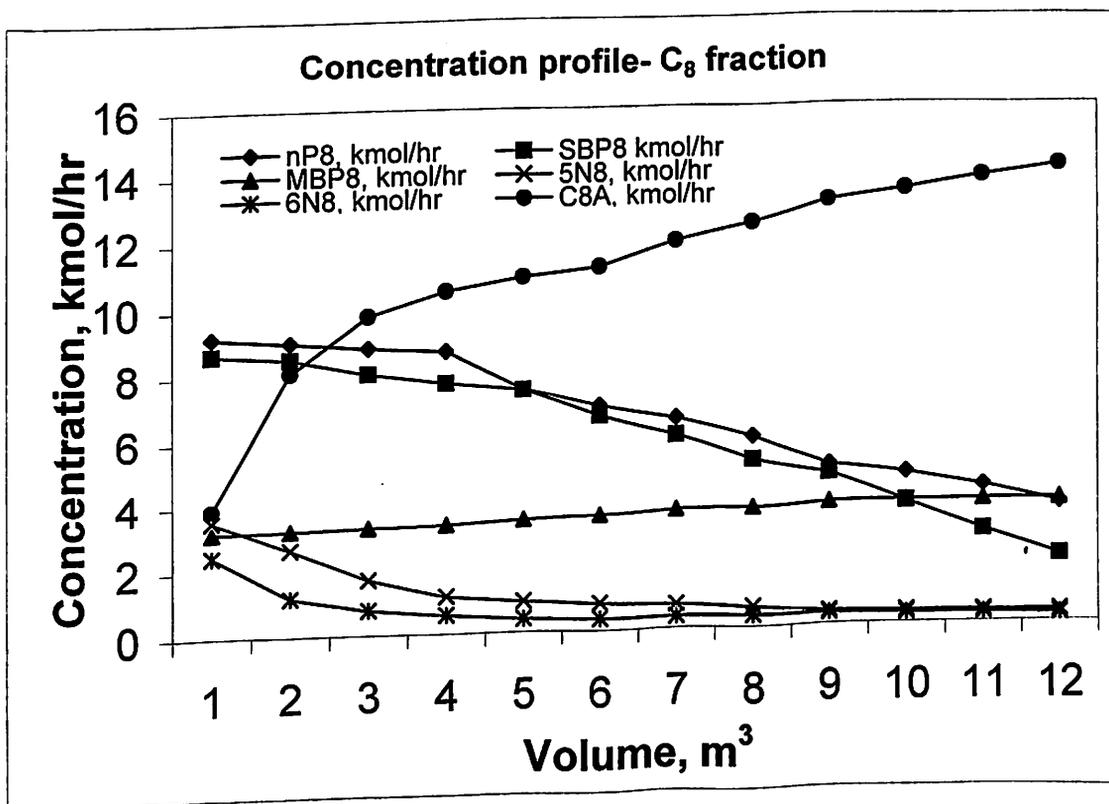


FIG 3.11: CONCENTRATION PROFILE OF C₈ FRACTION IN THE REACTOR FOR CASE-I

TABLE 3.27: CONCENTRATION VARIATION OF C₉ FRACTION CASE II

Volume, m ³	nP ₉ , kmol/hr	SBP ₉ , kmol/hr	MBP ₉ , kmol/hr	5N ₉ , kmol/hr	6N ₉ , kmol/hr	C ₉ A, kmol/hr
0	1.2119	1.4001	1.8858	0.2032	0.3949	0.223
1	0.9884	1.4271	1.8818	0.1842	0.1104	0.6246
2	0.8656	1.453	1.8785	0.167	0.09651	0.6657
2.72	0.84495	1.471	1.8764	0.1627	0.0831	0.6834
4	0.82119	1.5021	1.8727	0.1435	0.08131	0.6944
5.5	0.7761	1.54	1.869	0.1238	0.07834	0.7171
7	0.71447	1.5759	1.8658	0.1172	0.07228	0.7297
8.5	0.6329	1.5886	1.8648	0.111	0.06229	0.7458
10	0.61021	1.6221	1.8619	0.0958	0.05626	0.7671
11.5	0.5713	1.6221	1.8619	0.0958	0.05626	0.7707
13	0.5524	1.6221	1.8619	0.0958	0.04312	0.7802
14.3	0.5387	1.6221	1.8619	0.0958	0.03264	0.7907

TABLE 3.28: COMPARISON OF CALCULATED VALUES AND PLANT DATA OF C₉ FRACTION FOR CASE II

Reformate	Predicted by Model, %	Actual Plant, %	Error, %
nP ₉	0.6981	0.7350	5.02
SBP ₉	2.1019	2.3196	9.38
MBP ₉	2.4127	2.6483	8.89
5N ₉	0.1241	0.1210	2.59
6N ₉	0.04229	0.0412	2.66
C ₉ A	1.0246	1.1031	9.33

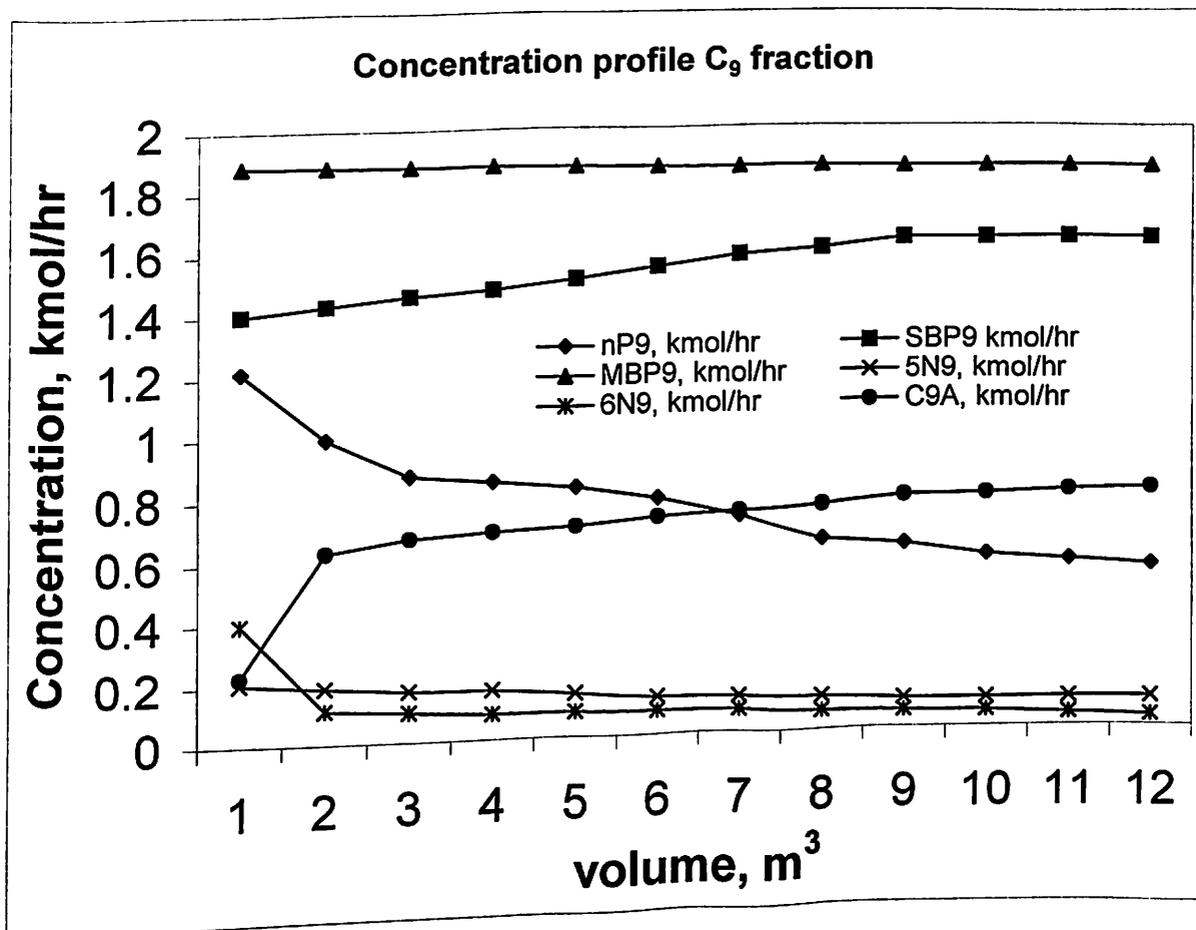


FIG 3.12: CONCENTRATION PROFILE OF C₉ FRACTION IN THE REACTOR FOR CASE-II

TABLE 3.29: CONCENTRATION VARIATION OF C₁₀ FRACTION CASE II

Volume, m ³	nP ₁₀ , kmol/hr	SBP ₁₀ , kmol/hr	MBP ₁₀ , kmol/hr	5N ₁₀ , kmol/hr	6N ₁₀ , kmol/hr	C _{10A} , kmol/hr
0	0.02160	0.02463	0.2822	0.10690	0.11610	0.0000
1	0.02040	0.02470	0.2822	0.09690	0.04160	0.08300
2	0.01920	0.02480	0.2822	0.08789	0.03808	0.08635
2.72	0.01810	0.02488	0.2822	0.07660	0.03687	0.08684
4	0.01709	0.02500	0.2823	0.07550	0.03678	0.08793
5.5	0.01630	0.02510	0.2824	0.06517	0.03488	0.09179
7	0.01407	0.02570	0.2825	0.06170	0.03142	0.09583
8.5	0.01265	0.02576	0.2825	0.05846	0.03608	0.09835
10	0.01103	0.02590	0.2826	0.05049	0.02862	0.11000
11.5	0.00987	0.02593	0.2827	0.05049	0.02762	0.113000
13	0.00963	0.02612	0.2828	0.05049	0.02620	0.11500
14.3	0.00912	0.02619	0.2828	0.05049	0.02450	0.11900

TABLE 3.30: COMPARISON OF CALCULATED VALUES AND PLANT DATA OF C₁₀ FRACTION FOR CASE II

Reformate	Predicted by Model, %	Actual Plant, %	Error, %
nP ₁₀	0.0118	0.011	7.43
SBP ₁₀	0.0339	0.033	2.84
MBP ₁₀	0.3664	0.350	4.70
5N ₁₀	0.0654	0.065	0.65
6N ₁₀	0.0317	0.031	2.41
C _{10A}	0.1542	0.150	2.80

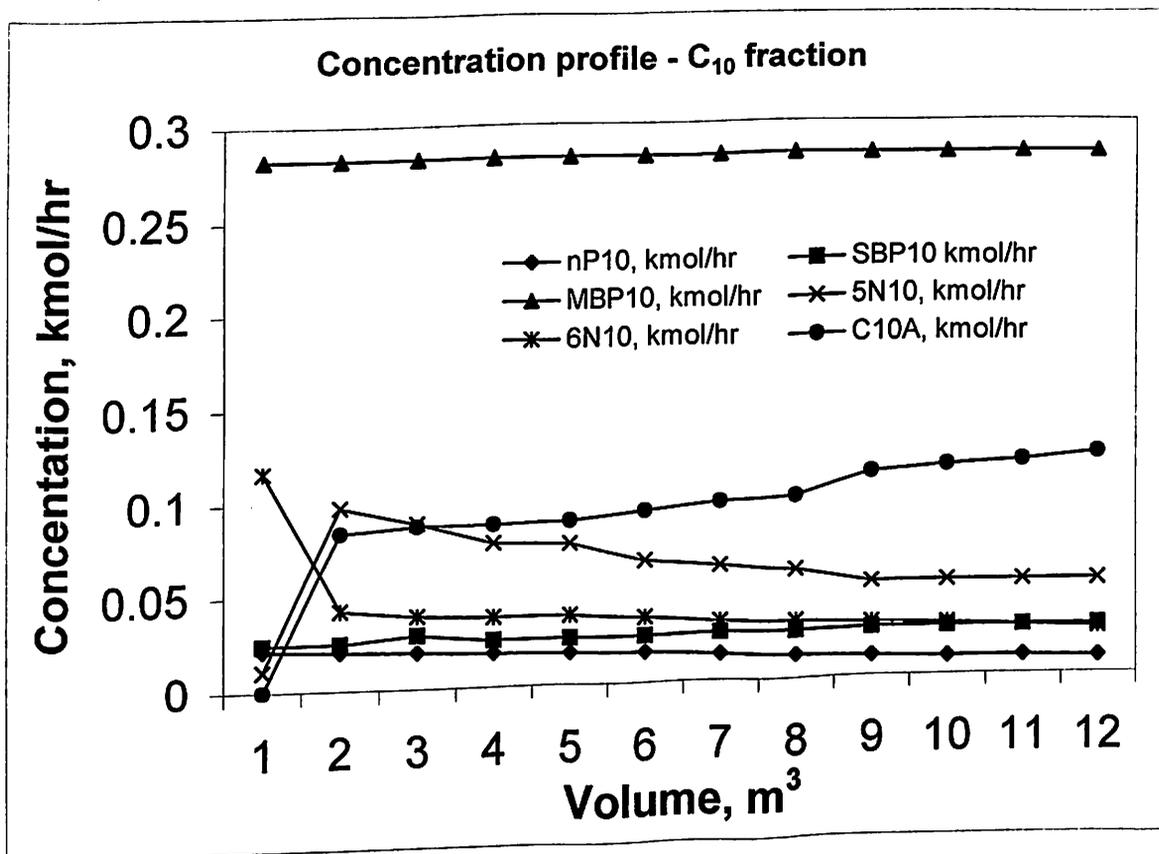
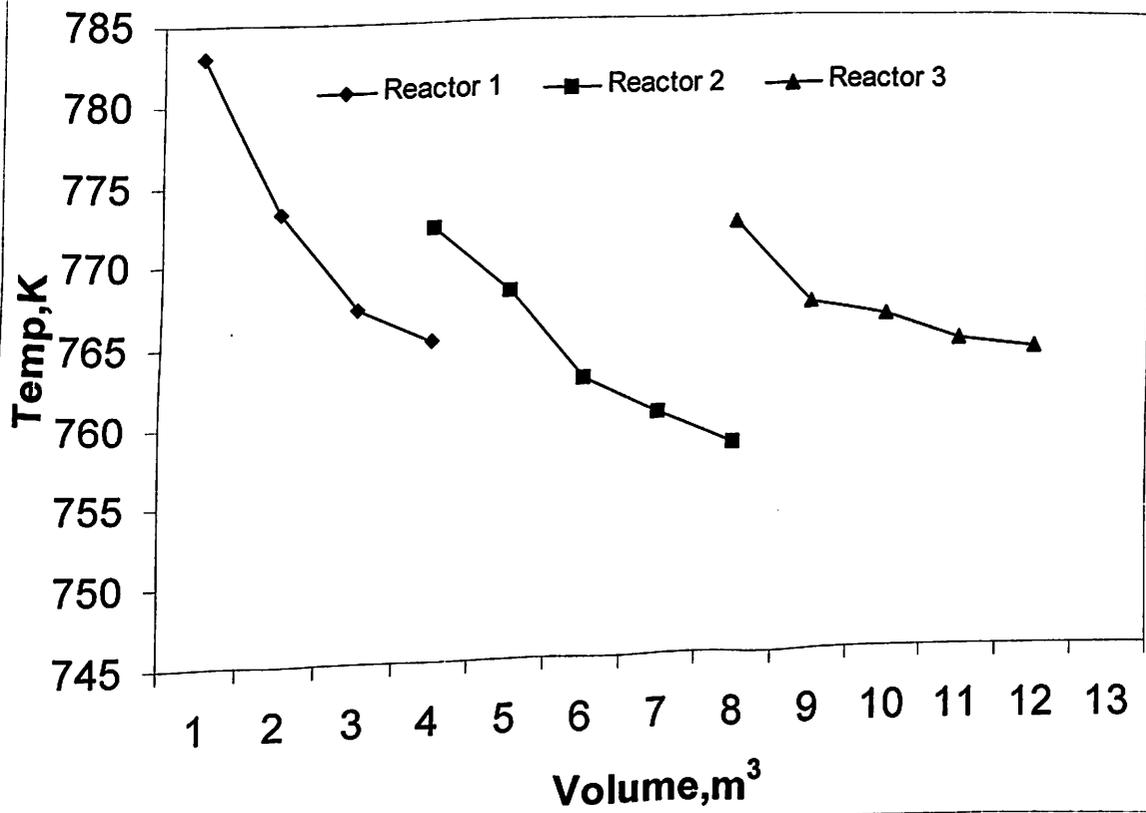


FIG 3.13: CONCENTRATION PROFILE OF C₁₀ FRACTION IN THE REACTOR FOR CASE-II

TABLE 3.31: TEMPERATURE DATA FOR CASE II

Volume, m³	Reactor 1	Reactor 2	Reactor 3
0	783		
1	773.13		
2	766.91		
2.72	764.87	772	
4		767.95	
5.5		762.37	
7		760.13	
8.5		758.16	772
10			766.87
11.5			765.83
13			764.31
14.3			763.79

Temperature profile case-2



RESULTS AND DISCUSSION

As can be seen from the above Tables ,Comparison of calculated values and plant data of C₅ to C₁₀ fractions, the aromatics composition at the exit of the third reactor match very well, with the error being distributed randomly and the maximum deviation being 4.58 percent. The program is designed to give the individual concentration of nonaromatics fractions i.e., nP₆, SBP₆, MBP₆, 5N₆, 6N₆ etc, the error being maximum of 6.4 percent.

We observe that in spite of the model being simplistic; it does predict the plant performance reasonably well even for the wide varying aromatics content in the feed.

CONCENTRATION PROFILE:

Fig-3.2 to Fig-3.7 shows the concentration profile for C₅ to C₁₀ fractions in the reactor for the case I, the aromatics increase rapidly in the first reactor at the cost of naphthenes. There is a insignificant change in the paraffins content in the initial part of first reactor and for the rest of reactors they seem disappear and contribute for the production of Isoparaffins as well as aromatics. In the beginning of the third reactor there is a slight decrease in the naphthene concentration after that it remains constant at the negligible level.

Fig-3.9 to Fig-3.12 shows the concentration profile for case II, qualitatively resembles the case I and the above remarks apply there too.

TEMPERATURE PROFILE:

Fig-3.8 and Fig3.14 shows the Temperature profile over the volume of reactor for the two cases. Since most of the reforming reactions are endothermic, drop in temperature in first reactor is balanced heating in the furnace before it is sent through the second reactor. Similarly the change from the second reactor is heated before it is send to the third reactor. The temperature decreases smoothly, in an exponential manner in all the cases.

CONCLUSION

A mathematical model of catalytic naphtha reformer employing detailed kinetic scheme was developed. The model was benchmarked with the industrial data to ensure that it adequately represented the actual plant variables at a base case operating point.

A simple procedure has been used extract the kinetic parameters for the reforming reactions using plant production data. These have been used in the model, to simulate a naphtha reformer plant. The simulation results have been found to be in close agreement with the plant data.

There is a slight discrepancy in the prediction which could be attributed to the innate character of the model and also to the fact that the complex naphtha has been simplified to consist of 33 components C_5 to C_{10} hydrocarbon fraction.

Concentration and Temperature profile have been obtained to provide information about the extent of conversion in the individual reactors. Inlet temperature to the reactor is another important parameter, which can significantly affect the reformer performance.

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