MODELING AND SIMULATION STUDY ON PARTIAL OXIDATION OF ISOOCTANE FOR THE PRODUCTION OF HYDROGEN

A DISSERTATION

Submitted in partial fulfillment of the
requirements for the award of the degree
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(With Specialization in Hydrocarbon Engineering)

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CANDIDATE DECLARATION

I hereby declare that the work presented in this Seminar report entitled "**Modeling and Simulation Study on Partial Oxidation of Isooctane for the Production of Hydrogen**" submitted in partial fulfilment of the requirements for the award of **Integrated Dual Degree** in Chemical Engineering with specialization in **Hydrocarbon Engineering** at the Indian Institute of Technology Roorkee, is an authentic record of my original work carried out during the period from June 2011 to June 2012 under the guidance of **Dr. Surendra Kumar**, Professor, Department of Chemical Engineering, IIT Roorkee.

I have not submitted the matter embodied in this Seminar Report for the award of any other degree.

Devesh Salvi

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CERTIFICATE

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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ABSTRACT

Hydrogen is projected to be one of the primary energy sources in the 21st century. It has the highest specific energy content of all conventional fuels and is the most abundant element. The three main methods for producing hydrogen from heavy hydrocarbons are: Steam reforming (SR), Partial oxidation (POX) and Auto-thermal reforming (ATR). In the present work, the catalytic partial oxidation of isooctane for the production of hydrogen over nickel/alumina catalyst for in fixed bed reactor has been considered. A steady state one-dimensional non-isothermal model have been developed to simulate the partial oxidation of isooctane using oxygen in first fixed bed reactor (FBR-1) and air in second reactor (FBR-2) as oxidants over a Nickel/alumina catalyst to produce hydrogen. The variations of conversion of isooctane and conversion of oxygen with inlet temperature, pressure, C/O ratio in feed and residence time have been shown in both reactors.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

Chapter-1

INTRODUCTION

1.1 HYDROGEN: IMPORTANCE AND APPLICATION

Hydrogen has the highest specific energy content of all conventional fuels and is the most abundant element in the universe .Nowadays, there is an increasing interest in hydrogen as an energy carrier because it creates almost no pollution. It is a clean fuel with no CO_2 emissions. Its combustion does not result in any emission other than water vapour (although under certain air/hydrogen ratios, oxides of nitrogen (NO_x) can also be produced) and hence it is the least polluting fuel that could be used in an internal combustion engine.

Hydrogen will be a key contribution to sustainable development, because in the future it may be produced in virtually unlimited quantities using renewable energy sources. Hydrogen is one of the clean fuel options for reducing motor vehicle emissions. Hydrogen is not an energy source. It is not a primary energy existing freely in nature. Hydrogen is a secondary form of energy that has to be manufactured like electricity. It is an energy carrier. Hydrogen has a strategic importance in the pursuit of a low-emission, environment-benign, cleaner and more sustainable energy system. Hydrogen has very special properties as a transportation fuel, including a rapid burning speed, a high effective octane number, and no toxicity or ozone-forming potential. It has much wider limits of flammability in air than methane and gasoline. Hydrogen has become the dominant transport fuel, and is produced centrally from a mixture of clean coal and fossil fuels, nuclear power, and large-scale renewable. In the current and medium term the production options for hydrogen are first based on distributed hydrogen production from electrolysis of water and reforming of natural gas and coal. Hydrogen production using steam reforming of methane is the most economical method among the current commercial processes.

Hydrogen comes from the Greek words “hydro” and “genes” [1]. The fact that hydrogen reacts with oxygen to produces energy and water is the basis of the so-called hydrogen energy. Hydrogen holds the promise as a dream fuel of the future with many social, economic and environmental benefits to its credit. It has the long-term potential to reduce the dependence on foreign oil and lower the carbon and criteria emissions from the transportation sector. Only in the last decade, the idea of a post-fossil fuel hydrogen-based economy started to gain mainstream interest.

Hydrogen has the highest energy content per unit mass of any fuel [7]. For example, on a weight basis, hydrogen has nearly three times the energy content of gasoline Hydrogen has a high energy yield of 122 kJ/g (kilo joule per gram), which is 2.75 times greater than hydrocarbon fuels.

It is being explored for use in combustion engines and fuel-cell electric vehicles. One of the important and attractive features of hydrogen is its electrochemical property, which can be utilized in a fuel cell. At present, H_2/O_2 fuel cells are available operating at an efficiency of 50–60% with a lifetime of up to 3000 h. The current output range from 440to 1720 A/m^2 of the electrode surface, which can give a power output ranging from 50 to2500 W

The global market for hydrogen is already greater than $40 billion per year; including hydrogen used in ammonia production (49%), petroleum refining (37%), methanol production (8%), and miscellaneous smaller-volume uses (6%). Sales of hydrogen have increased by 6% annually in the last five years, which is closely related to the increased use of hydrogen in refineries as a result of stricter standards for fuel quality. Present utilization of hydrogen is equivalent to 3% of the energy consumption and with a growth rate estimated at 5–10% per year.

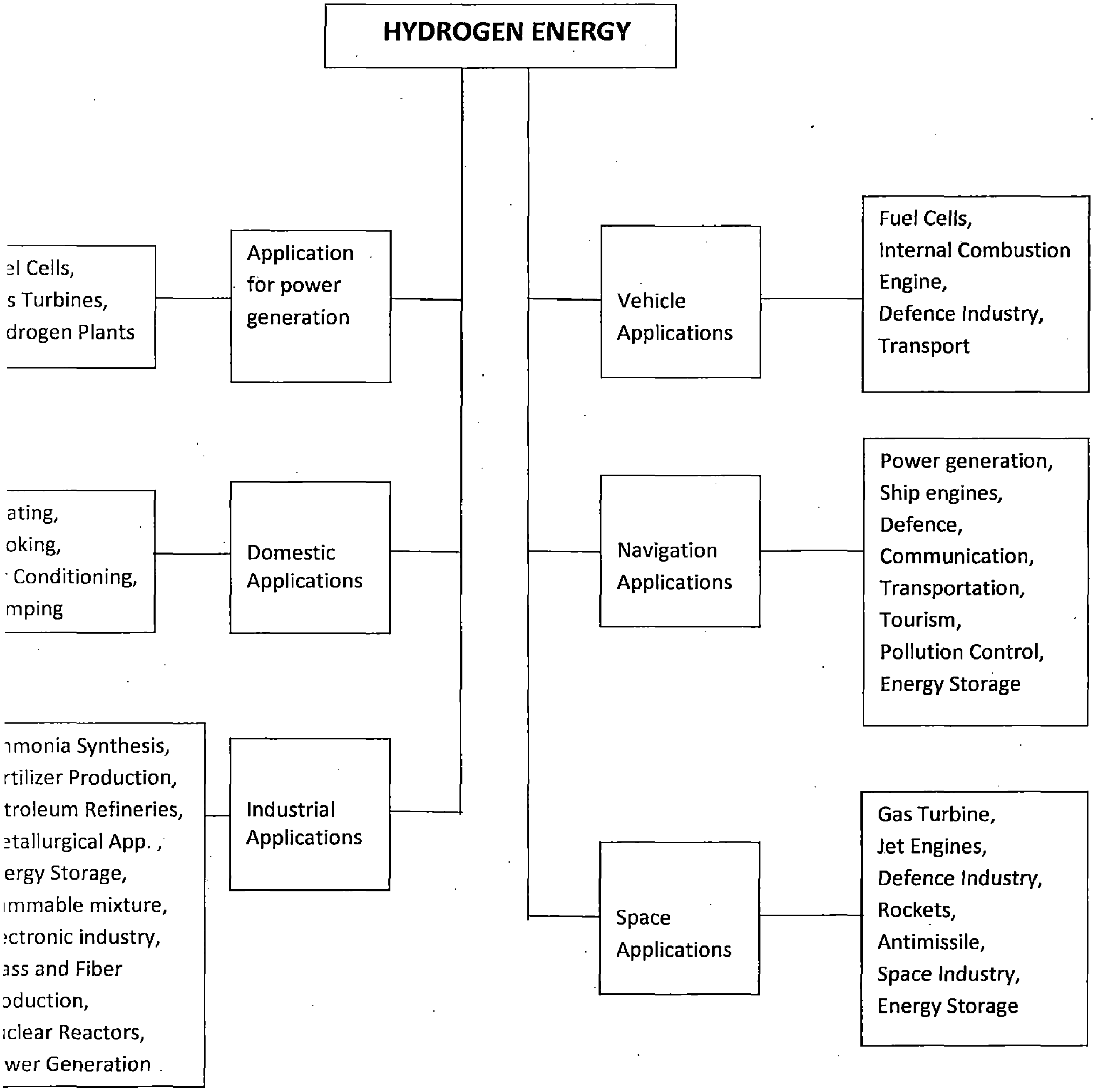

Figure-1.1 Application Areas for Hydrogen Energy

1.2 TECHNOLOGIES OF HYDROGEN PRODUCTION FROM HYDROCARBONS

The vast majority of hydrogen is bound into molecular compounds. To obtain hydrogen means to remove it from these other molecules. With respect to the energy required, it is easy to remove hydrogen from compounds that are at a higher energy state, such as fossil fuels. This process releases energy, reducing the amount of process energy required. It takes more energy to extract hydrogen from compounds that are at a lower energy state, such as water, as energy has to be added to the process.

A number of hydrogen generation routes have been explored. Methanol, ethanol, ammonia, gasoline and natural gas are some possible sources of hydrogen production. In addition, petroleum distillates, liquid propane, oil, gasified coal and even gas from landfills and wastewater treatment plants can also be processed to supply hydrogen. For stationary applications, natural gas is the fuel of choice due to its availability and ease in distribution. For automotive applications, gasoline is the most convenient fuel since it can be easily transported.

Hydrogen is produced commercially on a large scale mainly by steam reforming, partial oxidation, coal gasification and electrolysis. Alternative methods of hydrogen production include thermo chemical water decomposition, photo-conversions, photo-biological processes, production from biomass, and industrial processes. Although some of these methods show promise for the future, they are still largely experimental and capable of supplying only small amounts of hydrogen.

Before going into a detailed discussion of processes for the conversion of hydrocarbons to hydrogen, it would be useful to give a general classification of hydrocarbon-to-hydrogen technologies. There are several ways to categorize these technologies, for example, from a thermodynamic viewpoint (endothermic versus exothermic), by the use of catalysts (catalytic versus non-catalytic) or by the role of oxidants (oxidative versus non-oxidative). The last-mentioned classification (oxidative versus non-oxidative hydrocarbon-to-hydrogen processes) is used in this review because it best reveals the differences in process chemistry, the type of energy input, the role of catalysts, and the environmental implications of the technologies. Figure (on next page) provides the general classification of all the major technologies and methods for producing hydrogen from hydrocarbon-based feed-stocks. The various routes for hydrogen production from different primary energy resources are shown below in figure [7]:

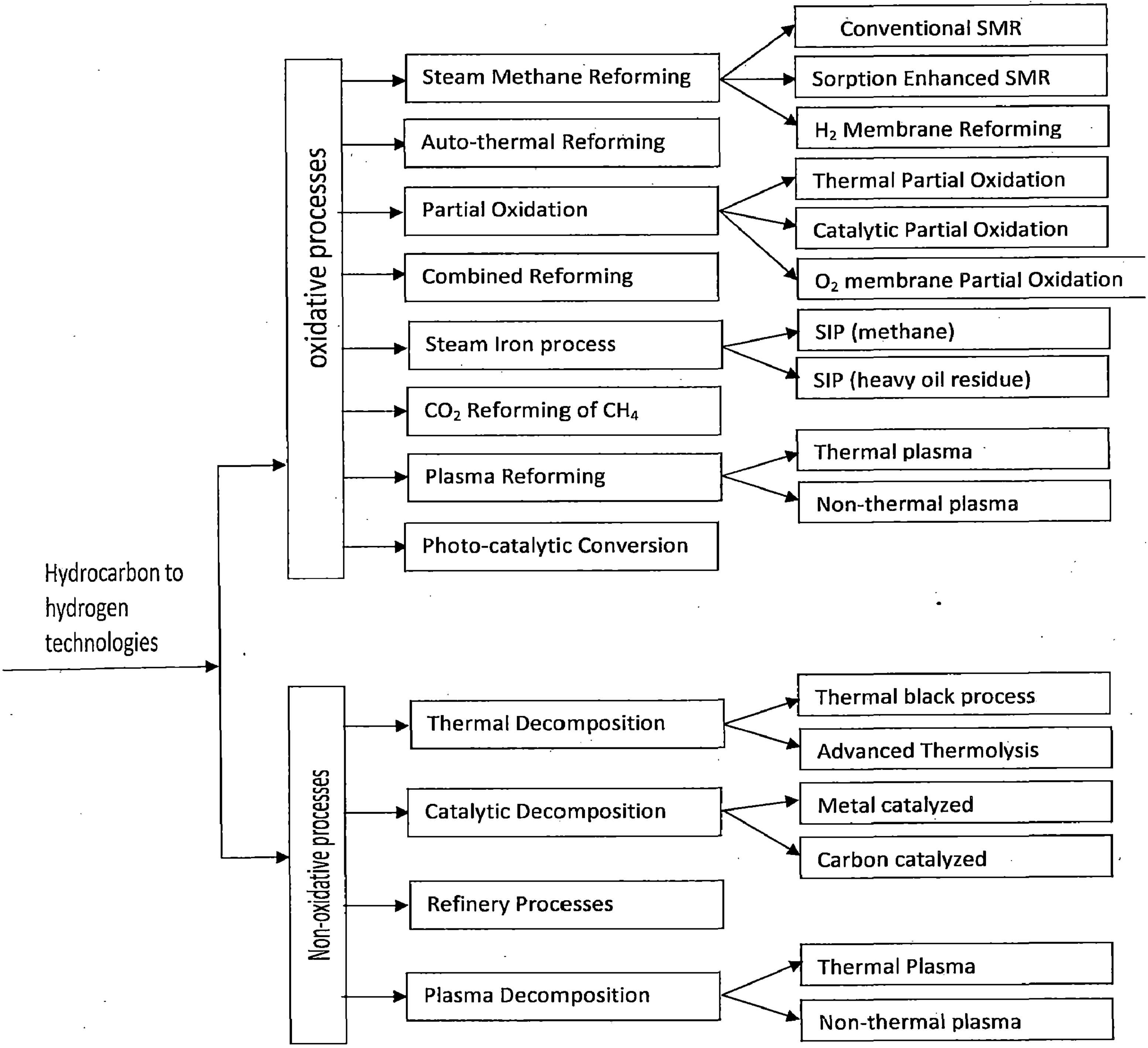

Figure-1.2 Various processes to produce hydrogen from hydrocarbons

Oxidative processing [7] of hydrocarbons to hydrogen occurs at elevated temperatures (typically, above 700°C) in the presence of oxidants such as oxygen (air), steam, CO_2, or a combination thereof. In general, the processes for oxidative conversion of hydrocarbons to hydrogen are well-established technologies, and most of the industrial hydrogen production processes (e.g., steam methane reforming [SMR], partial oxidation [PO], auto-thermal reforming [ATR], steam–iron process [SIP]) belong in this category. The oxidative conversion of hydrocarbons to hydrogen can be represented by the following generic chemical equation:

$$C_nH_m + \{\text{Oxidants}\} \rightarrow xH_2 + yCO + zCO_2$$

Depending on the nature of the oxidant, the oxidative process could be exothermic (e.g., when Oxidant is O_2), endothermic (when Oxidants are H_2O, CO_2 or mixture of both), or near thermo-neutral (when Oxidants are O_2-CO_2, or O_2-H_2O, or mixture of this components with the suitable molar ratio). High operational temperatures of the oxidative conversion processes are due to the relative "inertness" of methane and other saturated hydrocarbons (or alkanes) that make up most of the hydrocarbon feedstock for hydrogen production. However, water and CO_2 are also very inert compounds requiring high temperatures for their activation and interaction with other chemical compounds. Therefore, catalysts are widely used to accomplish these processes at the practical range of temperatures (750–950°C).

Non-oxidative conversion [7] of hydrocarbon feed-stocks to hydrogen generally occurs by the splitting of C–H bonds in hydrocarbons in response to an energy input (heat, plasma, radiation, etc.), and it does not require the presence of oxidizing agents. Among the non-oxidative hydrocarbon-to-H_2 conversion processes are thermal, catalytic, and plasma hydro-carbon decomposition processes. The following generic chemical reaction describes the non-oxidative transformation of hydrocarbons to hydrogen:

$$C_mH_n + [\text{energy}] \rightarrow xH_2 + yC + zC_pH_q$$

where, C_mH_n is the original hydrocarbon feedstock, C_pH_q represents relatively stable products of the feedstock cracking and [energy] is an energy input for example, thermal energy or electrical energy(e.g., plasma) or radiation energy.

In most cases, the non-oxidative conversion processes are endothermic and require some form of an energy input to accomplish the decomposition reaction. In general, these processes require elevated temperatures (>500°C), especially when methane and other light alkanes are used as a feedstock.

1.2.1 OXIDATIVE PROCESSING OF HYDROCARBONS

1.2.1.1 Steam reforming of Hydrocarbon

In the steam reforming process [7], a light hydrocarbon feedstock (such as natural gas, refinery gas, LNG, or naphtha) is reacted with steam at elevated temperatures (typically 700° C to 900° C), and elevated pressures (15 to 31 bar) in catalyst filled tubes to produce a synthesis gas. This gas consists primarily of hydrogen and carbon monoxide, but other gases such as carbon dioxide and nitrogen, as well as water vapour are also present. The typical ratio of this gas exiting the reformer is approximately 50% hydrogen, 10% carbon monoxide, with the balance being the other gases. Increasing the amount of steam used in the reaction will increase the hydrocarbon conversion rate, but the economic cost of the steam must be taken into account in the overall process. The typical steam to carbon ratio falls in the range of 2.8 to 3.2 to 1. The primary reforming reaction is:

$$C_xH_y + x\,H_2O \rightarrow x\,CO + (x+y/2)\,H_2,$$

which is highly endothermic. This process is currently the most popular process for producing hydrogen from natural gas. Almost 48% of the world's hydrogen is produced from Steam Reforming of Natural Gas, which is the most common and least expensive method of producing hydrogen, with an energy consumption rate of only about 1.23–1.35 GJ-Natural Gas/GJ-H_2. The process requires high process temperature and the most common practice for providing the needed heat for the process is via burning natural gas. Steam reformation of natural gas or methane produces a hydrogen rich gas that is typically on the order of 70–75% on a dry basis, along with smaller amounts of CH_4 (2–6%), CO (7–10%), and CO_2 (6–14%) .

Steam reforming of hydrocarbon offers an efficient, economical, and widely used process for hydrogen production, and provides near- and mid-term energy security and environmental benefits. The efficiency of the steam reforming process is about 65% to 75%, among the highest of current commercially available production methods. The cost of hydrogen produced by Steam Reforming is acutely dependant on hydrocarbon fuel prices and is currently the least expensive among all bulk hydrogen production technologies.

The disadvantage of steam reforming process is highly endothermic reaction. Thus, the high temperature is necessary to obtain the maximum yield of product. No sulphur resistant Steam reforming catalyst has been founded, resulting in the need for a very efficient and therefore probably large unit for removing the sulphur contained in fuel. During the production of hydrogen, CO_2 is also produced which is assumed to be the main responsible for the so-called "greenhouse effect". These processes use non-renewable energy sources to produce hydrogen and is not sustainable .The steam reforming process in centralized plants emits more than twice the CO_2 than hydrogen produced. Another problem with Steam reforming is that it is operating at or near its theoretical limits; the hydrogen produced is still expensive compared to the cost targets (according to U.S. Department of Energy's) for producing hydrogen for future automobiles and other applications.

1.2.1.2 Partial Oxidation of Hydrocarbons

The partial oxidation of hydrocarbons [7] is another major route to hydrogen production on a commercial scale. In partial oxidation process, a fuel and oxygen (or air) is combined in proportions such that a fuel is converted into a mixture of H_2 and CO. There are several modifications of the partial oxidation process, depending on the composition of the process feed and the type of the reactor used. The overall process is exothermic due to sufficient amount of oxygen added to a reagent stream. The partial oxidation process can be carried out catalytically or non-catalytically. The non-catalytic partial oxidation process operates at high temperatures (1100–1500°C), and it can utilize any possible carbonaceous feedstock including heavy residual oils (HROs) and coal. The catalytic process is carried out at a significantly lower range of temperatures (600–900°C) and, generally, uses light hydrocarbon fuels as a feedstock, for example, NG and naphtha. If pure oxygen is used in the process, it has to be produced and stored, which significantly adds to the cost of the system. In contrast, if the Partial oxidation process uses air as an oxidizer, the effluent gas would be heavily diluted with nitrogen resulting in larger water gas shift reactors and gas purification units.

Partial oxidation systems promise to have a much better dynamics than a steam reforming system. The reaction is exothermic so it doesn't need an external supply of energy as in case of steam reforming and can be heated up internally relatively quickly by exothermic reaction of fuel. A key advantage of a non-catalytic Partial oxidation process is that it can utilize all kinds of petroleum-based feed stocks from light hydrocarbons to Heavy Residue Oils and even petroleum coke. Heavy residues from refineries are the preferred feed stocks for the production of hydrogen for the following two reasons:

(1) Residual oils high in sulphur and heavy metals (e.g., Ni and V) are very difficult and costly to upgrade (e.g., by hydrogenation)

(2) There are environ-mental restrictions on their use as fuels (due to heavy SO_x and NO_x emissions)

Hydrogen production by partial oxidation of heavy residues is an economically viable process, and has been commercially practiced for decades. The major reaction during partial oxidation of sulphurous heavy oil fractions can be presented by the following generic chemical reaction:

$$C_mH_nS_p + m/2\ O_2 \rightarrow m\ CO + (n/2-p)\ H_2 + pH_2S$$

Partial oxidation reactions are thought to proceed in two distinct phases; a rapid, highly exothermic combustion phase where all free oxygen is consumed to form heat and the products of CO_2 and H_2O; and a much slower endothermic reforming phase where residual unconverted fuel reacts with the CO_2 and H_2O plus the reaction heat to form syngas products H_2 and CO. Besides this exothermic reaction, a number of other (both exothermic and endothermic) reactions also occur in the Partial oxidation reactor including the cracking reaction, incomplete carbon (coke) combustion and coke gasification

Major disadvantages of the Partial oxidation process are the need for large quantities of pure oxygen (thus, requiring an expensive air separation plant) and the production of large volumes of CO_2 emissions. It needs external cooling and generates a high concentration of CO, which is not desired for fuel cell applications.

1.2.1.3 Auto thermal Reforming (ATR)

This process is a combination of steam reforming and partial oxidation technologies in that the thermal energy for the production of syngas is provided by partial oxidation (combustion) of the hydrocarbon feed-stock in an adiabatic reactor [7]. The process has been used to produce hydrogen and CO-rich synthesis gas for decades. In the 1950s and 1960s, auto-thermal reformers were used to produce syngas for ammonia and methanol production. The auto-thermal reformer consists of three zones: combustion, thermal, and catalytic zones. The feed is introduced to the combustion zone (which is, essentially, a turbulent diffusion flame with the temperature as high as 3000°C at the core) and mixed intensively with steam and a sub stoichiometric amount of oxygen or air. The resulting combustion reaction can be presented as follows: (eg.CH_4)

$$CH_4 + 1.5\ O_2 \rightarrow CO + 3H_2O \qquad \Delta H= -519\ \text{kJ/mol}$$

In the thermal zone, above the catalyst bed, further conversion occurs by homogeneous gas-phase reactions. The main reactions in the thermal zone are homogeneous gas-phase steam reforming and shift reactions. Reactions between N_2 and hydrocarbon radicals leading to the formation of such by-products as NH_3 and HCN can also take place in the thermal zone. By proper adjustment of O_2/ CH_4 and H_2O/ CH_4 ratios, the partial combustion in the thermal zone provides the heat for the subsequent endothermic steam reforming reaction taking place in the catalytic zone.

In the catalytic zone, a reforming catalyst bed (typically, alumina-supported Ni catalyst) carries out steam reforming of hydrocarbons at an operating pressure in the range 1.8–6.7 MPa. Owing to the high endothermicity of the steam reforming reaction, the temperature decreases from typically 1200°C to 1300°C at the inlet of the catalyst bed to about 1000°C at the exit of the catalyst bed. Thus, the product gas composition is fixed thermodynamically through the pressure, exit temperature, and O_2/ CH_4 and H_2O/ CH_4 ratios .Oxygen consumption is high due to the simultaneous adiabatic steam reforming reaction (usually, the O_2 to carbon ratio is in the order of 0.60–0.65).

The ATR attract much attention due to the low energy requirement, the opposite contribution of the exothermic hydrocarbon oxidation and endothermic steam reforming, and also the high space velocity compared to the partial oxidation process. The sulphur tolerance of ATR system is also better than that of steam reforming. Because ATR uses less oxygen than Partial oxidation (per unit of H_2 produced), the economics are less sensitive to the price of oxygen. ATR requires no external fuel while offering some flexibility in feedstock (although ATR does not lend itself to heavy hydrocarbon feed-stocks). One of the advantages of the ATR process is that the pressure can be increased compared to conventional steam reforming, resulting in lower-energy requirement for syngas compression.

1.2.1.4 Plasma Reforming

There is a growing interest in electricity-assisted generations of syngas and hydrogen. In these processes, electricity alone or a mixed source of energy (i.e., electrical and chemical) can be used to provide the syngas generation process with the required energy input [7]. Use of electricity allows a better control and useful modularity of the syngas generation equipment. Hydrogen production by plasma reforming can be categorized as follows: thermal and non-thermal plasma reforming

In thermal plasma reforming, thermal plasma consists of an electric arc (with the temperatures exceeding 5000°C) through which a gaseous feedstock diffuses at a high velocity, generating ionized species. Thermal plasmas operate at very high power densities and they can catalyze chemical reactions through the intermediate formation of active radicals and ionized species. Thus, thermal plasma reformers use less hydrocarbon fuel since reactant heating is provided by the electric plasma torch. Other advantages of thermal plasma reformers include high conversion efficiencies, a rapid response, compactness, fuel flexibility, and no need for the use of catalysts (thus, no catalyst deactivation problem). The heat generation is independent of reaction chemistry, and optimum operating conditions can be maintained over a wide range of feed rates and gas composition. Disadvantages of plasma reformers are as follows: the difficulty of a high-pressure operation, the need for cooling electrodes (to reduce their thermal erosion), high-energy consumption, and dependence on electrical energy. Owing to the high-energy intensity, the process energetic may be less favourable than that of purely thermal processes, especially, endothermic reactions such as steam reforming.

Non thermal plasma reforming system (also referred as "cold" or non-equilibrium plasma) operate under non-equilibrium thermal conditions (i.e., electrons are at much higher temperature than the ions, radicals, and neutral molecules, which are at near room temperature). An electric discharge produces chemically active species, for example, electrons, ions, atoms, free radicals, excited-state molecules, and photons, which can catalyze chemical reactions involving hydrocarbons and oxidants (e.g., oxygen, steam, and CO_2). Non-thermal plasma reformers operate at much reduced electric currents and consumes less electrical energy compared to thermal plasma systems (since energy is not consumed in heating the bulk of the gas). Other advantages of using non-thermal plasma reactors relate to lower temperature and insignificant electrode erosion (thus, cooling of electrodes is not necessary), compactness etc.

1.2.1.5 Carbon Dioxide Reforming of Methane

The CO_2 reforming of methane is an alternative to Steam reforming and partial oxidation processes, where CO_2 plays the role of an oxidant [7]. Sometimes the process is also called stoichiometric reforming, but more often it is referred to as dry reforming. Like steam reforming, it is a highly endothermic process requiring high operational temperatures of 800–1000°C. Owing to the presence of CO_2 in the feedstock, the process produces synthesis gas with high CO/H_2 ratio (1:1) according to the following equation:

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad \Delta H = 247 \text{ kJ/mol}$$

With the growing concerns about negative environmental impact of CO_2 (i.e., global warming), the CO_2 reforming technology is getting more attention increasingly. It should be noted, however, that if the objective were to produce H_2 only, this process would not result in the overall reduction of CO_2 emission compared to steam Reforming (because CO_2 is produced in the water gas shift stage of the process). However, if the process targets the production of syngas with relatively high content of CO (e.g., for FT synthesis), then this approach can be conducive to increasing CO/H_2 ratio in the syngas. In this case, CO_2 from the feedstock will be sequestered in the form of synthetic fuels (e.g., FT gasoline or diesel) or oxygenated compounds (alcohols, esters, etc.). Another advantage of this approach is related to the fact that pure CO_2 is produced as a co-product of the methane reforming process.

Practical implementation of CO_2 reforming of methane faces several key challenges, technically and economically. At the preferred (from the economical viewpoint) pressure of the syngas plant (2.0–4.0 MPa), CO_2 reforming will result in the non-complete conversion of methane due to thermodynamic limitations. Furthermore, the process economy strongly depends on the pressure and the cost of CO_2 available. However, the most serious problem hindering the practical application of CO_2 reforming is the deactivation of metal catalysts due to the deposition of carbon (or coke). Carbon formation can be attributed to two reactions: methane decomposition and CO disproportionation. CO disproportionation is an exothermic reaction; it is favoured by temperatures below 700°C and high pressures. From a practical viewpoint, it is preferable to operate CO_2 reforming of methane at moderate temperatures and with the CH_4: CO_2 ratio close to unity, which would require a catalyst that kinetically inhibits the carbon formation under conditions that are thermodynamically favourable for carbon deposition. Iron, cobalt, and nickel based catalysts are particularly active in methane decomposition and CO disproportionation reaction, and noticeable deposition of carbon on the surface of these catalysts would occur at temperatures as low as 350°C.

1.2.1.6 Photo-production of Hydrogen from Hydrocarbons

Photo-catalytic production of hydrogen is a potentially attractive approach in converting solar photon energy to chemical energy of hydrogen [7]. Owing to the high dissociation energy of CH_3–H bond (4.48 eV), methane absorbs irradiation in vacuum ultraviolet (UV) region. The absorption spectrum of methane is continuous in the region from 1100 to 1600 A° (absorption coefficient k =500/atm/cm). Unfortunately, the wavelengths shorter than λ = 160 nm are present neither in the solar spectrum, nor in the output of most UV lamps. Therefore, the production of hydrogen and other products by direct photolysis of methane does not seem to be practical. However, the use of special photo-catalysts allows activating and converting hydrocarbons to H_2 under the exposure to the wavelengths extending well into near-UV area (300–360 nm) that are present in solar spectrum (about 4–5% of the total spectrum).

1.2.2 NON-OXIDATIVE PROCESSING OF HYDROCARBONS

1.2.2.1 Thermal Decomposition of Hydrocarbons

When hydrocarbons are heated to a high temperature, they thermally decompose into their constituent elements: hydrogen and carbon [7],

$$C_nH_m \rightarrow nC + m/2\, H_2$$

The amount of energy required to carry out this process depends on the nature of the hydrocarbon: it is the highest for saturated hydrocarbons (alkanes, cyclo-alkanes) and low for unsaturated and aromatic hydrocarbons (in fact, decomposition of acetylene and benzene are exothermic reactions). Methane is one of the most thermally stable organic molecules.

The dissociation energy for C–H bond in methane (E = 436 kJ/mol) is one of the highest among all organic compounds. Its electronic structure (i.e., the lack of π- and n-electrons), lack of polarity, and any functional group make it extremely difficult to thermally decompose the methane molecule into its constituent elements.

Since the 1950s, thermal decomposition of NG has been practiced for the production of carbon black (CB) with hydrogen being a by-product and supplementary fuel for the process. The process (called thermal black process) was operated in a semi-continuous mode at high operational temperatures. Recently, several new processes for methane thermal decomposition were reported in the literature.

1.2.2.2 Catalytic Decomposition of Hydrocarbons

It has long been known that certain transition metals (d-metals), most prominently, Fe, Co, and Ni, exhibited high catalytic activity toward the decompositions of methane and other hydrocarbons to hydrogen and carbon at moderate temperatures. In the 1960s, Universal Oil Products Co. (UOP) developed the HYPRO^{TM} process for the continuous production of hydrogen by catalytic decomposition of gaseous hydrocarbon streams.

For instance, methane decomposition reaction requires high temperatures; there have been attempts to use catalysts to reduce the temperature of thermal decomposition of methane [7].

Methane decomposition was carried out in a fluidized-bed catalytic reactor in the temperature range from 815°C to 1093°C. Supported Ni, Fe, and Co catalysts (preferably, Ni/Al_2O_3) were used in the process. The coked catalyst was continuously removed from the reactor to the regeneration section where carbon was burned off by air, and the regenerated catalyst was recycled to the reactor.

1.2.2.3 Plasma-Assisted Decomposition of Hydrocarbons

The objective of plasma-assisted decomposition of hydrocarbons is to produce hydrogen and carbon in an oxidant-free environment (as opposed to plasma-assisted Partial oxidation and steam reforming that produce hydrogen and CO_2), according to the following generic reaction [7]:

$$C_nH_m + \text{Energy} \rightarrow nC + m/2\ H_2$$

The plasma decomposition process is applicable to any hydrocarbon fuel, from methane to heavy hydrocarbons. Similar to oxidative plasma reforming, plasma decomposition processes all into two major categories: thermal and non-thermal plasma systems. In thermal plasma reactors, the energy required to accomplish an endothermic hydrocarbon decomposition process is provided by high-temperature plasma. Decomposition of paraffinic hydrocarbons including $C_{16}H_{34}$ by Ar–H_2 plasma was carried out by continuous injection of the hydrocarbon in the spouted-bed reactor. Controlling temperature, residence time, and H_2 concentration allows reaching the hydrocarbon decomposition yield of about 95%.

1.2.2.4 Other Refineries process

In refineries, hydrogen is produced by steam reforming of hydrocarbons or by its recovery from hydrogen-rich gases and refinery off-gases (that were formerly used as gaseous fuels for heating purposes) [7]. With the increasing quality demands for transportation fuels and other refinery products and with the increasing use of heavy sulphurous feed-stocks, the transfer of hydrogen within the refinery is rising. The following refinery processes produce gaseous streams from which the recovery of hydrogen could be economically viable:

1. Thermal cracking processes (e.g., cokers and vis-breakers)
2. Catalytic cracking (CC)
3. Catalytic reforming
4. Olefins production
5. Acetylene production

Thermal cracking processes, In cokers and visbreakers, heavy crude and residues are converted to petroleum coke, oil, light fractions (benzene, naphtha, LPG), and gas. Depending on the particular process, hydrogen is present in the process gases in a wide range of concentrations. The pressure swing adsorption (PSA) process is best suited for the recovery of H_2 from these gases because they feature a high-purity H_2, and its off-gas is suitable as a fuel for the process-heating purposes. If more H_2 is required in the refinery, it can be produced by steam reforming of light fractions (LPG and naphtha), or even by the gasification of petroleum coke.

Catalytic cracker, The CC is designed to produce light products from gas oil and increasingly from vacuum gas oil and residues. In the CC process, the molecular mass of the main fraction of the feedstock is lowered, whereas the remaining part is converted to coke, which is deposited on the catalyst. The catalyst is regenerated by burning the coke off with air, which also provides the heat input for the endothermic cracking process. During cracking processes (1) paraffins and naphthens are cracked to olefins and lighter alkanes, (2) monoaromatics are dealkylated without ring cleavage, and (3) polyaromatics are dealkylated and converted to coke. Hydrogen is produced only in the last-mentioned process, whereas the first two processes produce light hydrocarbons, and therefore, need a certain amount of hydrogen. Increase in coke production results in an increase in the overall hydrogen yield.

Catalytic reformers, Catalytic reforming is an important step to improve the quality of gasoline. During the reforming process, naphthens are dehydrogenated to aromatics.

As a representative example, hydrogen is produced by cyclohexane dehydrogenation to benzene as follows:

$$C_6H_{12} \rightarrow C_6H_6 + 3H_2 \qquad \Delta H^\circ = 206.2 \text{ kJ/mol}$$

Olefin production, during the production of ethylene and propylene by the steam cracking process, large amounts of hydrogen are formed as a by-product. The concentration of H_2 in crude gases from steam cracking of ethane, naphtha, and hydrogenated vacuum gas oil is (mol %) 33, 16, and 10, respectively. Because ethane, ethylene, propane, and propylene are fractionated at low temperatures, hydrogen is usually separated from methane by condensation, cryogenically. The resulting gas has the following composition (mol%): H_2=80–95, CO= 0.5–1, CH_4= 4.5–19, and C_2— 0.1.

Acetylene production, hydrogen is produced as a by-product in the production of acetylene by high-temperature thermal cracking in a plasma arc process. In a simplified form,

$$2CH_4 \rightarrow C_2H_2 + 3H_2$$

.2.3 OTHER PROCESSES

.2.3.1 Gasification of coal

Coal gasification is the process of producing coal gas, a type of syngas–a mixture of carbon monoxide (CO), hydrogen (H_2), carbon dioxide (CO_2) and water vapour (H_2O)–from coal [7]. Coal gas, which is a combustible gas, was traditionally used as a source of energy for municipal lighting and heat before the advent of industrial-scale production of natural gas, while the hydrogen obtained from gasification can be used for various purposes such as making ammonia, powering a hydrogen economy, or upgrading fossil fuels. It is noteworthy that hydrogen from coal only accounts for 18% of the world's hydrogen production. Its energy consumption is about 1.54–1.69 GJ-coal/GJ-H_2.

Hydrogen production from coal, with carbon capture technology, can provide a low cost, low emission, high volume stream of hydrogen to provide clean energy. The process used in production of hydrogen by gasification of coal is given as:-

Step 1: Gasification

Gasification turns coal into a very hot (up to 1800°C) synthesis gas, or syngas, which is composed of carbon monoxide, hydrogen and carbon dioxide, as well as small amounts of other gases and particles.

This is accomplished by mixing pulverized coal with an oxidant, usually steam, air or oxygen.

$$3C + O_2 + H_2O \rightarrow H_2 + 3CO$$

Step 2: Cooling and Cleaning

Next, the syngas is cooled and cleaned to remove the other gases and particles, leaving only carbon monoxide, carbon dioxide and hydrogen. During syngas cleaning, mercury, sulphur, trace contaminants, and particulate matter are removed.

Step 3: Shifting

Next, the syngas is sent to a "water gas shift reactor." During the shift reaction, the carbon monoxide is converted into more hydrogen and carbon dioxide by mixing it with steam.

Afterwards, the syngas consists mostly of hydrogen and carbon dioxide

$$CO + H_2O \rightarrow CO_2 + H_2$$

Step 4: Purification

Once the syngas has been shifted, it is separated into streams of hydrogen and carbon dioxide. The hydrogen, once cleaned, is ready for use. The carbon dioxide is captured and sent off for sequestration. Carbon sequestration is the process of utilizing natural and man-made processes to store carbon, on a long-term basis, in an effort to reduce or slow the build-up of carbon dioxide (the principal greenhouse gas) in the atmosphere. Carbon is naturally sequestered in the earth's terrestrial biosphere, and geologic and oceanic reservoirs.

There is now a stream of pure hydrogen ready for a variety of uses. It can be burned in a gas turbine for electricity generation, converted to electricity in a fuel cell, used as a fuel for an internal combustion engine or as a chemical for making fertilizer, semiconductors and many other products.

Hydrogen production from coal represents an excellent near- to mid-term opportunity to use domestic fossil energy resource to support the transition to a hydrogen economy. Coal is a relatively inexpensive resource making it an attractive energy source when considering options to produce hydrogen.

A concern regarding the utilization of coal in a hydrogen economy is that the resulting CO_2 emissions are greater than those from any other method of producing hydrogen. Increased demand for coal could significantly impact the cost of coal resources, which could negatively impact the use of coal for hydrogen production. The complex and expensive gasification process it undergoes presents the greatest drawback for its widespread production.

1.3 HYDROGEN MARKET

The markets partially define the requirements for the production technologies as well as potential partners to commercialize new hydrogen production technologies. It has been reported that 50 million tonnes of hydrogen are traded annually worldwide with a growth rate of nearly 10% per year for the time being [3]. It is primarily used as feed-stocks in the chemical industry, for instance, in the manufacture of ammonia and methanol, and in refinery reprocessing and conversion processes. However, with the environmental regulations becoming more stringent, there is now growing interest in the use of hydrogen as an alternative fuel.

Hydrogen is considered as a viable alternative fuel and "energy carrier" of future. It can easily be used in fuel cells for production of electricity for stationary applications and mobile electric vehicle operations. However, the demand on hydrogen is not limited to utilization as a source of fuel. Hydrogen gas is a widely used feedstock for the production of chemicals, hydrogenation of fats and oils in food industry, production of electronic devices, processing steel and also for desulphurization and re-formulation of gasoline in refineries.

1. **Industrial Market** There are thousands of industrial users of hydrogen. Most users use relatively small quantities. However, there are two industrial markets where the facility size matches the output of centralized high-volume hydrogen production systems.

    (i) **Ammonia production** Ammonia production (fertilizer) consumes about half the hydrogen produced today and is the primary chemical industry use of hydrogen. All nitrate fertilizers require hydrogen in their production processes. Ammonia is currently produced where inexpensive natural gas that provides inexpensive hydrogen and shipped to the customer. The low cost of shipping of ammonia favours very large-scale ammonia production plants with very high demands for hydrogen.

(ii) **Petrochemical:** The use of H_2 in the chemical and petroleum refining industries is of prime importance. Hydrogen is essentially a hydrogenating agent. Hydrogen use in the petroleum refining includes many processing schemes such as hydrocracking, hydrofinishing of lube oils, hydrodealkylation and hydrodesulphurization of petroleum fractions and residues. Hydrocracking of petroleum residue is becoming more important to produce lighter petroleum distillates of low sulphur and nitrogen content to meet stringent government mandated product specifications to control pollution. In the petrochemical field, hydrogen is used to hydrogenate benzene to cyclohexane and benzoic acid to cyclohexane carboxylic acid. These compounds are precursors for nylon production. It is also used to selectively hydrogenate acetylene from C_4 olefin mixture [13].

2. **Commercial Markets** Hydrogen is being considered for commercial applications in buildings with the co-production of electricity and heat. If highly economic hydrogen production is achieved, hydrogen may be used to generate electricity, hot water, building heating, and building cooling. This is a distributed market with relatively small hydrogen consumption in individual facilities. This market does not favour large-scale hydrogen production techniques

3. **Intermediate and Peak Electricity Production** The demand for electricity varies daily, weekly, and seasonally. As a result, the market price of electricity varies by an order of magnitude as a function of time. To meet this demand, the utilities buy lower-capital-cost peaking power units, typically gas turbines that burn natural gas. In addition, utilities have developed storage devices so that they can buy electricity during time of low demand and low cost and sell the electricity during times of high demand and high prices. The variability of the price of electricity creates the potential for a large hydrogen market aimed at producing electrical power at those times of day when the price of electricity is at its maximum. A hydrogen intermediate and peak electrical system (HIPES) has been proposed by Charles Forsberg [4,6] that consists of three components:

(i) **Hydrogen production:** A power plant unit with an associated hydrogen and oxygen production plant to produce H_2 and O_2 at a constant rate to minimize the production costs.

(ii) **Hydrogen storage:** One or more underground facilities for the low-cost storage of hydrogen and oxygen (optional). Underground caverns, depleted oil and gas fields, and aquifers are the traditional approaches to the low cost storage of natural gas to meet seasonally variable natural gas demand. Underground storage is the only known low-cost technology for storing compressed gases; however, the storage economics demand very large facilities. This storage characteristic favours large-scale centralized hydrogen production.

(iii)**Peak electric production:** Large banks of FC (or other systems) convert hydrogen to electricity during periods of high demand for electrical power and associated high prices for electricity. For every megawatt of steady state hydrogen production, there would be several megawatts of FC.

While hydrogen is produced at a constant rate, the fuel-cell electrical production is highly variable—from zero to many times the rate of energy production from the reactor when the price of electricity is high. The economic feasibility of HIPES is based on: (1) the low cost of large-scale bulk storage of hydrogen and (2) projected costs and efficiencies of fuel cells or other technologies to convert hydrogen to electricity. HIPES, as an electric energy storage system, has the unique capability to economically store very large quantities of energy as compressed hydrogen over periods of weeks or months to address weekly and seasonal variations in electric demand. This is not a viable option all kinds of peak electric systems such as pumped hydro systems where the cost of energy storage over time becomes excessive. HIPES, if successful, may be an enabling technology for a nuclear-H_2 renewable economy. The fundamental problem for large-scale use of renewable is to match electricity production to electricity demand. Were there no electricity storage problem, wind or solar would become economic wherever their production cost is below the price of electricity, not the cost of electricity plus energy storage. HIPES may be an enabling technology to meet electricity demand when a significant fraction of the electricity is produced with renewable and the renewable electrical output does not match the consumer demand [5].

1.4 CATALTIC PARTIAL OXIDATION OF ISOOCTANE

The production of synthesis gas based on heterogeneous catalytic reactions using O_2 (air) as an oxidant is referred to as catalytic Partial oxidation (CPO). Although the process is potentially able to process a wide range of hydrocarbon feed-stocks, including heavy hydrocarbons, in our case it is isooctane. The catalytic partial oxidation of isooctane can be presented by the following equation:

$$C_8H_{18} + 4\,O_2 \rightarrow 8\,CO + 9\,H_2 \qquad \Delta H_{298} = -660.9\ \text{kJ/mol}$$

Partial oxidation is highly exothermic reaction. Therefore, it doesn't require an external supply of energy. The conversion of heavy hydrocarbons to hydrogen by catalytic partial oxidation tends to suffer from coke deactivation. Hence, there has been emphasis on the development of highly active and coke-resistant catalyst for Partial oxidation.

The catalytic partial oxidation of hydrocarbons has been extensively researched for several decades. Most commonly used catalysts for the catalytic partial oxidation reaction include refractory supported Ni and noble metal–based (e.g., Rh, Pt, Pd, Ir, Ru) catalysts in the form of pellets, monoliths, and foams. Short monolithic honeycomb and foam structures made out of metal oxides usually serve as catalyst carrier. Due to the short residence time, high fuel throughput and syngas yields can be achieved in compact reactors operated nearly adiabatically. These features make catalytic partial oxidation reactors attractive for on-board supply of hydrogen and reformate fuel from conventional logistic as well as synthetic fuels.

1.5 OBJECTIVE OF THE THESIS

Thesis objectives have been planned as below:

1. Development of a steady state one-dimensional non-isothermal model to simulate the partial oxidation of isooctane using oxygen in first fixed bed reactor (FBR-1) and air in second reactor (FBR-2) as oxidants over a Nickel/alumina catalyst to produce hydrogen.
2. To develop flow rates profiles of all four components ($F^t_{C_8H_{18}}, F^t_{CO}, F^t_{O_2}, F^t_{H_2}$) of reactants and products and temperature profile in FBR-1 and FBR-2 with residence time (t) in reactors and to develop profile for the variation of conversion of isooctane and conversion of oxygen with inlet temperature, pressure, C/O ratio in feed and residence time.
3. Comparison of performance of FBR-1 (using oxygen as oxidant) and FBR-2 (using air as oxidant) in terms of conversion of isooctane and conversion of oxygen and to find out dependency of the conversion on factors, C/O ratio in feed, residence time, inlet temperature and pressure in both reactors.

1.6 ORGANIZATION OF THESIS

Thesis consists of four chapters. Chapter 1 include the introduction of thesis, importance of hydrogen production and major routes of hydrogen production and finally the objective of thesis. Chapter 2 gives a brief literature reviewed. Chapter 3 contains details of model developed, assumptions, operating and boundary conditions. Chapter 4 consists of result and discussion, comparison of performance of both reactors.

1.7 CHEMICAL UNDER CONSIDERATION

Our objective is production of hydrogen form partial oxidation of iso-oactane. A brief description about isooctane is as follows:

1.7.1 ISOOCTANE

2,2,4-Trimethylpentane, also known as isooctane, isooctane, is an organic compound with the formula $(CH_3)_3CCH_2CH(CH_3)_2$. It is one of several isomers of octane (C_8H_{18}). It is an important component of gasoline, frequently used in relatively large proportions to increase the knock resistance of the fuel. Isooctane is produced on a massive scale in the petroleum industry by distillation of petroleum. It can also be produced from isobutylene by dimerization using an Amberlyst catalyst to produce a mixture of isooctenes. Hydrogenation of this mixture produces 2,2,4-trimethylpentane. In common with all hydrocarbons, inhalation or ingestion of large quantities of isooctane is harmful. In rare cases a stronger reaction can occur.

TABLE -1.1 Physical Properties of Isooctane

ISOOCTANE PROPERTIES	
Physical appearance	Colourless, transparent liquid, flammable, not soluble in water, soluble in ether, soluble in alcohol, acetone, benzene, chloroform
Molecular formula	C_8H_{18}
Molar mass	114.140g mol^{-1}
Flash point	-12.22°C (10°F)
Auto ignition point	411°C(772°F)
Odour	Odourless
Specific gravity /Density	692 mg mL^{-1}
Melting point	-107 °C(-160.6 °F),
Boiling point	99 °C(210°F)
Vapour pressure	5.5 kPa (at 21 °C)
Refractive index(N_D)	1.391
Explosive limits	1.10-6.00 vol %
Viscosity, kinematic	0,503 cSt at 20 °C (68 °F)

Chapter-2

LITERATURE REVIEW

This chapter contains a review of the existing research, to the extent available, on the catalytic partial oxidation of isooctane over various catalysts e.g. rhodium, Ni/β"-Al_2O_3 and Ni/$Ce_{0.75}Zr_{0.25}O_2$ and their characteristics and performance has been presented

Pengpanich Sitthiphong et al. (2006) [16] studied the partial oxidation of isooctane over catalysts Ni/Al_2O_3 and Ni/$Ce_{0.75}Zr_{0.25}O_2$. The partial oxidation products were mainly H_2 and CO for Ni/$Ce_{0.75}Zr_{0.25}O_2$ catalyst, with hydrogen selectivity up to 53% in the temperature range of 550–800 K with a C/O feed ratio of 1. The H_2/CO ratio was in the range of 1.3–1.7 depending on the operating temperature. At temperatures above 700 K, the presence of methane was detected. The main products of isooctane partial oxidation over Ni/Al_2O_3 catalyst were CO_2 and i-C_4H_8 at temperatures below 650 K while H_2 and CO along with small amount of hydrocarbons such as CH_4, C_2H_4, C_2H_6 and C_3H_6 were obtained at temperatures above 650-800 K, yielding a H_2/CO ratio of about 1.3. As a result, the hydrogen selectivity was lower than that of Ni/$Ce_{0.75}Zr_{0.25}O_2$ catalyst. For both catalysts, the carbon dioxide and carbon monoxide selectivities were decreased whilst the hydrogen and hydrocarbons selectivities were increased with increasing C/O feed ratio. The Ni/$Ce_{0.75}Zr_{0.25}O_2$ catalyst can be operated over a wider C/O feed ratio range than the Ni/Al_2O_3 catalyst, resulting in less amount of carbon formed.

Characterisations of both catalysts experimentally studied were the surface areas, the degree of Ni dispersion, crystalline structure and the amount of coke formation in the spent catalysts.

Experimental procedure for catalytic activity tests, a fixed-bed quartz tube micro-reactor (i.d. Ø 6 mm) was used for conducting the catalytic activity tests for isooctane partial oxidation. Typically, ca. 10 mg of catalyst sample diluted in 90 mg of Al_2O_3 was packed between the layers of quartz wool. The reactor was placed in an electric furnace equipped with K-type thermocouples. The catalyst bed temperature was monitored and controlled by Shinko temperature controllers. Isooctane was vaporized from a saturator at 10 °C using He as carrier gas. The concentration of isooctane was maintained at 0.8 mol%. Typically, the feed composition was altered to obtain C/O ratios in the range between 0.6 and 1.6, balanced with He. The total flow rate of feed gases was kept at 150 ml/min (GHSV = 80,000 h^{-1}) using

Aalborg mass flow controllers. The product gases were chromatographically analyzed using a Shimadzu GC 14A equipped with a CTR 1 (Alltech) column for a TCD detector and Porapak ®Q (Alltech) column for an FID detector. The conversions (X) were determined by dividing the moles of reactant consumed by the mole of initial reactant. The selectivities (S) reported in this work were calculated by the ratio of the moles of a specific product to the total moles of all products based on dry basis.

It was concluded that $Ni/Ce_{0.75}Zr_{0.25}O_2$ catalyst is more active than Ni/Al_2O_3 catalyst for Partial oxidation of isooctane. Under the Partial oxidation reaction conditions, synthesis gas was produced at temperatures above 550 K on the $Ni/Ce_{0.75}Zr_{0.25}O_2$ catalyst, whereas Ni/Al_2O_3 required temperatures above 650 K. Alkanes and olefins (CH_4, C_2's, C_3's and C_4's) were produced over the Ni/Al_2O_3 catalyst; however, only CH_4 was formed over the $Ni/Ce_{0.75}Zr_{0.25}O_2$ catalyst. This suggests that Ni/Al_2O_3 may be used for the simultaneous production of H_2 for fuel cells and of value-added chemicals. Both catalysts are quite stable when operated under normal conditions, yet the $Ni/Ce_{0.75}Zr_{0.25}O_2$ catalyst is more stable when rich conditions are applied. The addition of steam promotes a water-gas shift reaction, resulting in a larger amount of hydrogen production and less amount of coke formation. Although the isooctane conversion of both catalysts remains unchanged, H_2 selectivity over Ni/Al_2O_3 catalyst significantly decreased due to the phase change of Al_2O_3 support, in the presence of steam.

Pengpanich Sitthiphong et al. (2008) [17] studied $Ni/Ce_{0.75}Zr_{0.25}O_2$ catalyst doped with different amount of Sn by co-impregnation method. Sn is well known to decrease carbon deposition in many processes such as aromatization and dehydrogenation of paraffins. Addition of a small amount of Sn (<0.5 wt. %) lowered the catalytic activity for isooctane partial oxidation by less than 5% while the extent of carbon deposition was decreased by more than 50%. However, Sn loadings higher than 1 wt.% caused a massive drop in catalytic activity. This indicates that as long as the Ni surface is only partially covered with Sn species, the active sites for the partial oxidation of isooctane remain intact, while the surface site ensembles required for carbon formation are blocked.

Characterisations of catalyst experimentally studied were the surface areas, the degree of Ni dispersion, crystalline structure, morphology of the catalyst, redox properties over the resultant material, surface composition of the catalyst and the amount of coke formation in the spent catalyst.

Experimental procedure for catalytic activity tests, a fixed-bed quartz tube micro-reactor (i.d. Ø 6 mm) was used for conducting the catalytic activity tests for isooctane partial oxidation. Typically, ca. 10 mg of catalyst sample diluted in 90 mg of α-Al_2O_3 was packed between the layers of quartz wool. The reactor was placed in an electric furnace equipped with K-type thermocouples. The catalyst bed temperature was monitored and controlled by Shinko temperature controllers. Isooctane was vaporized from a saturator at 10 °C using He as carrier gas. The concentration of isooctane was maintained at 0.8 mol%. Typically, the feed composition was altered to obtain C/O ratios in the range between 0.6 and 1.6, balanced with He. The total flow rate of feed gases was kept at 150 ml/min (GHSV = 80,000 h^{-1}) using Aalborg mass flow controllers. The product gases were chromatographically analyzed using a Shimadzu GC 14A equipped with a CTR 1 (Alltech) column for a TCD detector and Porapak ®Q (Alltech) column for an FID detector. The conversions (X) were determined by dividing the moles of reactant consumed by the mole of initial reactant. The selectivities (S) reported in this work were calculated by the ratio of the moles of a specific product to the total moles of all products based on dry basis

It was concluded that the addition of small amounts of Sn (<0.5 wt.%) into $Ni/Ce_{0.75}Zr_{0.25}O_2$ catalysts decreases the amount of carbon deposition, while maintaining most of the catalytic activity for i-C_8H_{18} Partial oxidation. This might be due to partial coverage of NiO particles with Sn species, disrupting the active site ensembles responsible for coking. When added in high amounts, a total coverage of Ni particles by Sn leads to loss of catalytic activity. Furthermore, addition of Sn could also reduce the amount of whisker carbon growth by retarding the solubility of carbon in Ni particles.

Hartmann M. et al. (2009) [8] experimentally and numerically studied Catalytic partial oxidation of isooctane over a rhodium/alumina coated honeycomb monolith at short-contact times for varying fuel-to-oxygen ratios. The conversion on the catalyst and in the gas-phase is modelled by detailed reaction mechanisms including 857 gas-phase and 17 adsorbed species. Elementary-step based heterogeneous and homogeneous reaction mechanisms are implemented into two-dimensional flow field description of a single monolith channel. In the experimental part of this study, a recently developed experimental set-up for catalytic partial oxidation of liquids is used, in which well-defined inlet and boundary conditions are realized.

Experimental procedure, the C/O ratio is used as parameter for the description of the composition of the mixture entering the catalyst. The C/O ratio is varied between 0.8 and 1.2

at a constant dilution with 80 vol.% nitrogen. A total flow rate of 4 slpm is used corresponding to a gas hourly space velocity (GHSV) of 85,000 h^{-1} referred to standard conditions (298.15 K, 1013.25 mbar). Fuel and synthetic air are fed to the reactor at 463 K. At the reactor outlet, a part of the product stream (0.5–2.0 slpm) is directed to a process FT-IR with high-optical-throughput sampling cell in a tempered line at 418 K. The FTIR analyzes the infrared active components CO, CO_2, H_2O, CH_4, $H_2C{=}CH_2$, $CH_3{-}CH{=}CH_2$, $H_2C{=}O$, $CH_3{-}CH{=}O$. After cooling the product stream down to 268 K to remove high boiling liquids, the infrared inactive components H_2 and O_2 are analyzed by a sector field mass spectrometer and a paramagnetic gas analyzer, respectively.

Assumption taken in modeling, (1) Due to the thermal insulation, the radial temperature gradient across the catalyst is small. Furthermore, uniform inlet conditions are ensured. (2) All channels of the monolith behave essentially alike, and one representative channel needs to be analyzed only. This single channel is then approximated by an axis-symmetric cylinder leading to the axial and radial spatial coordinates as independent variables of the flow field simulation. (3)Due to the short residence time, being on the order of milliseconds, the transport in axial direction is mainly determined by convection implying that axial diffusion can be neglected, which reduces the elliptical structure of the steady-state Navier–Stokes equations to a parabolic one by application of a boundary-layer approximation.

It was concluded very high hydrogen and carbon monoxide selectivity was found at stoichiometric conditions (C/O = 1), while at lean conditions more total oxidation occurs. At rich conditions (C/O > 1), homogeneous chemical conversion in the gas-phase is responsible for the formation of by-products such as olefins that also have the potential for coke formation, which was observed experimentally and numerically. This study also reveals that the chemical models applied – even though the most detailed ones available were used – need further improvement. Potential extensions of the models are seen in the implementation of more sophisticated coking models and a more detailed description of adsorption of higher hydrocarbons (surface chemistry) and the evaluation of the gas-phase mechanism applied.

Hartmann M. et al. (2010) [9] studied catalytic partial oxidation of isooctane experimentally and numerically over a rhodium/alumina coated honeycomb monolith at millisecond contact times by varying both fuel-to-oxygen ratio and flow rates and at varying flow rates. The quantity of by-products strongly depends on the flow rate. Both fuel conversion and hydrogen yield increase with increasing flow rate, i.e., decreasing residence time. Therefore, an elementary-step-like heterogeneous reaction mechanisms implemented into a two-dimensional flow field description of a single monolith channel, coupled with a heat balance of the entire monolithic structure. In a previous work of this author, a detailed numerical simulation for catalytic partial oxidation of isooctane over rhodium was conducted. In particular, the formation of undesired by-products and the role of homogeneous gas-phase reactions were considered in this work. It has been shown that the formation of soot precursors occurs through homogeneous gas-phase reactions at rich operating conditions and high temperatures. It presents an experimental and numerical study on the impact of the mass flow rate on conversion, selectivity, and operating temperature in an auto-thermal short-contact time reactor at atmospheric pressure. In addition to the mass flow rate which has been varied between 2 and 6 splm, the fuel-to-oxygen ratio has been changed from oxygen excess to oxygen deficiency conditions.

Experimental procedure, the C/O ratio is used as parameter for the description of the composition of the mixture entering the catalyst. The C/O ratio is varied between 0.8 and 1.3 at a constant dilution with 80 vol.% nitrogen. To investigate the effect of residence time on the catalytic partial oxidation of higher hydrocarbon fuels, the total flow rate of the inlet mixture has been varied from 2 to 6 slpm in small steps of 1 slpm. These flows correspond to gas hourly space velocity (GHSV) between 42 500 h^{-1} at 2 slpm and 127 000 h^{-1} at 6 slpm referred to standard conditions (298.15 K, 1013.25 mbar).

Assumption taken in modeling, (1) Due to the thermal insulation, the radial temperature gradient across the catalyst is small. Furthermore, uniform inlet conditions are ensured. (2) All channels of the monolith behave essentially alike, and one representative channel needs to be analyzed only. This single channel is then approximated by an axis-symmetric cylinder leading to the axial and radial spatial coordinates as independent variables of the flow field simulation. (3)Due to the short residence time, being on the order of milliseconds, the transport in axial direction is mainly determined by convection implying that axial diffusion can be neglected, which reduces the elliptical structure of the steady-state Navier–Stokes equations to a parabolic one by application of a boundary-layer approximation (4) Heat losses due to radiation, in particular of the front and back side of the catalytic monolith, may have a severe effect on the temperature profile. The amount of heat loss primarily depends on the temperature of the solid structure of the catalyst.

The resulting PDEs are semi-discretized by a method of lines leading to a large-scale, structured, differential algebraic equation (DAE) system, which is solved using the computational code DETCHEM^{CHANNEL}.

It was concluded that this combined experimental, modeling, and simulation study led to a much better understanding of the relation between flow rate, chemical heat release, and thermal heat losses in catalytic partial oxidation of isooctane – serving as a logistic fuel model component – over a rhodium coated monolithic catalyst. Two-dimensional simulations of the flow field in the single catalytic channels coupled with detailed models for heterogeneous fuel conversion can substantially support the understanding of the reaction sequences and help to understand the experimentally observed behaviour. Although the simulation-assisted discussion of the experimental behaviour was conducted for one C/O ratio only, it was exemplarily shown how molecular based models can support a better understanding of the reactor behaviour.

Hussam H. Ibrahim et al. (2006) [10] studied the kinetics of the catalytic partial oxidation of isooctane for hydrogen production over a stable Ni/Al_2O_3 catalyst at atmospheric pressure in the temperature range of 663–913 K, ratio of weight of catalyst to the molar feed rate of isooctane (W/F^0_{iC8}) in the range of 7.09-30.89 kg mol^{-1}, and molar feed ratio $O_2/i\text{-}C_8H_{18}$ of 4.0 in a 12.7mm diameter Inconel micro-reactor housed in an electrically controlled furnace. The objective of the present study is to develop a mechanistic based kinetic model to describe the catalytic partial oxidation of isooctane to produce hydrogen using this stable Ni/Al_2O_3 catalyst. The developed models are based essentially on the Langmuir–Hinshelwood–Hougen–Watson (LHHW) and Eley–Rideal (ER) hypotheses and these were cross-examined with actual experimental kinetic data. Out of the 18 models developed, 10 were eliminated due to poor predictive efficiency. A LHHW mechanism requiring the dissociative adsorption of isooctane and molecular adsorption of oxygen on a single site was the most likely pathway for the partial oxidation of isooctane.

Experimental procedure, An Inconel fixed bed reactor (ID = 12.7mm) housed in a furnace with a single heating zone was used for catalyst performance evaluation. Liquid isooctane was introduced by a syringe pump while the gas flows were metered and regulated by an Aalborg digital flow controller. The air to isooctane molar ratio was 12.0. Experimental kinetic data were collected at atmospheric pressure; temperatures of 863, 883, 903 and 913 K; and W/F^0_{iC8} of 255.6, 198.0, 162.0 and 136.8 kg-cat s kg-iC_8^{-1}. Catalyst particle size of 150 μm and feed flow rate of 390mL min^{-1} were used to eliminate pore and external diffusional limitations, respectively. The pressure drop along the reactor was calculated for the particle size used and found to be insignificant ($< 5 \times 10^3$ Pa) at the highest reaction temperature.

Assumption taken in modeling, (1) the rate-determining step (RDS) could be controlled by the surface reaction step, adsorption step or desorption step; (2) there is the presence of uniformly energetic adsorption sites; and (3) there is monolayer coverage. The only differing assumption between LHHW and ER mechanisms was the use of a dual site mechanism for the reaction in the former case and a single site mechanism in the latter case.

This work investigated the kinetics of the partial oxidation of isooctane over a stable Ni/Al_2O_3 catalyst. The chemical reaction was modelled using rate models developed from the LHHW and ER mechanisms. Out of the eighteen models proposed, eight converged but only four exhibited acceptable the percentage absolute average deviation (AAD %) and comparable activation energy as compared to the power law model. A LHHW mechanism requiring the dissociative adsorption of isooctane and molecular adsorption of oxygen on a single site appeared to be the most likely pathway for the partial oxidation of isooctane. The reaction order of 1.5 for this model indicates a strong coverage of nickel by isooctane. The activation energy estimated from the LHHW model was 2.81×10^5 J mol^{-1}.

Oscar G. Marin Flores et al. (2009) [15] studied the performance of molybdenum dioxide (MoO_2) as a catalyst for the partial oxidation of isooctane. Metallic character and high oxygen mobility exhibited by this oxide appear to enhance its catalytic activity, which can be explained in terms of the Mars–van Krevelen mechanism. An oxygen-to-carbon ratio (O/C) of 0.72 seems to stabilize the catalytic performance, which could reach H_2 yields of 78% and carbon conversions of 100%, at 700°C and 1 atm, after 20h on stream. In addition, the catalyst was tested for sulphur tolerance using thiophene as model sulphur compound. Our findings indicate that the catalytic activity is barely affected even at sulphur concentrations as large as 500 ppm, after 7 h on stream. Finally, the catalyst performance was compared to that of a nickel catalyst using premium gasoline as fuel. MoO_2 displayed a stable performance whereas the Ni catalyst deactivated due to coke formation. The objective of this work is to understand how the various operating conditions affect the partial oxidation of gasoline over bulk MoO_2 catalyst. The section one of this paper characterizes the physical properties of bulk MoO_2. The body of the present work combines thermodynamic analysis and experimental results to investigate the mechanistic process of MoO_2 toward the isooctane reforming reaction. Finally, the catalyst was tested to understand how the presence of sulphur compounds and coking precursors would influence their reforming activity and long-term stability.

Experimental procedure, it was performed in a 12 mm fixed-bed tubular (quartz) reactor. The liquid feed, consisting of either isooctane or premium gasoline, was vaporized at 200°C and 350°C, respectively. The vapour obtained was mixed along with air, employed as oxygen source for the partial oxidation, using a silicon carbide bed to enhance the mixing. Calibrated syringe pumps and mass flow controllers were employed to control the flow rates. The exit stream was cooled down to 5°C to separate water, non-reacted fuel, and other possible condensable compounds from the off-gas. The dry gas product was analyzed using an SRI chromatograph to monitor H_2, CO, CO_2, and CH_4 concentrations. The GC columns used for this purpose were Molecular Sieve 13X and HyesepD. The carrier gas was a mixture of 10% hydrogen and 90% helium.

It was concluded that the catalytic activity of MoO_2 for the partial oxidation of isooctane appears to be the result of the dual metallic–acidic character of the catalyst surface combined with its remarkable oxygen mobility. The mechanism of reaction proposed by Mars– van Krevelen seems to be responsible for the stability of the catalyst. At 700°C and after 20h on stream, MoO_2 displayed a stable performance for the partial oxidation of isooctane with a H_2 yield of 78% and a conversion of 100%. MoO_2 exhibits a significant sulphur tolerance. The adsorption of sulphur compounds seems to affect the selectivity by enhancing the total oxidation of the fuel at the expense of its partial oxidation. MoO_2 is able to reform actual gasoline displaying a higher coking resistance when compared to that exhibited by an active Ni catalyst.

Chapter-3

MODEL DEVELOPMENT

3.1 INTRODUTION

A model is a set of assumptions about the operation of the system, logical, algorithm, and mathematical. Mathematical model of any process is a set of equations including the necessary input data to solve the equations, whose solution gives a specified data representative of the process to a corresponding set input that allows us to predict the behaviour of chemical process system. Processing modeling has made substantial progress over decades. Today, computer simulation is used extensively to analyze the dynamic chemical process or design controllers and study their effectiveness in controlling the process. The simulation operations make it possible to evaluate the influence of variables on any process theoretically. Steady state simulation of parameter system involves the solution of algebraic equations, while dynamic simulation involves the solution of ordinary differential equations. Also by comparing the experimental results with simulation results, one can decide if it is necessary to develop a more detailed model or it is possible to introduce simplifying assumptions to the model. The simulation is also used to fix the experimental conditions needed for design, optimization, and control. Engineers are now capable of building mathematical models with a degree of details and prediction.

In chemical reaction engineering, kinetic modeling is the concept of mathematical description of chemical reactions which occur in a reactor. The kinetic models are based on description of transport processes, and the reaction mechanisms involved in a chemical process. The time evolution of mole fraction of the reacting species in a batch reactor or plug flow reactor is governed by the ordinary differential equations. The governing model non-linear equations are to be solved by using numerical methods. The numerical solution is always an approximation. Arrhenius equation is used to find the temperature dependency of the reactions involved in transformation of isooctane to synthesis gas.

In this chapter, a steady state one-dimensional non-isothermal model have been developed to simulate the partial oxidation of isooctane in two fixed bed reactors over a Nickel/alumina catalyst bed to produce hydrogen. Oxygen is used as oxidant in first fixed bed reactor (FBR-1) and air as oxidant in second reactor (FBR-2). For both reactors, material balance equation for each component and energy balance equation have been written and a computer program written by MATLAB environment (version 9) is used to perform all the calculation.

3.2 KINETIC CONSIDERATION

In development of model, one of the major reaction namely partial oxidation of isooctane is considered in fixed bed reactors. The intrinsic kinetics of partial oxidation of isooctane has been studied extensively in literature on noble metal based catalysts (Ni, Ce, Sn, and Rh). In these sense, Hussam H. Ibrahim et al. (2006) [10] deduced a power law equation, fitted to an experimental data obtained on a commercial catalyst (Ni/Al_2O_3) and valid for temperature range 663-913K.

The overall reaction considered in the development of model is given as:

$$C_8H_{18} + 4\,O_2 \rightarrow 8\,CO + 9\,H_2 \qquad \Delta H_{298} = -660\ kJ/mol$$

The power law rate expression for this reaction over a Nickel/alumina is given as:

$$r_A = k_0\, e^{(-E/RT)}\, C_A^{\ m} \tag{3.1}$$

Where values of constants are $k_0 = 4.33 * 10^{18}$ kg-cat^{-1}s^{-1}

Activation energy (E) = $2.99 * 10^5$ J mol^{-1}

And reaction order (m) = 0.82

3.3 STEADY STATE MODELING OF FIXED BED REACTOR-1 (FBR-1) USING OXYGEN AS OXIDANT:

3.3.1 MODEL ASSUMPTIONS

In order to develop a one-dimensional steady state non-isothermal mathematical model for fixed bed reactor (FBR-1), a tubular reactor is considered with radius of 12 mm and length of 80 mm and loaded with catalyst (Ni/Al_2O_3) where catalyst density is 2100 kg/m^3. In this reactor, isooctane and oxygen is entering form one side and reaction is taking place over catalyst bed in temperature range 775-820 K at various C/O ratio. Along the length of reactor, isooctane is converted to synthesis gas. Thus, on the other side of reactor product gas and unconverted reactants are leaving the reactor. The following figure represents a scheme of this fixed bed tubular reactor:

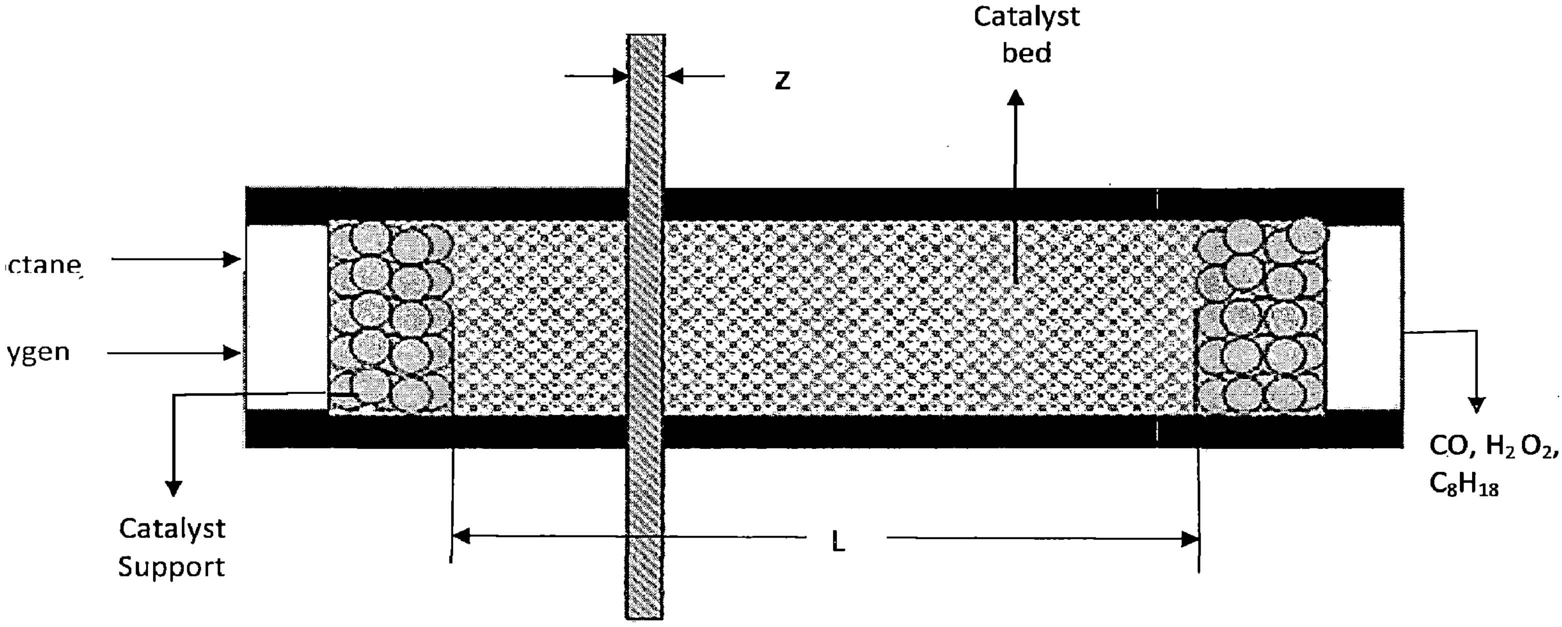

Figure –3.1 Schematic diagram of fixed bed reactor-1(FBR-1)

The small element z is considered along the length of reactor and material balance equation for each component and energy balances have been written for this small element. The following assumptions are taken in writing these balance equation:

1. Operation is adiabatic and isobaric.
2. Concentration and temperature gradients in radial direction are neglected.
3. Axial dispersion is neglected.
4. The deposition of carbon on catalytic surface is neglected resulting in no deactivation of catalyst.
5. Internal mass transfer resistance of catalyst particles is neglected due to small size of particles.
6. Ideal gas law holds true.

3.2.2 MATERIAL AND ENERGY BALANCE EQUATIONS

With the above specified assumptions, the component mass balance and energy balances over a differential reactor volume (z) have been written for the reaction zone. The subscript 'i' represents the reaction components in a sequence of C_8H_{18}, O_2, CO, H_2. F^t_i and T are the molar flow rates of components 'i' and temperature in reaction zone respectively. The general balance equations are as follows:

Component mass balance equation for any component 'i' is given as:

$$\frac{dF_i^t}{dz} = \pi R_1^2 \rho_B (1 - \varepsilon_B) \mu_i r_A \tag{3.2}$$

Energy balance equation is given as:

$$\frac{dT}{dz} = \frac{1}{\sum_{i=1}^{6} F_i^t \, Cp_i} \{\pi R_1^2 \rho_B (1 - \varepsilon_B) * (-\Delta H_r r_A)\} \tag{3.3}$$

Where Cp_i = heat capacity of i^{th} component, J $mol^{-1}K^{-1}$,
F_i^t= molar flow rate of i^{th} component, mol s^{-1},
r_i= formation or consumption rate of i^{th} species in reaction zone, mol kg-cat^{-1} s^{-1},
R_1= inner radius of membrane tube, m
T= temperature inside the tube of reactor, K
z = reactor length at any point, m
ε_B = void fraction of packing, m^3m^{-3},
μ_i= stoichiometric coefficient of component 'i^{th}' in reaction,
ρ_B= bulk density of catalyst, kg m^{-3}
υ = volumetric flow rate in reactor m^3/sec,
P = pressure in the reactor, N/m^2,
R = universal gas constant (8.314 J $mol^{-1}K^{-1}$)

These balance equations (3.2 and 3.3) are written in terms of spatial variable z, along the length of reactor. Based on assumption stated above these equations are converted in terms of residence (t) time using following relation:

$$\text{Residence time(t)} = \frac{\text{Total volume(V)}}{\text{Volumetric flow rate}(\upsilon)} = \frac{\pi R_1^2 \, z}{\upsilon} \tag{3.4}$$

And according to ideal gas law,

$$P\upsilon = (\, F^{t}_{C_8H_{18}} + F^{t}_{O_2} + F^{t}_{CO} + F^{t}_{H_2} \,)\ RT \tag{3.5}$$

Using these above equations 3.4 and 3.5 we can write dz in terms of dt:

$$dz = \frac{(\, F^{t}_{C_8H_{18}} + F^{t}_{O_2} + F^{t}_{CO} + F^{t}_{H_2} \,)RT}{P * \pi R_1^2} * dt \tag{3.6}$$

Using above equation 3.6, the energy and material balance equation are written in terms residence time (t). For this fixed bed reactor, four gaseous components are present in reaction zone (C_8H_{18}, O_2, CO, H_2). As a result, the mathematical model consist five ordinary differential equations (ODEs) which are written in term of residence time given as:

Material balance equation for isooctane (C_8H_{18}):

$$\frac{dF^{t}_{C_8H_{18}}}{dt} = \frac{\rho_B(1-\varepsilon_B) * (\, F^{t}_{C_8H_{18}} + F^{t}_{O_2} + F^{t}_{CO} + F^{t}_{H_2} \,) * RT * -r_A}{P} \tag{3.7}$$

Material balance equation for oxygen (O_2):

$$\frac{dF^{t}_{O_2}}{dt} = \frac{\rho_B(1-\varepsilon_B) * (\, F^{t}_{C_8H_{18}} + F^{t}_{O_2} + F^{t}_{CO} + F^{t}_{H_2} \,) * RT * -4r_A}{P} \tag{3.8}$$

Material balance equation for carbon monoxide (CO):

$$\frac{dF^{t}_{CO}}{dt} = \frac{\rho_B(1-\varepsilon_B) * (\, F^{t}_{C_8H_{18}} + F^{t}_{O_2} + F^{t}_{CO} + F^{t}_{H_2} \,) * RT * 8r_A}{P} \tag{3.9}$$

Material balance equation for hydrogen (H_2):

$$\frac{dF^{t}_{H_2}}{dt} = \frac{\rho_B(1-\varepsilon_B) * (\, F^{t}_{C_8H_{18}} + F^{t}_{O_2} + F^{t}_{CO} + F^{t}_{H_2} \,) * RT * 9r_A}{P} \tag{3.10}$$

Energy balance equation:

$$\frac{dT}{dt} = \frac{\rho_B(1-\varepsilon_B) * \left(\, F^{t}_{C_8H_{18}} + F^{t}_{O_2} + F^{t}_{CO} + F^{t}_{H_2} \,\right) * RT * (-\Delta H_r r_A)}{P * (F^{t}_{C_8H_{18}} C_{pC_8H_{18}} + F^{t}_{H_2} C_{pH_2} + F^{t}_{O_2} C_{pO_2} + F^{t}_{CO} C_{pCO})} \tag{3.11}$$

The heat capacity equations for each component in terms of temperature which are used for solving the set of ODE are given as:

$$C_{p_{C_8H_{18}}} = 24.5425 + 0.60685 * T - 1.9086 * 10^{-4} * T^2 \qquad (3.12)$$

$$C_{p_{CO}} = 22.2237 + 0.014793 * T - 3.2676 * 10^{-6} * T^2 \qquad (3.13)$$

$$C_{p_{O_2}} = 25.1967 + 0.0100815 * T - 2.8961 * 10^{-6} * T^2 \quad \text{And} \qquad (3.14)$$

$$C_{p_{H_2}} = 12.9436 + 0.0056478 * T - 3.3824 * 10^{-6} * T^2 \qquad (3.15)$$

Consequently, the solution of these ordinary differential equations provides the axial profiles of five variable($F^t_{C_8H_{18}}$,$F^t_{O_2}$, F^t_{CO},$F^t_{H_2}$ and T) in FBR-1 with residence time(t).

3.2.3 BOUNDARY AND INTIAL OPERATING CONDITIONS

Thus, all the boundary conditions required to solve the set of ODEs are available at the inlet end of reactor i.e. at z = 0. So, the boundary conditions are as follows:

$$F_i^t \Big|_{z=0} = F^t_{i_{in}} \qquad (3.16)$$

$$T \Big|_{z=0} = T^t_{in} \qquad (3.17)$$

In view of the fact that all boundary conditions are given at z = 0, therefore, the set of ODEs constitutes the initial value problem. In this work, the set of ODEs is solving by using ODE solver ''ode45'' in MATLAB R2009a.

All initial conditions for solving these ODE equations are given below:

$$F^t_{C_8H_{18}} = 2.5 * 10^{-3} \text{ mol sec}^{-1} \qquad (3.18)$$

$$F^t_{O_2} = 10 * 10^{-3} \text{mol sec}^{-1} \quad \text{For} \frac{C}{O} \text{ratio} = 1 \qquad (3.19)$$

$$F^t_{CO} = 0 \qquad (3.20)$$

$$F^t_{H_2} = 0 \qquad (3.21)$$

$$T_{inlet} = 800 \text{ K} \qquad (3.22)$$

The standard initial conditions, operating conditions, and reactor specifications are given in Tables:

Table-4.1 Initial and operating conditions for simulation of reactors [10]

Feed composition	
Inlet flow rate of C_8H_{14} (mol s^{-1})	2.5 * 10^{-3}
Inlet flow rate of CO (mol s^{-1})	0
Inlet flow rate of H_2 (mol s^{-1})	0
C_8H_{18}/O_2 ratio in FBR-1	0.25

Table-4.2 Reactor configurations for simulation of reactors [11]

Reactor configuration	
Length of reactor L (mm)	80mm
Tube radius R_1 (m)	12 * 10^{-3}
Catalyst density ρ_B (kg m^{-3})	2100
Porosity of catalyst bed (ε_B)	0.43
feed inlet temperature(K)	800
pressure P_s (bar)	14

After Solving all equations using these initial conditions and boundary condition flow rates profiles and temperature profiles obtained for all four components ($F^t_{C_8H_{18}}, F^t_{CO}, F^t_{O_2}, F^t_{H_2}$).

3.4 STEADY STATE MODELING OF FIXED BED REACTOR-2 (FBR-2) USING AIR AS OXIDANT:

3.4.1 MODEL ASSUMPTIONS:

In order to develop a one-dimensional steady state non-isothermal mathematical model for fixed bed reactor (FBR-2), we considered a same tubular reactor and loaded with catalyst (Ni/Al_2O_3). In this reactor, isooctane and air instead of oxygen with significant amount of nitrogen are entering form one side and reaction is taking place over catalyst bed in temperature range 775-820 K at various C/O ratio and unreacted nitrogen is leaving the reactor with product gas and unreacted reactants. The assumptions taken for this reactor are same as for fixed bed reactor -1(FBR -1).

3.4.2 MATERIAL AND ENEGRY BALANCE EQUATIONS

With the specified assumptions, the component mass balance and energy balances over a differential reactor volume (Δz) have been written for the reaction zone. The subscript 'i' represents the components in reactor in a sequence of C_8H_{18}, O_2, CO, H_2, and N_2. F^t_i and T_I are the molar flow rates of components 'i' and temperature in reaction zone respectively

For this fixed bed reactor, five gaseous components are present in reaction zone (C_8H_{18}, O_2, CO, H_2 and N_2). As a result, the mathematical model consist five ordinary differential equations (ODEs) which are written in term of residence time (t) given as:

Material balance equation for isooctane (C_8H_{18}):

$$\frac{dF^t_{C_8H_{18}}}{dt} = \frac{\rho_B(1-\varepsilon_B) * (F^t_{C_8H_{18}} + F^t_{O_2} + F^t_{CO} + F^t_{H_2} + F^t_{N_2}) * RT * -r_A}{P} \quad (3.23)$$

Material balance equation for oxygen (O_2):

$$\frac{dF^t_{O_2}}{dt} = \frac{\rho_B(1-\varepsilon_B) * (F^t_{C_8H_{18}} + F^t_{O_2} + F^t_{CO} + F^t_{H_2} + F^t_{N_2}) * RT * -4r_A}{P} \quad (3.24)$$

Material balance equation for carbon monoxide (CO):

$$\frac{dF^t_{CO}}{dt} = \frac{\rho_B(1-\varepsilon_B) * (F^t_{C_8H_{18}} + F^t_{O_2} + F^t_{CO} + F^t_{H_2} + F^t_{N_2}) * RT * 8r_A}{P} \quad (3.25)$$

Material balance equation for hydrogen (H_2):

$$\frac{dF^t_{H_2}}{dt} = \frac{\rho_B(1-\varepsilon_B) * (F^t_{C_8H_{18}} + F^t_{O_2} + F^t_{CO} + F^t_{H_2} + F^t_{N_2}) * RT * 9r_A}{P} \quad (3.26)$$

Energy balance equation:

$$\frac{dT}{dt} = \frac{\rho_B(1-\varepsilon_B) * \left(F^t_{C_8H_{18}} + F^t_{O_2} + F^t_{CO} + F^t_{H_2} + F^t_{N_2}\right) * RT * (-\Delta H_r r_A)}{P * (F^t_{C_{8H_{18}}} C_{pC_8H_{18}} + F^t_{H_2} C_{pH_2} + F^t_{O_2} C_{pO_2} + F^t_{CO} C_{pCO} + F^t_{N_2} C_{pN_2})} \quad (3.27)$$

The heat capacity (C_p) equations for each component in terms of temperature which are used for solving the set of ODE are given as:

$$C_{p_{C_8H_{18}}} = 24.5425 + 0.60685 * T - 1.9086 * 10^{-4} * T^2 \tag{3.28}$$

$$C_{p_{CO}} = 22.2237 + 0.014793 * T - 3.2676 * 10^{-6} * T^2 \tag{3.29}$$

$$C_{p_{O_2}} = 25.1967 + 0.0100815 * T - 2.8961 * 10^{-6} * T^2 \tag{3.30}$$

$$C_{p_{H_2}} = 12.9436 + 0.0056478 * T - 3.3824 * 10^{-6} * T^2 \text{ And} \tag{3.31}$$

$$C_{p_{N_2}} = 12.6884 + 0.046156 * T - 1.76926 * 10^{-5} * T^2 \tag{3.32}$$

Consequently, the solution of these ordinary differential equations provides the axial profiles of five variable($F^t_{C_8H_{18}}$,$F^t_{O_2}$, F^t_{CO},$F^t_{H_2}$ and T) in FBR-1 with residence time(t).

3.4.3 BOUNDARY AND INTIAL OPERATING CONDITIONS

Thus, all the boundary conditions required to solve the set of ODEs are available at the inlet end of reactor i.e. at z= 0. So, the boundary conditions are as follows:

$$F^t_i \Big|_{z=0} = F^t_{i_{in}} \tag{3.33}$$

$$T_1 \Big|_{z=0} = T^t_{in} \tag{3.34}$$

In view of the fact that all boundary conditions are given at z = 0, therefore, the set of ODEs constitutes the initial value problem. In this work, the set of ODEs is solving by using ODE solver "ode45" in MATLAB R2009a.

All initial conditions for solving these ODE equations are given below:

$$F^t_{C_8H_{18}} = 2.5 * 10^{-3} \text{ mol sec}^{-1} \tag{3.35}$$

$$F^t_{air} = 47.619 * 10^{-3} \text{mol sec}^{-1} \text{ For} \frac{C}{O} \text{ratio } = 1 \tag{3.36}$$

$$F^t_{CO} = 0 \tag{3.37}$$

$$F^t_{H_2} = 0 \tag{3.38}$$

$$T_{inlet} = 800 \text{ K} \tag{3.39}$$

The standard initial conditions, operating conditions, and reactor specifications for FBR-2 are same as for FBR-1.

Chapter-4

RESULT AND DISCUSSION

4.1 INTRODUCTION

This chapter explains all the parameters which have significant impact on the performance of the reactors. The performance of both reactors FBR-1 and FBR-2 for production of synthesis gas from partial oxidation of isooctane have been studied under various conditions. The solutions of the set of these ordinary differential equations for these reactors resulted into axial profile of all components and temperature profile and by using these profiles the performance of the reactors have been analyzed. It is analyzed in terms of conversion of isooctane, conversion of oxygen, inlet temperature of feed and C/O ratio in feed.

Figure 4.1 and Figure 4.2 shows flow rate profiles of all components in FBR-1 and FBR-2 respectively at inlet temperature 810 K, pressure 14 bar and C/O ratio = 1. In both reactors, the conversion of isooctane and oxygen at these conditions is complete but the time taken for complete conversion of isooctane is less in FBR-1 as compare to FBR-2. The presence of N_2 in air increased the time taken for complete conversion because the concentration of oxygen is reduced and rate of reaction is slow. The temperature profiles for the same conditions are shown in Figure 4.5 and Figure 4.6 for FBR-1 and FBR-2 respectively. From Figure 4.5 it can be seen that the temperature profile reached its maximum value and maintained this constant value for rest residence time because at this time the reactants are completely reacted and there is no further reaction in reactor. In Figure 4.6 the temperature profile reached its maximum value just at end of the residence time because the presence of N_2 in air and concentrations of reactants are less. The temperature increase in reactor for FBR-1 is more as compare to FBR-2 because the temperature of inert N_2 is also increased during reaction so the some amount of reaction heat is taken away by N_2 and the overall temperature increase in FBR-2 became less. Figure 4.3 and Figure 4.4 also shows flow rate profiles of all components in FBR-1 and FBR-2 respectively but at inlet temperature 800 K, pressure 14 bar and C/O ratio = 1. The conversion of isooctane and oxygen in both reactors is not complete at these conditions. Overall, in FBR-1 the conversion of isooctane is high compare to FBR-2 but the temperature increase in the reactor is more in FBR-1.The overall performance of FBR-1 is better than FBR-2.

4.2 MODEL VALIDATION

The mathematical model for partial oxidation of isooctane over nickel/alumina has been validated on the basis of percentage conversion of isooctane and percentage conversion of oxygen and C/O ratio in feed. For this purpose the experimental studies of Pengpanich Sitthiphong et al. [16] on the partial oxidation of isooctane using pure oxygen in the fixed bed reactor has been considered. Pengpanich Sitthiphong et al. experimentally studied the partial oxidation of isooctane over catalysts Ni/Al_2O_3 and $Ni/Ce_{0.75}Zr_{0.25}O_2$ using pure oxygen at atmospheric pressure in a fixed bed reactor of diameter of 6 mm. The experiment is carried out on both catalysts but here the experimental results for Ni/Al_2O_3 is considered and the experiment is performed on Ni/Al_2O_3 under following conditions: C/O ratio in range of 0.6-1.6 and flow rate of feed is 150 ml/min over temperature range 650-800 K. The conversion profile of isooctane and oxygen with respect to varying C/O ratio in feed of this experimental work under the condition mentioned above are compared with model results for same experimental conditions.

The Figure 4.15 and figure 4.16 shows the conversion profile of isooctane and oxygen respectively with respect to varying C/O ratio form experimental work and from model for same conditions. From comparisons of the results, it can clearly be seen that model prediction are in good agreement with experimental predictions. Thus mathematical model for isooctane partial oxidation simulates the laboratory reactor as well.

4.3 EFFECT OF C/O RATIO OF FEED

The effect of varying Carbon to Oxygen (C/O) ratio in feed on conversion of isooctane and oxygen is studied while other operating conditions are kept constant. The profile of conversion of isooctane and oxygen with varying C/O ratio are shown in Figure 4.7 and Figure 4.10 respectively for operating conditions, pressure 14 bar, inlet temperature 800 K and constant residence time. Form Figure 4.7, it can be seen that the conversion of isooctane is high for both reactor when C/O ratio is very less(< 0.8) because oxygen is present in excess and while increasing the C/O ratio in feed the conversion of isooctane is reduced because the amount of oxygen is decreasing in feed in both reactor. In FBR-2, at less C/O ratio the amount of nitrogen present in the reactor is more than high C/O ratio ,because of this the conversion of isooctane is less compare to FBR-1.So the conversion in FBR-1 is always high at any C/O ratio as compare to FBR-2 because of inert N_2 presence.

Figure 4.10 shows that at less C/O ratio when the amount of oxygen in feed is more, the conversion of oxygen is not high because at this condition the isooctane is almost completed converted, no further reaction taking place in reactor and excess oxygen is present. While increasing C/O ratio in feed, the conversion of oxygen is increasing because the amount of oxygen is reduced.

4.4 EFFECT OF INLET TEMPERATURE OF FEED

The effect of varying inlet temperature of feed on conversion of isooctane and oxygen is studied while other operating conditions are kept constant. Figure 4.8 and Figure 4.11 shows the isooctane conversion profile and oxygen conversion profile with varying inlet temperature for operating condition, pressure 14 bar, C/O ratio= 0.8 and constant residence time(20sec). The reaction is highly exothermic and it can be seen from both graphs that slight increase in inlet temperature, the conversion of isooctane and oxygen is significantly changed. For high temperature as 815 K, the conversion of isooctane is complete for both reactors. The conversion in FBR-1 is always high at any inlet temperature as compare to FBR-2 because of inert N_2 presence.

Figure 4.13 shows the isooctane conversion profile with varying pressure inside the reactor for operating condition pressure 14 bar, C/O ratio= 1 and constant residence time(20sec) and at these conditions the conversion of oxygen is same as the conversion of isooctane.

4.5 EFFECT OF PRESSURE INSIDE THE REACTOR

The variation of pressure inside the reactor also affects the conversion of isooctane and oxygen is studied while other operating conditions are kept constant. For reactions, the number of moles increases with reaction, the conversion of reactants drops when pressure increased. The profile of conversion of isooctane and oxygen with pressure inside reactor are shown in Figure 4.9 and Figure 4.12 respectively for operating conditions, inlet temperature

800 K, C/O ratio= 0.8 and constant residence time(20sec). It can be seen from graphs that conversion is reduced when pressure is increased because the number of moles increasing in the reactions. When the pressure is very less, the conversion of isooctane is complete. The conversion in FBR-1 is always high at any inlet temperature as compare to FBR-2 because of inert N_2 presence.

The profile of conversion of isooctane with pressure inside reactor are shown in Figure 4.14 for operating conditions, inlet temperature 800 K, C/O ratio= 1 and constant residence time(20sec) and at these conditions the conversion of oxygen is same as the conversion of isooctane.

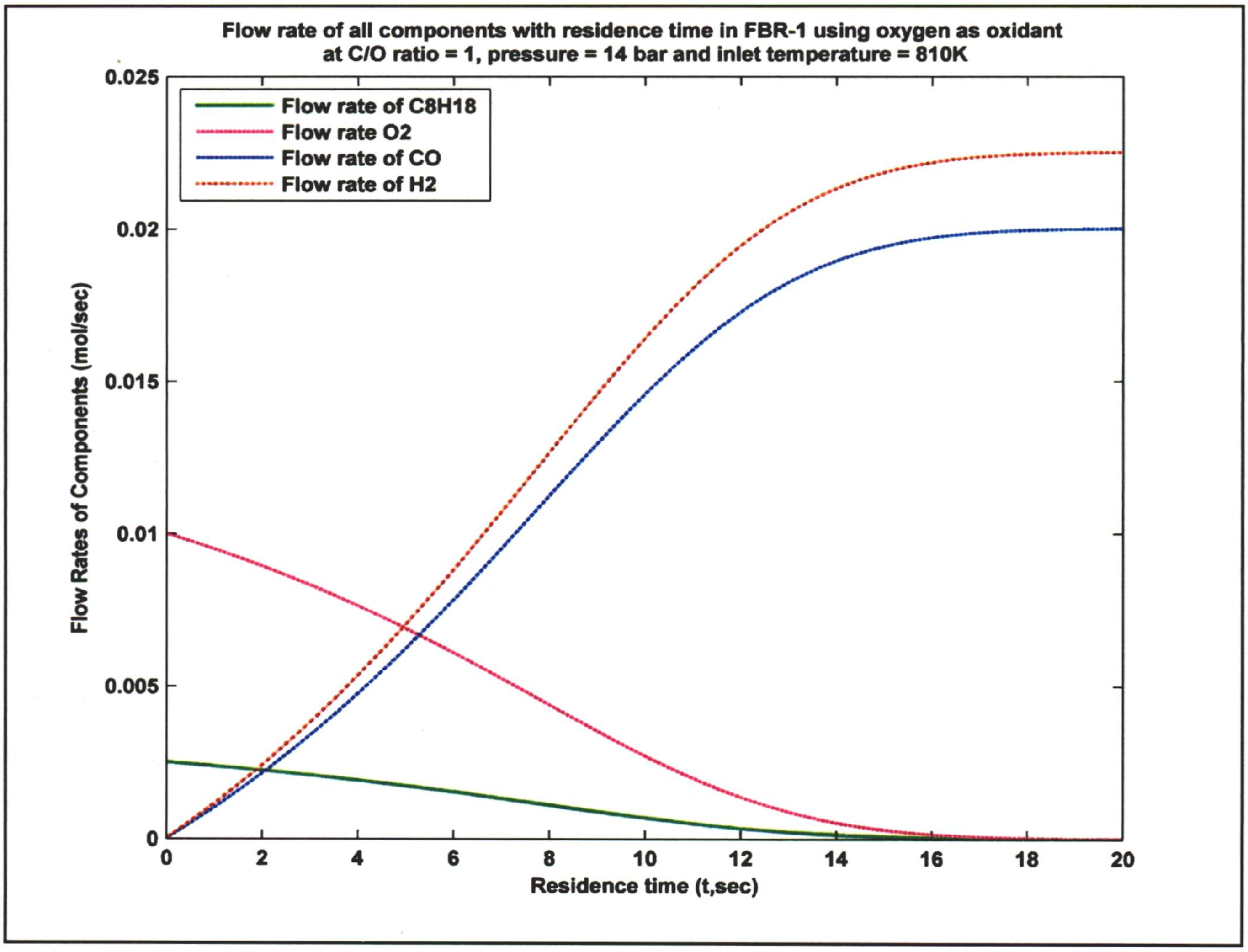

Figure 4.1 Flow rate profile for all components with reactor residence time in FBR-1 at inlet temp 810K, C/O ratio =1 and pressure 14 bar

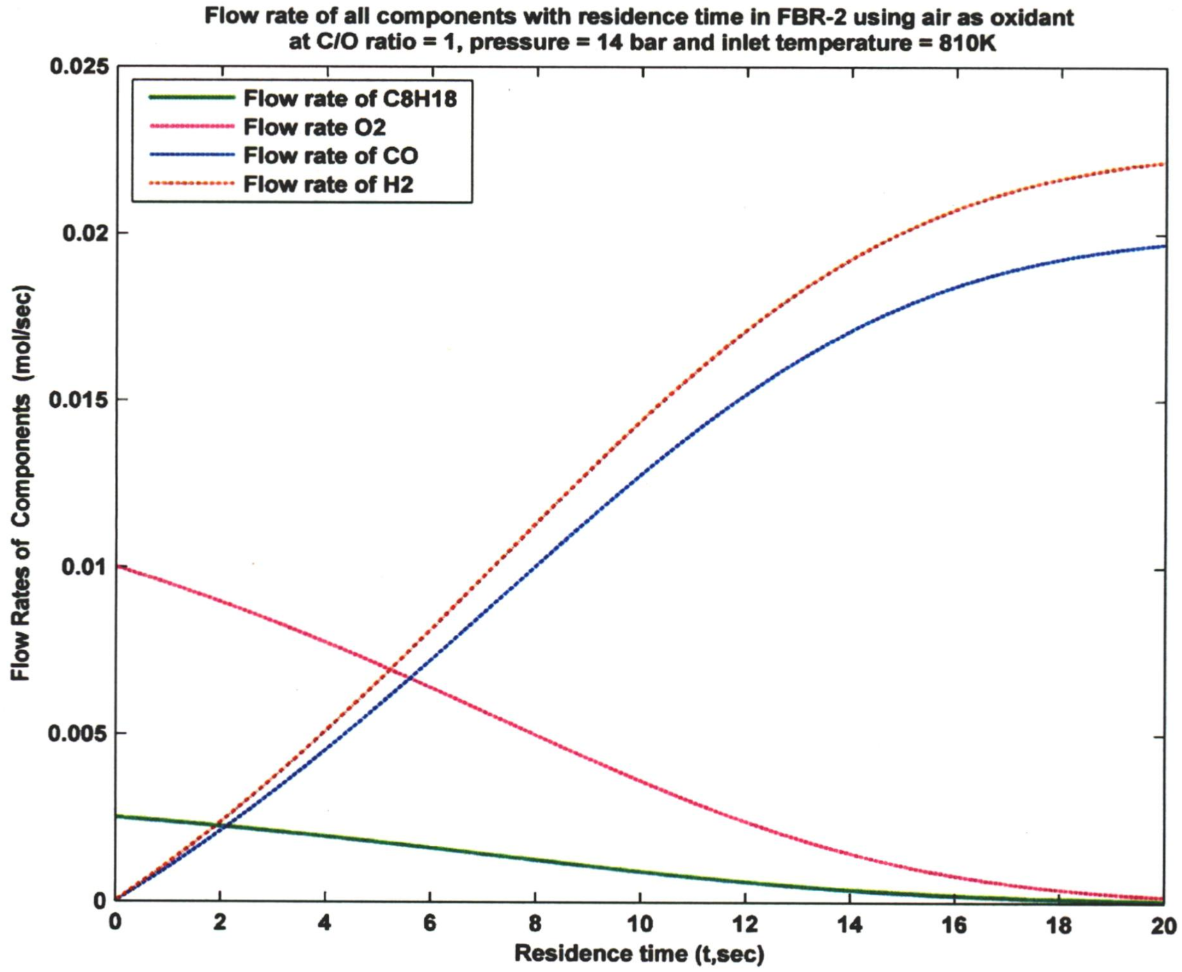

Figure 4.2 Flow rate profile for all components with reactor residence time in FBR-2 at inlet temp 810K, C/O ratio =1 and pressure 14 bar

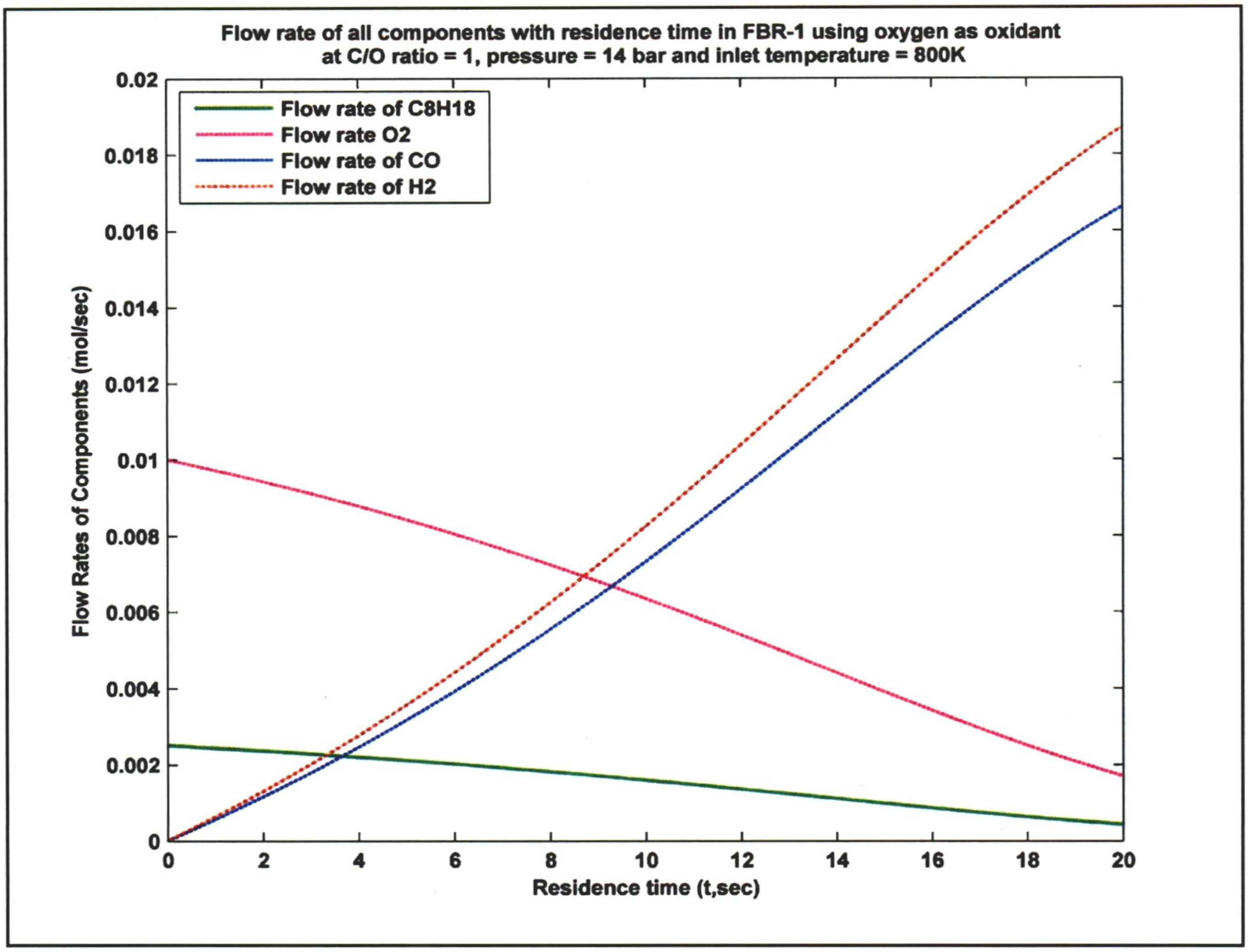

Figure 4.3 Flow rate profile for all components with reactor residence time in FBR-1 at inlet temp 800K, C/O ratio =1 and pressure 14 bar

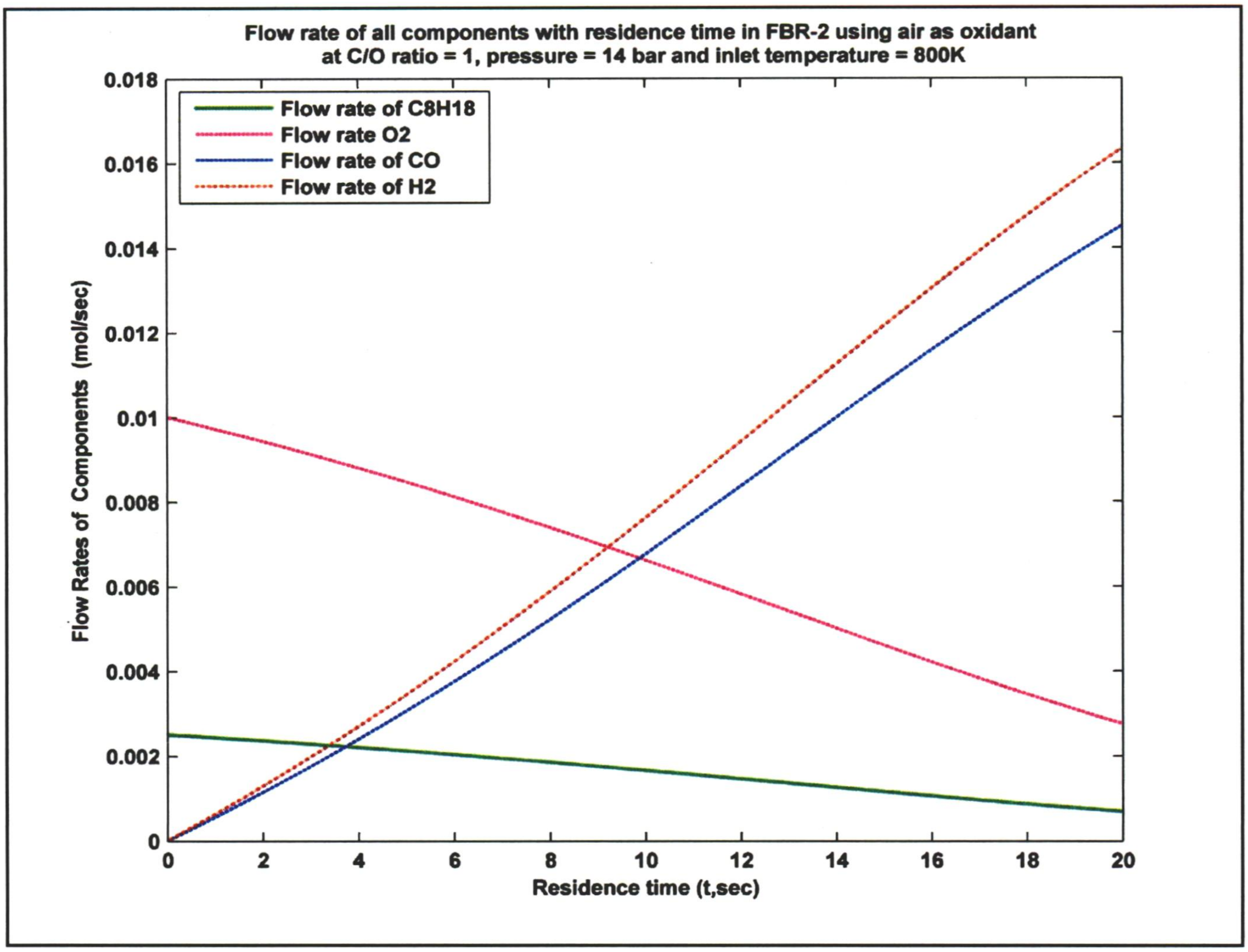

Figure 4.4 Flow rate profile for all components with reactor residence time in FBR-2 at inlet temp 800K, C/O ratio =1 and pressure 14 bar

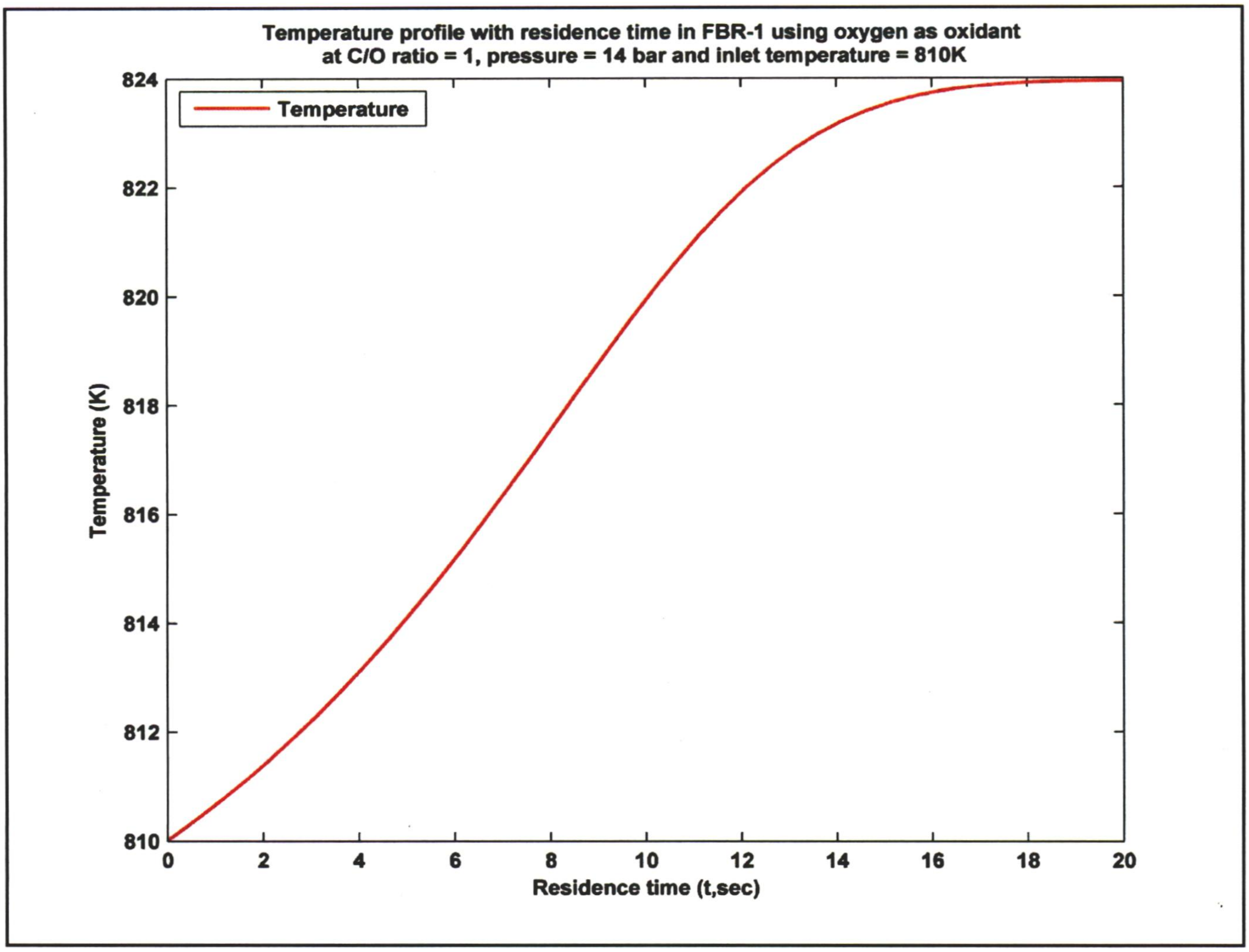

Figure 4.5 Temperature profile with reactor residence time in FBR-1 at inlet temp 810K, C/O ratio =1 and pressure 14 bar

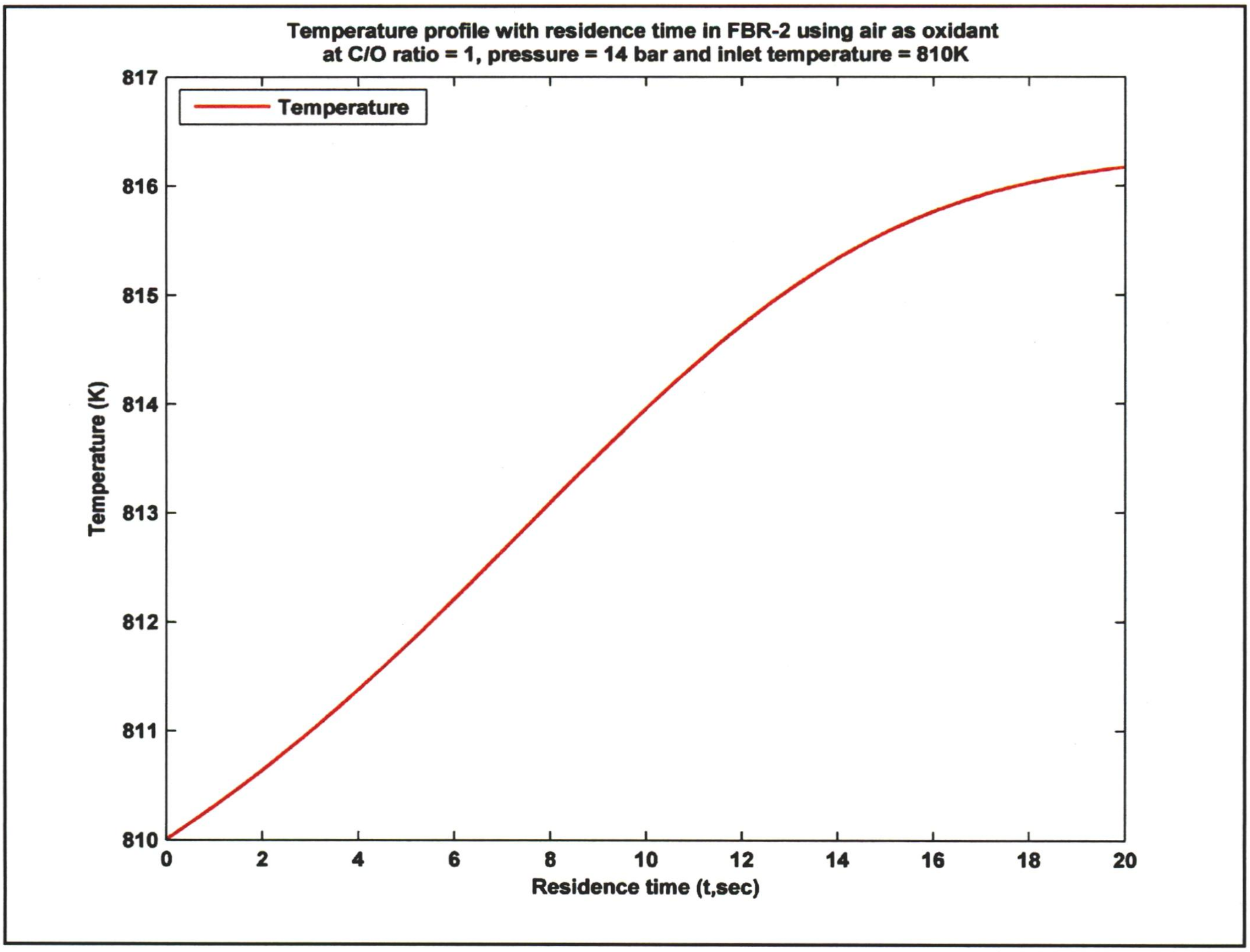

Figure 4.6 Temperature profile with reactor residence time in FBR-2 at inlet temp 810K, C/O ratio =1 and pressure 14 bar

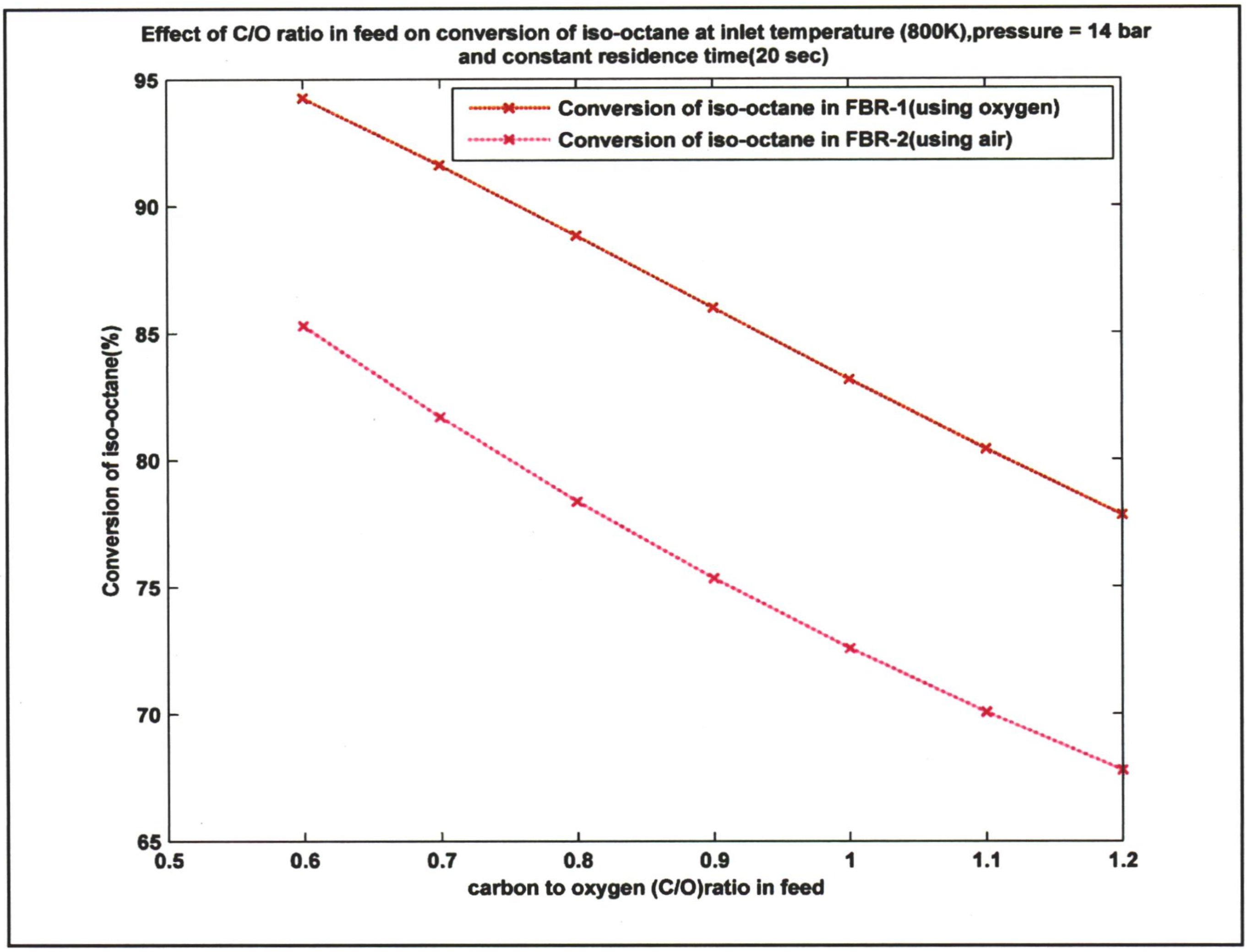

Figure 4.7 Effect of C/O ratio in feed on conversion of isooctane at inlet temp 800K, Constant residence time (20 sec) and pressure 14 bar

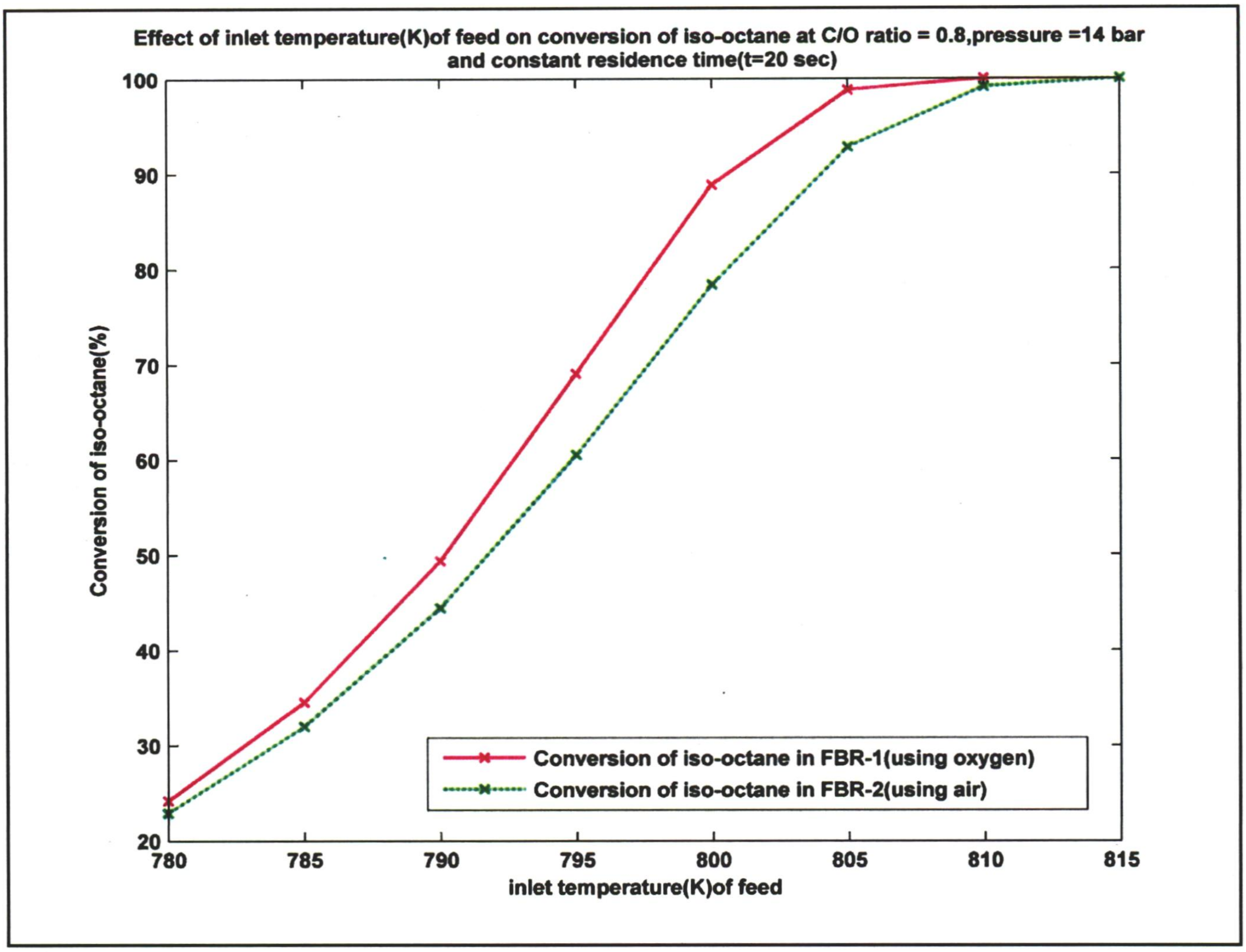

Figure 4.8 Effect of inlet temperature on conversion of isooctane at C/O ratio = 0.8, Constant residence time (20 sec) and pressure 14 bar

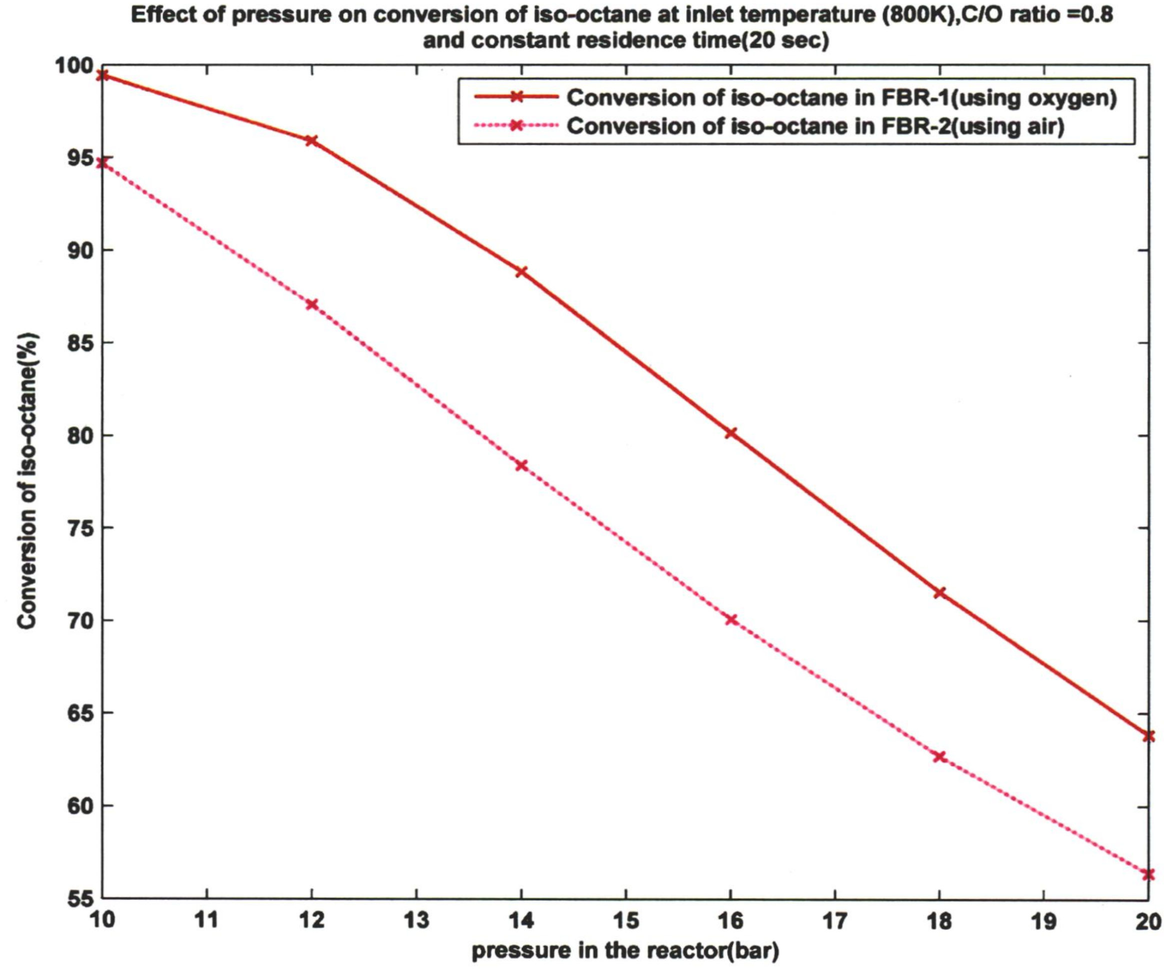

Figure 4.9 Effect of pressure inside the reactor on conversion of isooctane at inlet temperature 800K, C/O ratio = 0.8 and Constant residence time (20 sec)

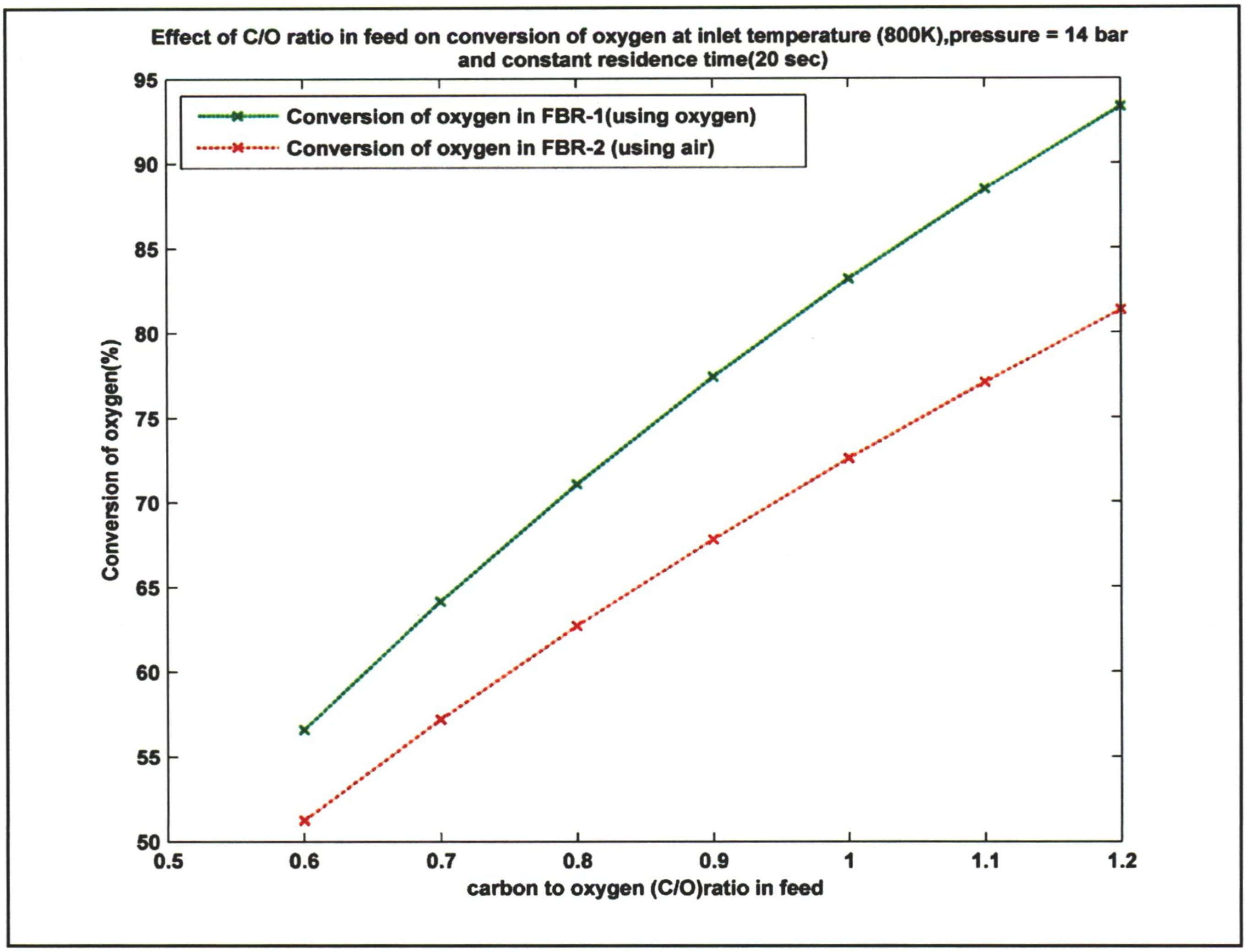

Figure 4.10 Effect of C/O ratio in feed on conversion of oxygen at inlet temp 800K, Constant residence time (20 sec) and pressure 14 bar

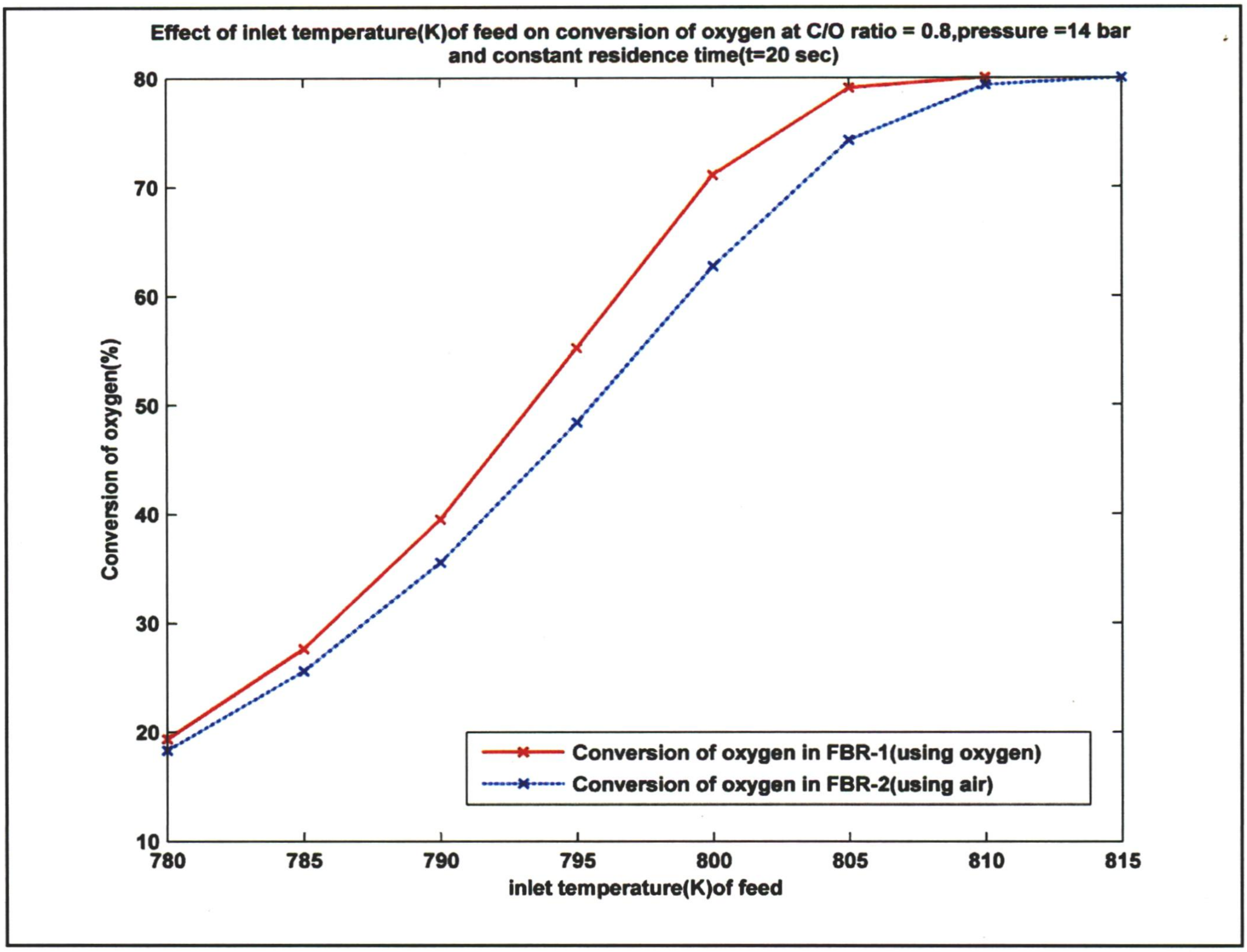

Figure 4.11 Effect of inlet temperature on conversion of oxygen at C/O ratio = 0.8, Constant residence time (20 sec) and pressure 14 bar

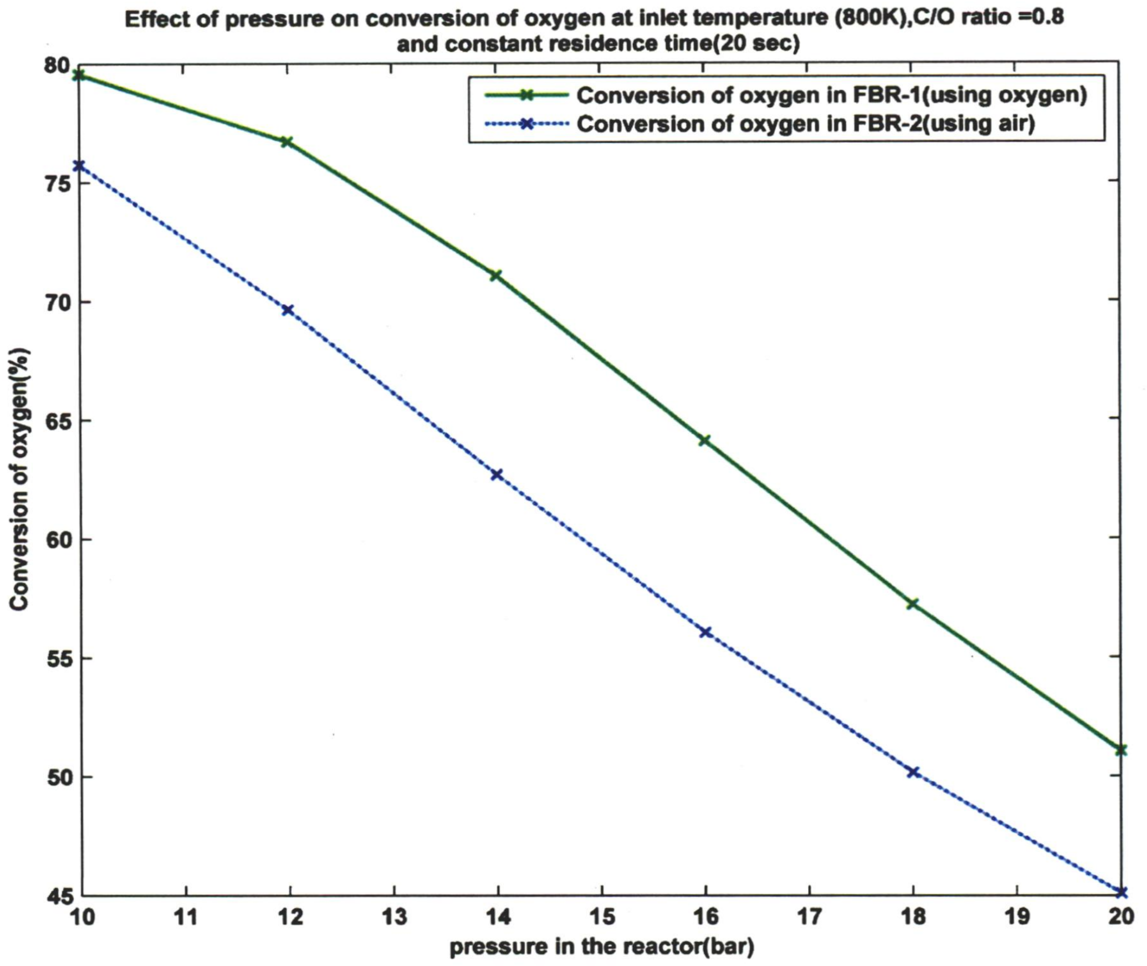

Figure 4.12 Effect of pressure inside the reactor on conversion of oxygen at inlet temperature 800K, C/O ratio = 0.8 and Constant residence time

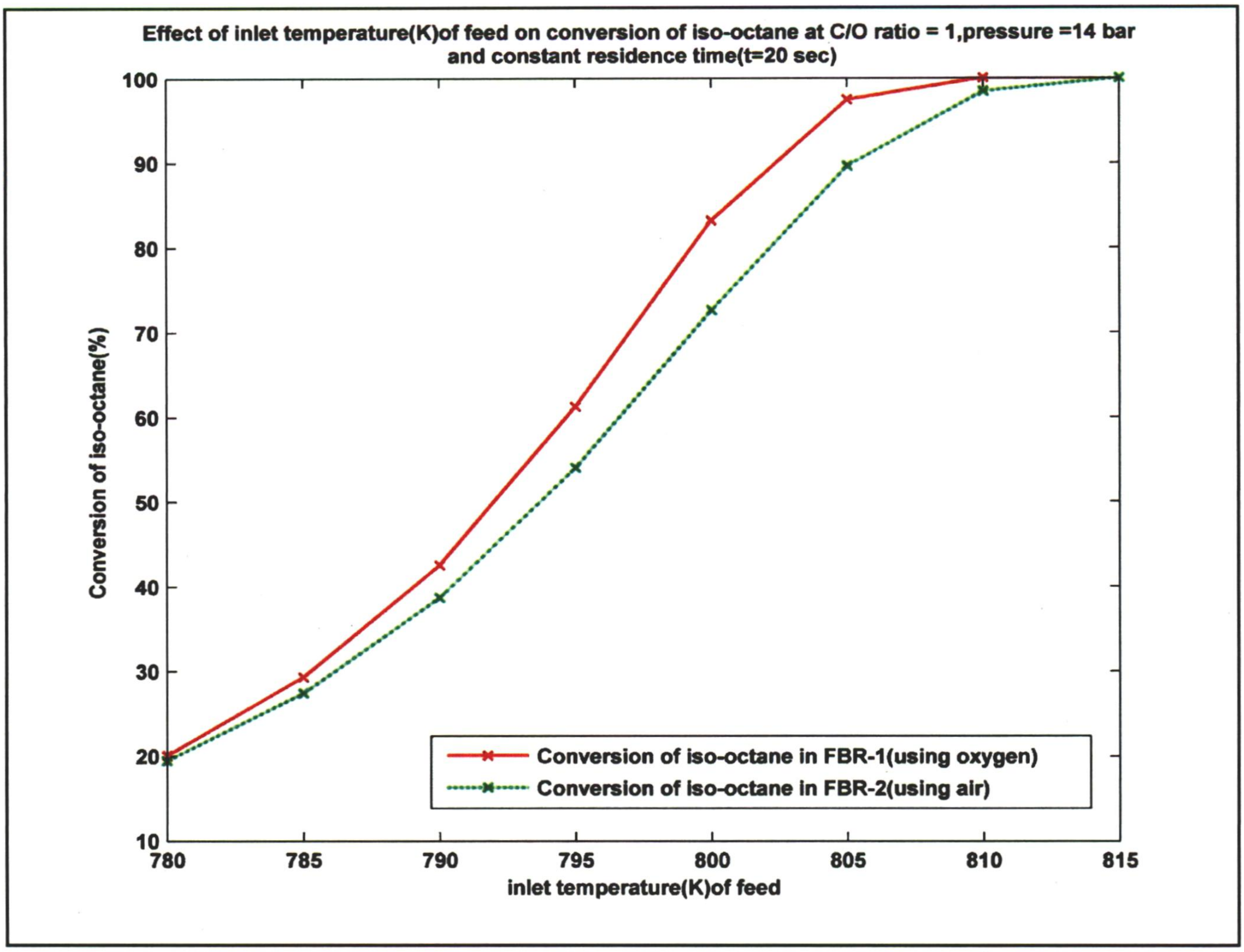

Figure 4.13 Effect of inlet temperature on conversion of isooctane at C/O ratio = 1, Constant residence time (20 sec) and pressure 14 bar

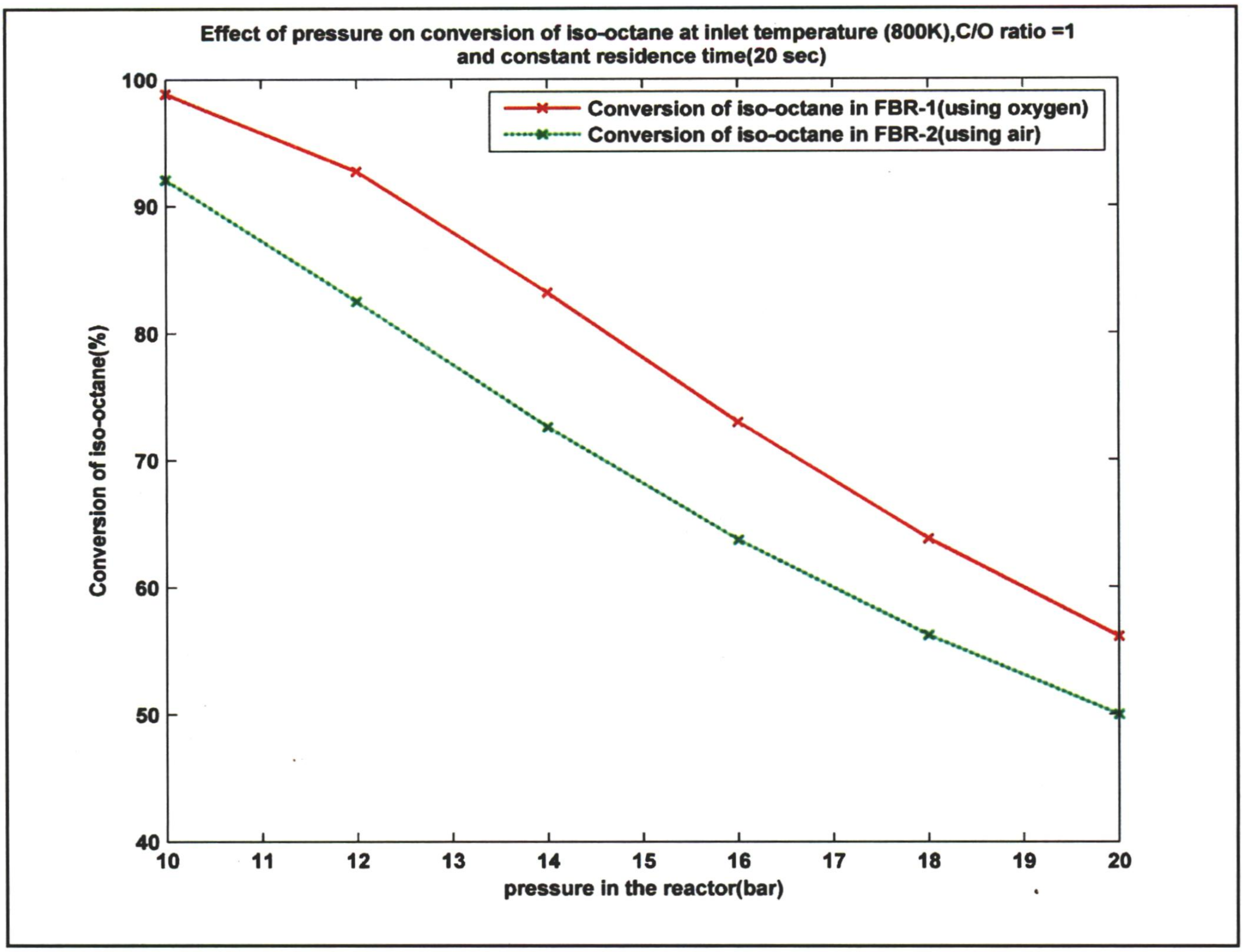

Figure 4.14 Effect of pressure inside the reactor on conversion of isooctane at inlet temperature 800K, C/O ratio = 1 and Constant residence time (20 sec)

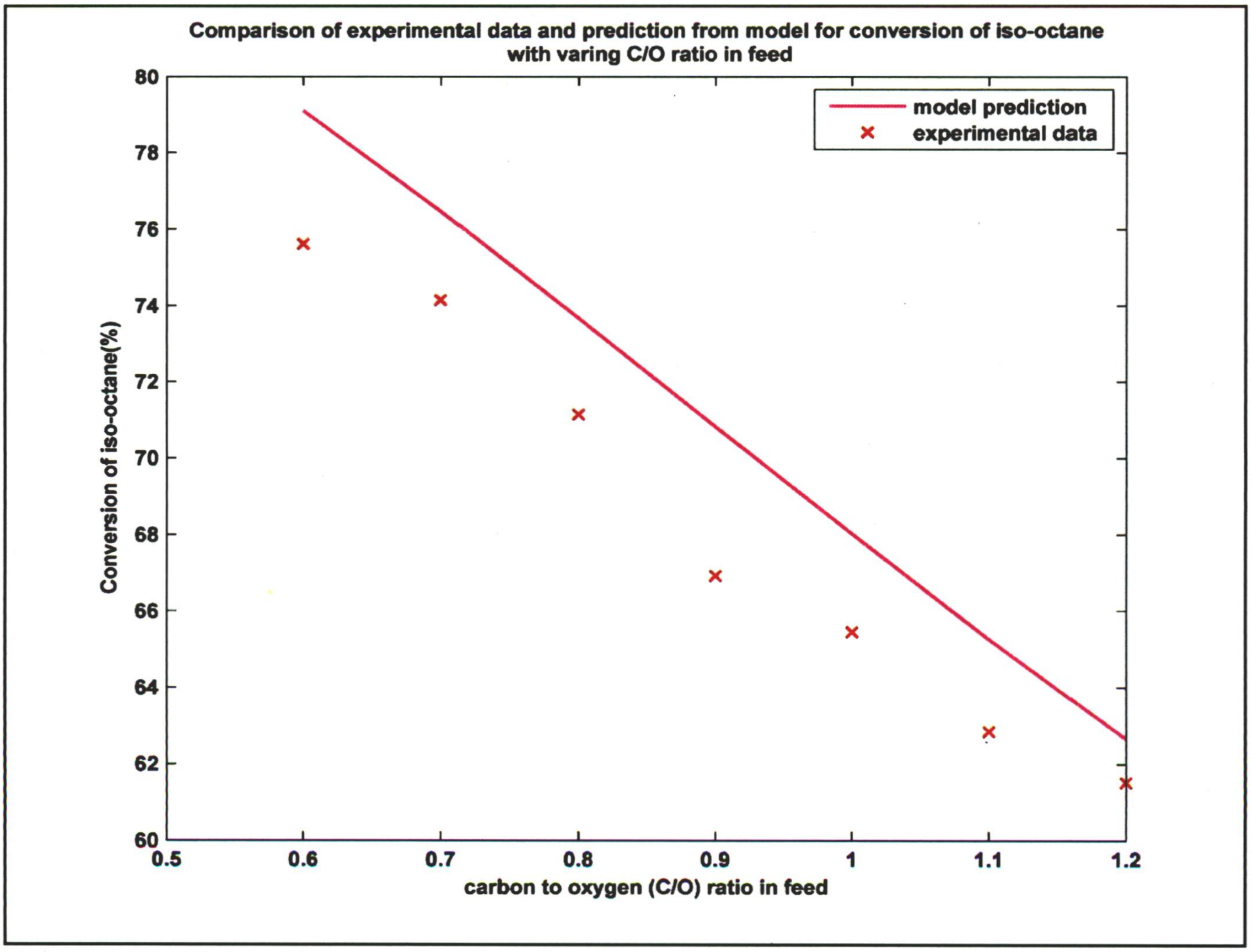

Figure 4.15 Validation of conversion of isooctane with varying C/O ratio calculated from model with the experimental data [16]

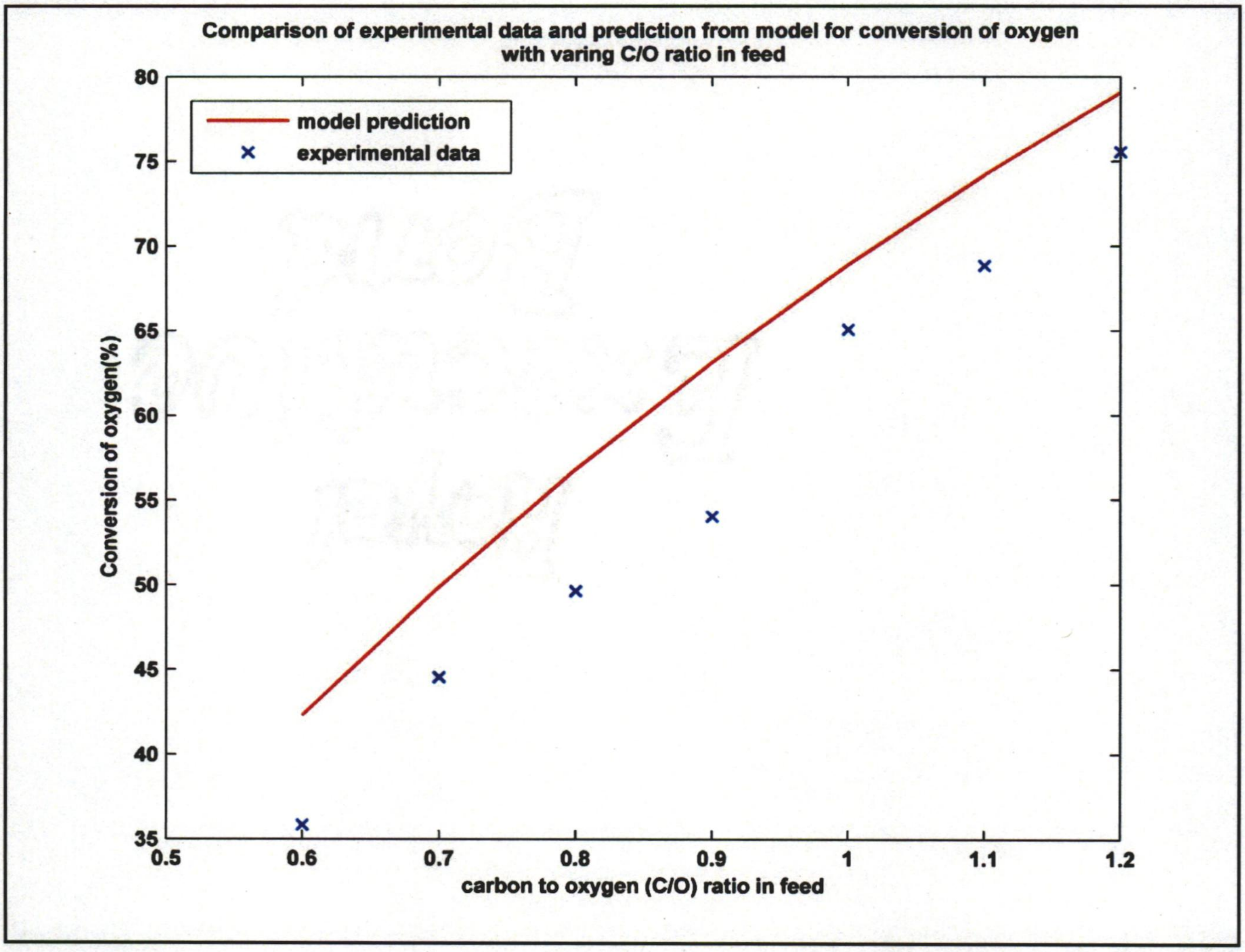

Figure 4.16 Validation of conversion of oxygen with varying C/O ratio calculated from model with the experimental data [16]

Chapter-5

CONCLUSION AND RECOMMENDATIONS

Hydrogen is projected to be one of the primary energy sources in the 21st century. Its combustion and oxidation is pollution free and supplies sufficient energy for transportation and other applications. The polymer electrolyte membrane fuel cell (PEMFC) is a potential candidate for direct electricity production from hydrogen for transportation applications and also for distributed and portable power generation. Petroleum-derived fuels such as gasoline are attractive sources of hydrogen because of their existing production, distribution, and retailing infrastructure. Also, gasoline has a much higher energy density and larger hydrogen content compared to methanol and ethanol. The conversion of hydrocarbons to hydrogen carried out using one of three major techniques: steam reforming, partial oxidation and auto-thermal reforming. Partial oxidation is chosen for this work for the reasons that:

1. The reaction is exothermic, making it much more energy-efficient than steam reforming
2. A smaller reformer can be used to achieve a high conversion of the hydrocarbon selectively in favour of the production of H_2 at short contact times; and
3. The partial oxidation setup is more compact and mechanically simpler than the steam reforming, since no additional heating is required.

In this work, a one-dimensional non-isothermal steady state mathematical model was developed to simulate the partial oxidation of isooctane for the production H_2 using oxygen in first fixed bed reactor (FBR-1) and air in second reactor (FBR-2) as oxidants over a Nickel/alumina catalyst. The performances of two reactors (FBR-1 and FBR-2) were compared in terms of conversion of isooctane and oxygen. FBR-1 and FBR-2 are fixed bed reactors with pure O_2 and air in feed respectively. The effect of C/O ratio in feed, inlet temperature of feed and pressure inside the reactor was investigated. The H_2/CO ratio in syngas in reactor is more favourable. The syngas from partial oxidation of isooctane reaction can be directly used as a feed for methanol synthesis or Fischer–Tropsch reaction. The observation of present research work leads to the conclusion that the hydrogen production is the maximum in case of FBR1, FBR2 gives poor performance. The membrane reactor can be used instead of plug flow reactor because it helps in separation of Nitrogen from air and improve the efficiency and the reaction should be carried out at low pressure for high conversion.

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