Computational Analysis for the Catalytic Combustion of Hydrocarbons

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2018

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NUST201463884MSCME67814F

This work is submitted as a MS thesis in partial fulfillment of the requirement for the degree of

(M.S in Chemical Engineering)

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May 2018

Dedication

This thesis is dedicated to my Parent

Acknowledgments

Praise is due to **Allah** whose worth cannot be described by speakers, whose bounties cannot be counted by calculators, whom the height of intellectual courage cannot appreciate, and the diving's of understanding cannot reach; He for whose description no limit has been laid down, no eulogy exists, no time is ordained, and no duration is fixed. Countless salutation upon "**HOLY PROPHET HAZRAT MUHAMMAD (S.A.W.W.)."**

I would like to acknowledge and express my sincere gratitude to my research supervisor, **Dr. Muhammad Ahsan** for his endless support, supervision and affectionate guidance to steer me in the right direction whenever he thought I needed it. I would also like to extend my gratitude to my research **co-supervisor, Dr. Arshad Hussain** and my Guidance committee members; **Dr. Sara Farrukh** and **Dr. Iftikhar Ahmad** for their valuable suggestions and guidance.

I would also like to thank **Dr. Arshad Hussain** (Principal, School of Chemical and Materials Engineering) and **Dr. Bilal Niazi** (HOD, Department of Chemical Engineering) for providing a research-oriented platform to utilize my skills in accomplishing this research work effectively.

In the end, I must express my very profound gratitude to my parents for providing me with unfailing support and continuous encouragement throughout my years of study and through the process of researching and writing this thesis. This accomplishment would not have been possible without them.

Waqas Ahsan

Abstract

Combustion is a rapid exothermic reaction process that liberates a substantial amount of energy. The high temperature exothermic reaction occurs between fuel-air mixture usually atmospheric oxygen. Complete combustion occurs when there is a lot amount of oxygen in the reaction.

VOCs are the volatile organic compounds that are mostly emitted during highly combustible reactions. These compounds are considered to be very dangerous for our environment. Hence, these substances are important to eliminate from the environment. In order to eliminate this substance from the environment, Catalytic combustion is considered to be the most efficient technique.

Catalytic combustion is an environmentally friendly technology which has attained the stage of commercialization in the last few years. This is a phenomenon in which a catalyst is added to the reaction to enhance the performance of the process to reduce the number of undesired substances that are produced during the reaction.

CFD Computational Fluid Dynamics is a fluid mechanics branch which numerically describes the fundamentals and fluid regimes of the process. Many types of research and developments regarding numerical simulation are being done because of the rapid increase in depending on computer models to help save resources and decrease product development time. In this research, a CFD Two-dimensional code (2D) and Three-dimensional code (3D) has been developed for the combustion reactor under catalytic surface activity. This process describes the fluid regimes of the catalytic combustion phenomenon.

Platinum group metals highly recommended in Natural gas drove gas turbines because of their superior activity with methane combustion. These catalysts are best known for their efficiency in conversion of catalytic combustion of methane into carbon dioxide and by-product water. Combustion involving catalytic surface activity depends on the different aspects of the reaction, for example, the fuel-air ratio, the material support using for the catalytic surface and the material pre-treatment for loading on the surface for catalytic activity.

Several fundamental issues are still open, and their understanding would result in an improvement of the technology. Therefore, this research majorly emphasizes at the identification of some of the parameters which govern the methane combustion activity of the platinum group metals. Currently, Catalytic Combustion of methane simulated under the influence of Platinum group metals as a catalyst where different fluid regimes, contours of static temperature and mass fractions profiles of CO, O_2, H_2, CO_2, H_2O, and CH_4 are obtained.

Keywords: Catalytic Combustion; Computational Fluid Dynamics (CFD); Laminar Finite Rate Species Transport Model.

Table of Contents

List of Figures

List of Tables

Nomenclature

|	
A	Pre – exponential factor
b	Temperature constant
C_i	Molar concentration of specie I, mol m^{-3}
C_p	Specific heat at constant pressure, kJ K^{-1} mol^{-1}
D	Diffusion coefficient, m^2 s^{-1}
E_a	Activation energy of the reaction, kgmol^{-1}
h	Enthalpy, J kg^{-1}
M	Molar mass of species, kg mol^{-1}
N_c	Number of elementary surface reactions
N_g	Number of gas phase species
N_s	Number of surface species
p	Pressure, Pa
q	Heat of reaction, J kg^{-1}
R	Universal gas constant, J K^{-1} mol^{-1}
R_i	Generation rate, kg m^{-3} s^{-1}
S_{oi}	Adsorption coefficient of specie i
u	Axial velocity, m s^{-1}
X	Co – ordinate distance in x direction, m
Y_i	Mass fraction of species i
λ	thermal conductivity, w m^{-1} k^{-1}
ρ	density, kg m^{-3}
τ	number of active sites occupied
μ	viscosity, kg m^{-1} s^{-1}
Γ	surface site density of catalyst, mol m^{-2}

Chapter-1

Introduction

1.1 Background:

In the current age of modernization and industrialization, fossil fuels have a huge impact on the human life. Being the most important and highly contributing source of energy, they contribute significantly to the pollution too [1]. There is a growing need to meet the growing global energy demands and reduce the impact of fossil fuels on the environment. Two solutions have been proposed in this regard. One is to use the renewable energy sources such as solar, wind and tidal energy, etc. to meet the energy demands without impacting the environment. Other is to use and enhance the technologies for the clean and efficient use of fossil fuels. Among the fossil fuels, natural gas is considered as one of the cleanest fuels [2]. Natural gas releases a higher amount of thermal energy per unit of CO_2 produced. Further, the production of nitrogen oxides (NO_x) and Sulfur dioxide (SO_2) is also lower. Therefore, the combustion of natural gas is considered as cleanest and most efficient among all the fossil fuels. This quality makes the use of natural gas more versatile. Currently, natural gas is being used as fuel for automobiles and power generation, etc. [3].

The complete combustion of methane, the major component of natural gas is given by the following equation:

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O \qquad\qquad (1)$$
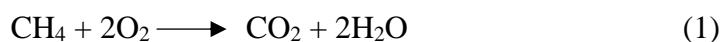
The conventional burning of natural gas has some drawbacks. For example, the only products of methane combustion should be carbon dioxide and water based on the overall reaction. However, as a result of nitrogen oxide, i.e., NO_2 and NO are also produced. The production of NO_x is because of traditional burners operating at a temperature as high as 2000 K. The produced oxides are environmental pollutants causing the concerns. Furthermore, the incomplete conversion of methane in traditional combustion will result in the release of unconverted methane into the environment. The homogenous combustion of methane can only happen in a certain range of the flammability limits (5 to 16 % by

volume of methane in the air). It can be considered that methane cannot be combusted with conventional combustion. These drawbacks have limited the use of conventional natural gas combustors. For example, the careful adjustment of the air and gas ratio for efficient burning; use of spark plugs for initiating combustion; the use of materials capable of sustaining high temperatures during the burning process, etc. In consideration of the environmental pollution use of the appropriate treatment of the effluent gas before release in the atmosphere is also required.

1.2 Global warming and greenhouse gases

In the current age, global warming is the burning issue and of serious concerns for the humanity. The changes resulting from the increase in temperature due to global warming has devastating consequences. The temperature rise can result in melting of the glaciers, change in weather patterns, change in hydrologic cycles and precipitation patterns etc. These changes can cause increased rains, flooding, the rise in sea levels, etc.

Major contributors to the global warming are the greenhouse gases (GHG), as considered by many researchers. GHG comprises less than one percent of the atmosphere. The increased amount of GHG in the atmosphere is due to the high usage of fossil fuels [4]. The increasing industrialization, use of fossil fuels for power generation, increased number of automobiles and other transportation have resulted in more usage of fossil fuels as the primary fuel source. The result is more release of GHG into the atmosphere. The result is the increased concentration of GHG into the atmosphere, which results in global warming. Therefore, the decrease in GHG emission can help coup the global warming and its effects on the earth's ecosystem [5].

1.3 General catalytic combustion

In 1818, Sir Humphrey Davy discovered the relationship of catalyst and combustion whole studying the safety lamps in coal mines. He discovered that oxygen and methane on hot platinum wires could produce a considerable amount of heat in flameless combustion. In 1836, the observations of the earlier chemists were summarized by Berzelius. He summarized that small amount of the foreign substances could greatly change the rate and course of chemical reactions. The effect of these foreign substances was termed as a catalytic effect. Further, in 1894, Ostwald expanded the Berzelius'

definition of the catalyst by stating that, a catalyst is a substance increasing the rate of a reaction without being consumed. Since their first discovery, the catalysts have played a great role in the chemical production, engineering, and industrial growth.

The interest in the catalytic combustion and its catalysts has increased recently because of wide applications of the process [6]. The potential applications of this technology are in the power generation systems, [7] [8] in reduction of fugitive methane levels [9], in catalytic converters used in vehicles to reduce GHG emissions [10] and in catalytic oxidation crucial for production of intermediate raw materials which are then used to synthesize high value end products.

The overall process of catalytic combustion in can spit into following steps:

1. Mass transfer of the reactants from the bulk fluid to the external surface of the catalyst and then diffusion of reactants in the catalyst pores.
2. Adsorption of the reactants on the surface of the catalyst.
3. Chemical reaction on the surface of the catalyst.
4. Desorption of the products from the catalyst surface.
5. Diffusion of the products in the catalyst pores and then the mass transfer of the products from the external catalyst surface to the bulk fluid.
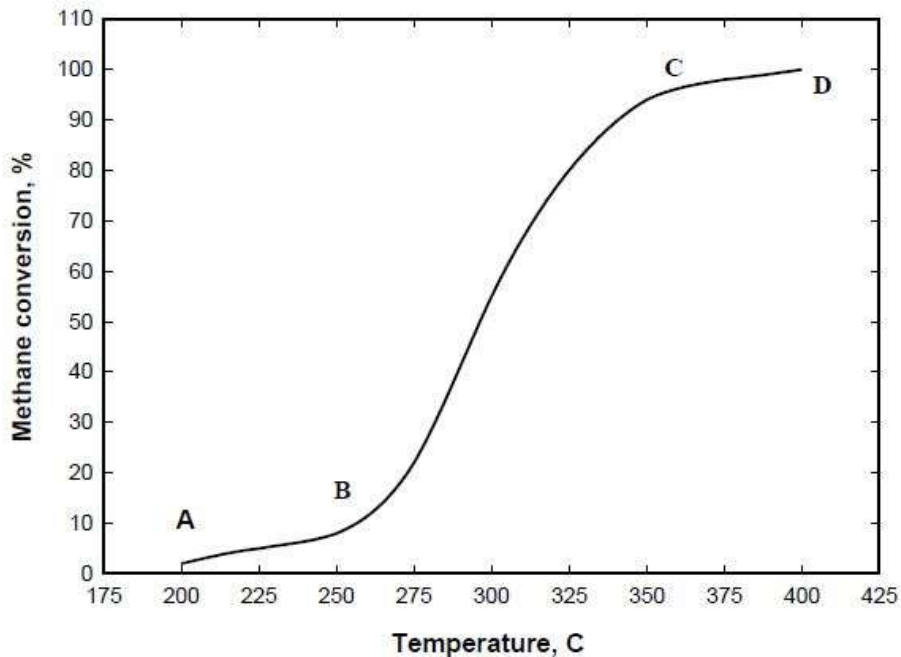
Figure 1 Catalytic Combustion of Methane as a function of Temperature

The above-mentioned steps occur at the same time. The rate of reaction is the rate of determining step or the rate of reaction and that is determined by the rate-limiting step. Determining step is the step with the highest resistance, and the rate-limiting step is the slowest step in the chemical reaction. Catalytic combustion is an exothermic process, resulting in the high release of heat energy. The release of high energy results in the increased temperature of the reacting mixture. The general pattern of catalytic combustion is widely studied and well established. It can be seen in Figure 1 that increase in the temperature of reactants by point A will initiate the combustion.

The initiation temperature in the catalytic combustion process depends on various factors including the catalyst and type of hydrocarbon feed. With the increase in temperature to a certain point, the rate of reaction will increase exponentially. In Figure 1, that temperature point can be seen at B, where after reaching that temperature level the rate of reaction is increasing rapidly and exponentially. After a further increase in the temperature, appoint will arrive where the mass transfer may become the controlling step. It can be observed in Figure 1, the region around the point C. With further increase in temperature, a point will reach where all the reactants are consumed. In Figure 1, that

point can be observed at temperatures above D. In catalytic combustion the porosity of the catalyst and support are the crucial factors in understanding the behavior of catalyst. As discussed above, the reaction in catalytic combustion reaches the final point when one of the reactants if fully utilized. A huge amount of heat energy is produced as a result of the consumption of the reactants. This huge amount of heat energy can increase the temperature too. Therefore, the stability of the catalyst at such high temperatures is another crucial factor in determining the performance of the catalyst-based systems [7].

Therefore, in determining the right catalyst the crucial factors such as reactivity of the catalyst, heat and mass transfer effects, and maximum temperature should be taken in view.

1.4 Combustion catalyst

Metal oxides and noble metals have been widely used as combustion catalysts. Generally, noble metals have higher activity as compared to the metal oxides [11]. The catalysts used in combustion process can either be supported or without support. Usually, catalysts with support are preferred because of the better utility of the precious catalyst spread over the support. It provides better yield, better activity and uses less amount of catalyst giving the maximum surface area of the catalyst. The catalysts with support have better thermal stability. Another advantage of the support is that it can also play a role in the oxidation reaction. In oxidation reaction, the support may provide the storage capacity.

Generally, the ideal catalyst for the combustion should have following characteristics;

1. High Activity
2. Low ignition temperature
3. High thermal stability
4. Stable activity
5. Resistance to poison
6. Low price
7. Non-toxicity

It is not necessary that the catalyst should comprise of all above characteristic. However, the above qualities can be used to determine the quality of catalyst and can help in choosing the right catalyst for the desired application.

1.5 Rare earth materials and other oxides

Rare earth metals and metals oxides have been used for the catalytic combustion without further change. They have the ability to be used as efficient catalysts as have been shown by several studies. Furthermore, rare earth metals can also be used as additives. These additives are used to increase the activity of the metal oxides for catalytic combustion. The increase in the activity is due to the increase in a number of basic sites and decrease the number of acid sites due to the presence of rare earth metals. The general formula for this catalyst is A-BO$_x$. Where, A is rare earth metal and BO$_x$ is the metal oxides.

Another type of the catalyst combustion is the perovskite-type catalysts. Perovskites are mixed metal oxides with applications in multiple fields such as transistors and fuel cells etc [12]. These catalysts are cheaper and stable. They have shown significant activity for the application in methane combustion. These perovskite-type combustion catalysts are relatively more thermally stable and withstand higher temperatures as compared to the noble metals. Therefore, it can be said that perovskite-type catalysts for methane combustion are more potentially viable than noble metals in terms of the cost and thermal stability.

1.6 Noble metals

Noble metals are those metals which show resistance to corrosion and oxidation in damp air. This group of metals consists of metals such as Ruthenium, Silver, Iridium, Gold, Platinum, Rhodium and Palladium etc [13]. Noble metals such as Platinum (Pt), Rhodium (Rd), and Palladium (Pd) have been considered as the most effective catalysts for the catalytic combustion of the methane [14]. These catalysts have shown relatively higher activity as compared to the other catalysts. These noble metal catalysts can be used with or without support. Another quality of the noble metal catalysts is their significant resistance to sintering. These catalysts have shown high efficiency as compared to the metal oxides and other catalysts being used for catalytic combustion of the methane. The noble metals have limited availability and are relatively much expensive. Most used

catalysts for the catalytic combustion of the methane are Pd, Rh and Pt. They are the most used noble metal catalysts because of their more availability as compared to other noble metals. These catalysts show significantly higher activity for the catalytic combustion of methane as compared to other catalysts at relatively lower temperatures. They also tend to have higher stability as compared to other catalytic combustion catalysts. Several parameters affect the activity of the catalysts for the catalytic combustion of the methane. These parameters include metal loading, presence or absence of support and pretreatments etc. Several studies have reported the activity and performance of the noble metals for the catalytic combustion of the methane. The studies have suggested that the Pd/silica catalyst having loading of 2.55% wt used for the mixture of CH_4, CO, NO and traces of H_2 and CO_2 started the reaction at 250°C, the mixture ignited at 350°C and the complete combustion occurred at 400°C. The reaction was not dependent on the concentration of the methane. For the Pt catalyst the temperatures reported were 450°C, 675°C and 900°C [Salaun, et. al, 2009]. However, Pt catalysts show more resistance to the poisons such as sulphur (Meeyoo, et. al., 1998), water (Gelin, et. al., 2003) and Pt catalysts hardly sinter at low temperatures (Hurtado, et al., 2004). It was concluded through various studies that Pt catalysts are more stable. They are less prone to sintering too.

1.7 Effect of different parameters on the activity of catalysts

1.7.1 The effect of feed composition

The feed ratio (ratio of $[O_2/CH_4]$) has considerable impact on the methane combustion using catalysts. For high O_2 concentration feed using Pt catalyst over alumina support the combustion produces carbon dioxide [15]. For feed with less O_2 concentration carbon monoxide is also produced. The shift to the carbon monoxide is the result of temperature. The conversion of methane to carbon dioxide and water tends to increase with increase in temperature. The complete combustion of the oxygen and complete conversion to carbon dioxide can be achieved with further increase in the temperature.

1.7.2 The effect of precious metal loading

It has been discussed in several studies that the precious metal loading has a significant effect on the activity of the catalyst. It was discussed by [16] that for methane conversion less than 10 percent, increase Pt loading (0.1 to 2% wt) significantly increased the

combustion of methane. Likewise, increase in (2.7 to-10 % wt) on γ-Al2O3 support also showed an increase in methane combustion. Though the combustion rate of methane increased with increase in the catalyst loading the activity rate per unit surface area of the catalyst decreases [17]. Further experiments showed that increasing Pt loading above 10 wt% caused the rate of reaction to decrease significantly.

1.7.3 Structure sensitivity

Extensive studies have been conducted to study the catalytic combustion of methane using noble metal catalysts. These studies also include the effects of various parameters on the activity of the catalyst, combustion of methane and optimum parameters. One of these parameters includes the structure sensitivity of the catalyst. It was observed by Hicks et al. [18] that structure sensitivity could be caused by different reactivities of oxygen on the surface of the catalyst. These catalysts may include Pd, Rh, and Pt. For the Pt catalyst, two different types of Pt particles were used by the researchers to study the structure sensitivity. One being the dispersed and other the crystallites. The authors concluded that the crystallites showed more activity as compared to the dispersed Pt. Similar behavior was observed for the palladium catalyst too.

Table 1 Different Studies of Catalytic Oxidation of Methane

Catalyst/support	Temperature (°C)	O_2/CH_4	Pretreatment of Catalyst	CH_4 Conversions	Reaction rate
CO_3O_4	450	O_2 rich	-	-	0.78
0.5% Pd/Al_2O_3	450	O_2 rich	-	-	22.5
0.5% Pt/Al_2O_3	450	O_2 rich	-	-	1.02
Pd	290-480	2	Reduced with H_2 at 480°C	5-80%	-
0.155% Pd/Al_2O_3	275-475	4	Heated to 500°C in He containing 1% O_2	Upto 80%	-
0.153% Rh/Al_2O_3	350-500	4		Upto 25%	-
0.2% Pt/Al_2O_3	300-500	4		Upto 10%	
0.2% Pt/SiO_2	450	2	Reduced with H_2 at 300°C	-	$1.6*10^{-5}$
0.2% Pt/Al_2O_3	450			-	$2.3*10^{-5}$

Catalyst					
0.2% Pt/SiO$_2$-Al$_2$O$_3$	450	2		-	$7.4*10^{-5}$
2.7% Pt/γ-Al$_2$O$_3$	410	0.45	Heated to 500°C in H$_3$ or H$_2$	-	0.296
2.7% Pd/γ-Al$_2$O$_3$	410	0.45		-	0.35
2.7% Pt/TiO$_2$	410	0.45		-	0.22
2.7% Pd/TiO$_2$	410	0.45		-	0.269
3.0% Pt/ThO$_2$	410	0.45		-	0.076
3.0% Pd/ThO$_2$	410	0.45		-	0.09
1.93% Pd/Al$_2$O$_3$(I)	310-600	4	I: Reduced with H$_2$ at 600°C	50%	-
1.93% Pd/Al$_2$O$_3$(II)	310-600	4	II: Pretreated with O$_2$/CH$_4$ at 600°C	50%	-
Pd/γ-Al$_2$O$_3$	289-432	1% CH$_4$/air	Calcinated at 600°C	2.4-74%	-
Pd/SiO$_2$	290-422	1% CH$_4$/air		0.3-22.4%	-
1.95% Pt/Al$_2$O$_3$(I)	280-600	4	I: Reduced with H$_2$ at 600°C	0-100%	-
1.95% Pt/Al$_2$O$_3$(II)	280-600	4	II: Pretreated with O$_2$/CH$_4$ at 600°C	0-100%	-
1.95% Pd/Al$_2$O$_3$(I)	400	4	I: Reduced with H$_2$ at 600°C	-	8.58
1.95% Pd/Al$_2$O$_3$(II)	400	4	II: Pretreated with O$_2$/CH$_4$ at 600°C	-	41.6
0.16% Pd/Al$_2$O$_3$	250-700	5	Calcinated with air at 500°C	Upto 100%	-
0.14% Rh/Al$_2$O$_3$	370-700	5		Upto 80%	-
0.2% Pt/Al$_2$O$_3$	400-700	5		Upto 80%	-
2.18% Pd/Al$_2$O$_3$(I)	275-430	4	I: Reduced with H$_2$ at 600°C	2-100%	-
2.18% Pd/Al$_2$O$_3$(II)	250-415	4	II: Pretreated with O$_2$/CH$_4$ at 600°C	6-100%	-
2.18% Pd/Al$_2$O$_3$(III)	310-555	4	III: Pretreated with O$_2$/CH$_4$ at 600°C	4-100%	-

CHAPTER-2

Literature Review

2.1 Literature review:

This chapter includes the discussion regarding CFD based analysis of different combustion processes. This section also reviews the preceding work carried out to evaluate the parameters affecting the performance of the catalytic combustion through experimental and computational strategies. Computational Fluid Dynamics (CFD) has made things very easy by predicting the behavior of different fluid regimes` of the reaction process. This software is well established for different types of reaction engineering. Combustion of fossil fuels has been known as the primary component for the energy sources. The importance of combustion process and its usage has been enhanced by the increase in demand for energy in the present era. But this process is also intimidated as the source for the emission of extensive pollution of the environment. The reason behind this pollution is the components that are emitted during this process which causes a lot of damage to the environment. That is why these environmental pollutants are the major challenge in the development and planning departments of the energy sector. For achieving the requirement of environmental standards, it is necessary to come up with the efficient procedure which reduces such components emission and maximizes the efficiency of the combustion process. Catalytic combustion is known as the efficient process in order to eliminate such substances which are dangerous for the environment. The reason behind is because this process requires very low energy and still performs quiet efficient conversion by removing these organic compounds. A lot of research has already been carried out in the past regarding CFD and methane combustion. This research is also done by keeping in mind whatever the previous work has been done and what results have been achieved. In this section of the thesis, we will discuss the previous researches that have been carried out involving catalytic combustion and their analysis through different simulation-based software like Aspen Plus, Computational Fluid Dynamics (CFD), MATLAB etc.

Methane combustion is a process which is used on a large scale for the production of heat and power for different industrial units. Catalytic combustion is regarded as the fast-exothermic reaction usually carried out in a fluid bed reactor. Different experimental researches have been done on this process historically, and by the innovation of computer technologies in the market, researchers have developed software's which can predict the results for such experimental results by simulating required input data. Computational Fluid Dynamics (CFD) is a latest emerging approach which is used to predict simulation-based results by incorporating required information in the software. CFD provides an internal visualization aid compared to other computer-based software's like Aspen Plus, MATLAB, etc.

Veldsink [19] studied the intrinsic kinetics of the methane oxidation on industrially available copper oxide with alumina support. He studied the kinetic rate of methane combustion taking place in the presence of a catalyst at temperatures ranging from 723k to 923k. Copper oxide was used on alumina support as a catalyst for the catalytic combustion process. This study was carried out in order to know the capabilities of this process for a membrane reactor. He concluded that this could be studied without limitations of heat and mass transfer in packed bed reactors. He also concluded that the catalyst used was quite efficient for such purpose as it long lasted and stable for high temperatures. He also derived rate equations and explained that there was no methane adsorption was found on a catalyst surface. Dangi and Abraham [20] performed complete catalytic combustion of benzene and methyl tert-butyl ether. They obtain experimental parameters from pure component experiments and then put into their model for the prediction of the simulation. They concluded from their research that complete oxidation of benzene and methyl tert-butyl ether results in the production of carbon dioxide and water due to the complete destruction at a temperature ranging from 400-500 ^{0}C. They also discussed details of the adsorption of material on the catalyst surface at low temperature. Mars van krevelen model was used for their model assumptions. Membrane reactor is the latest technology to remove nitrogen, organic materials and other wastewater contaminants from water [21]. Computational Fluid Dynamics (CFD) is a promising approach to improve the performance of membrane reactor. The efficiency of the membrane reactor relies on mass transfer phenomena which depends upon flow patterns

and flow velocity. A tubular hollow membrane is used, and a stimulus response approach is used to investigate the flow patterns. Plascencia-Jatomea, et al. (2015) [22] developed a CFD based model by assuming laminar flow and solve navier stokes equation for incompressible flow. A deviation from ideal hydrodynamic behavior is observed due to mixed flow and channeling effects. With the velocity flow patterns, stagnant zone is determined in the membrane in which degradation reactions can take place. This stagnant zone can provide the room for improvement of membrane reactor design. Anthony G Dixon [23] performed his analysis on CFD by using fixed bed reactors. He explained through his research that Computational Fluid dynamics is the appropriate software which has the capability to give details of the temperature and flow fields. It can provide highly reliable information of the flow field regimes. Zakharov and Zolotarski [24] investigated about transfer of mass and flow of gas by using two stage system which involved catalytic oxidation occurring at nitric acid plants through the simulation of gauze pad honeycomb chemical reactor system. Rodrigo [25] used CFD software to predict the influencing parameters involving in the catalytic oxidation of vanillic acid. He performed the analysis within a trickle bed reactor to execute numerical simulations. Additionally, Deutschmann and Quiceno [26] reported the high temperature catalytic partial oxidation of methane over platinum gauze. Their work is evident that even for complex catalytic geometries, Computational Fluid Dynamic CFD is the best software available which has the capability to implement comprehensive homogeneous reaction scheme. Jiang and Khadilkar [27] reported the modelling of multiphase flow distribution by using simulation through CFD under steady and unsteady state conditions. The flow distribution was carried in the catalytic packed bed reactors under the influence of steady or unsteady state conditions. The reactors used were scale cylindrical or rectangular shaped packed bed reactors. The distribution of porosity in packed bed reactors were applied by using pseudo-randomly allotted cell section holdup distribution.

2.2 Objective

In this study, Computational Fluid Dynamics (CFD) based simulation is performed for the catalytic combustion of Methane. In order to incorporate reaction mechanism of the catalytic combustion process, chemkin mechanism file is created which includes the information regarding the chemical reactions involving catalytic combustion of methane and the species that are involved in the process. After the incorporation of required input data to the software, simulation analysis is performed, and results are obtained.

CHAPTER-3

Computational Fluid Dynamics Based Modeling

Computational fluid dynamics is a subfield of fluid dynamics which takes account of data structure and numerical analysis to analyze and solve problems which are based on fluid flow. In order to perform the calculations, computers are required to simulate the gases and liquids interaction with surfaces described by boundary conditions. Better solutions can be achieved through high speed supercomputers. Through continuous research, many software's are developed which can enhance the speed and accuracy of complex simulation problems such as turbulent and transonic flows. These software's are validated by experimental comparison using wind tunnel and final validations are done by flight tests.

3.1 Background

Navier-Stokes equations are the fundamental basis of all CFD problems and these equations define many single-phase fluid flow problems [28]. To simplify these equations, viscous terms are removed to yield the Euler equations. To simply further these equations and yield potential equations, vorticity terms are removed. Finally, linear potential equations are obtained by removing the subsonic and supersonic flow terms.

Earlier Lewis Fry Richardson divided the physical space into cells and applied finite difference method which resembles with modern CFD calculations. Although he failed to get the required results latter these calculations which he mentioned in his book "Weather prediction for numerical process" provide the basis for modern CFD calculations.

3.2 Methodology

3.2.1 Preprocessing

The preprocessing consists of the following steps:

- Computer-aided design (CAD) can be used to define the physical bound and geometry of the problem. From there, fluid volume is extracted.
- The volume which is occupied by the fluid is then divided into discrete cells (mesh). The mesh may be uniform or non-uniform, pyramidal or polyhedral, tetrahedral, structure or unstructured cells.
- Now the physical mesh is defined using fluid motion, radiation, enthalpy and species conservation or non-conservation equations.
- Boundary conditions are specified.

3.2.2 Processing

Simulations are processed until the convergence is reached and the differential equations are solved as steady-state or transient.

3.2.3 Post processing

Finally, the post-processing is done to aid the visualizing and analysis of the solution.

3.3 Simulation Environment

3.3.1 Gambit 2.4.6

There are many geometries made in software such as Gambit, Solid Works, Auto CAD, IGES, etc. Gambit is most basic, and user-friendly software compares to others. So, Gambit 2.4.6 is used to prepare geometry. In this work, two-dimensional geometry and three-dimensional geometry are prepared with the help of vertices. Vertices are connected with each other to form the edges which can be further used to form faces. Unstructured meshes are prepared, and boundary conditions are labeled at edges while different zones are labeled at faces. Errors in geometry are resolved through the bottom console of Graphical user interface (GUI). GUI of Gambit 2.4.6 is shown in Figure 2.
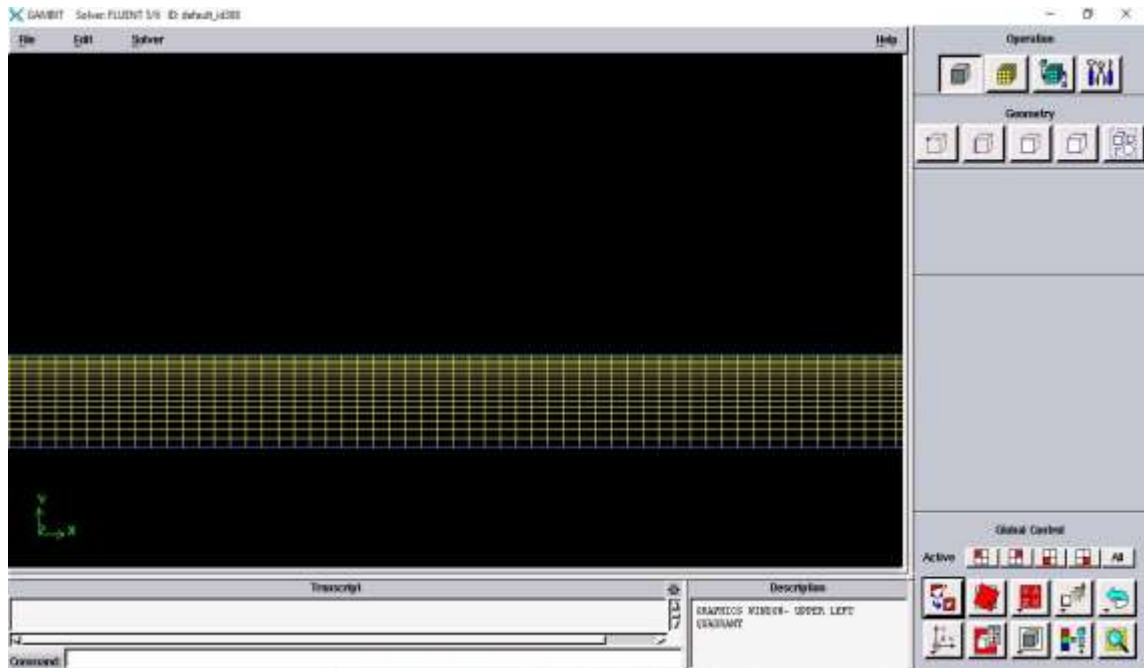
Figure 2 Combustion Reactor Mesh

3.3.2 ANSYS Fluent

Geometry is exported from Gambit to the Fluent software which performs required simulation. Control volume method is used to solve the mass, energy, and species conservative equations. Mesh quality is calculated in ANSYS Fluent. The boundary and zone conditions which are labeled in Gambit software are now specified one by one in Fluent. Under solution method, pressure velocity coupling scheme is chosen and specified the spatial discretization for gradient, pressure, momentum, turbulent kinetic energy, turbulent dissipation rate, and species. Under solution control method, relaxation factors are adjusted for pressure, velocity, density, and other parameters. Residual monitors for absolute convergence are specified to find out the absolute convergence. After that initialization of solution is done and then iteration is performed at different equations until the absolute convergence is achieved. Figure 3 shows the GUI of the ANSYS Fluent tool.
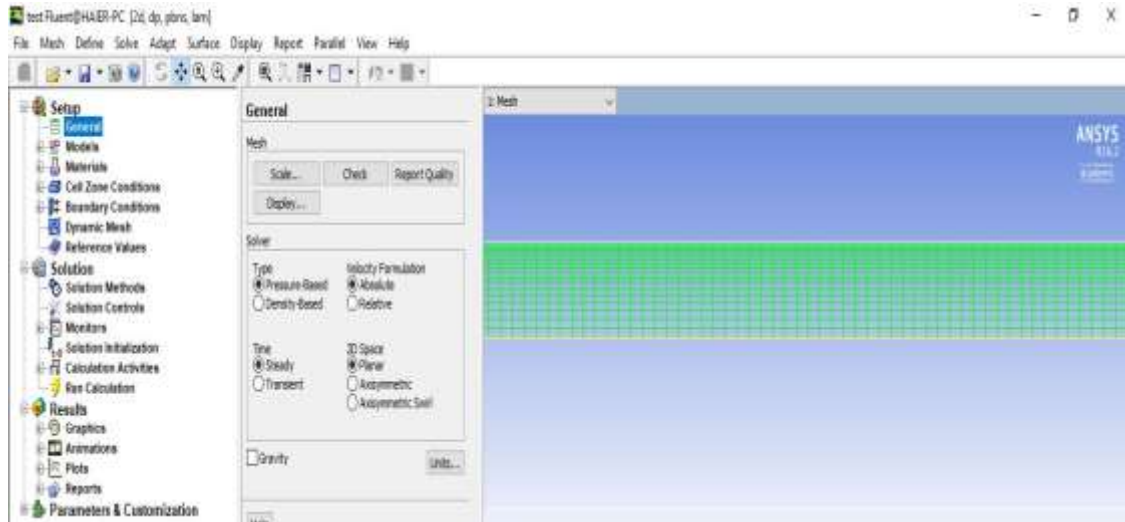
Figure 3 Mesh Import to Ansys Fluent

Four reaction models; laminar finite-rate, finite-rate/eddy-dissipation rate, eddy-dissipation and eddy-dissipation concept are present in the fluent to deal with reactions and incorporate turbulence-chemistry interactions. In laminar finite-rate, Arrhenius expressions are used to calculate reaction rate and turbulence effects are ignored. In finite-rate/eddy-dissipation rate, both Arrhenius expression and mixing can influence the reaction. The smaller value of Arrhenius rate and mixing rate is considered the rate of reaction. In eddy-dissipation model, the reaction rate is controlled and determined by turbulence while in eddy dissipation concept model, Arrhenius expression is also incorporated in turbulent flames. Laminar finite-rate model is not recommended in turbulent conditions due to non-linearity in Arrhenius chemical kinetics. The values of different reaction parameters in these reaction models which includes a pre-exponential factor, activation energy, mixing law constants, stoichiometric coefficients and rate exponent are required to incorporate different reactions as shown in Figure 4 and Figure 5.
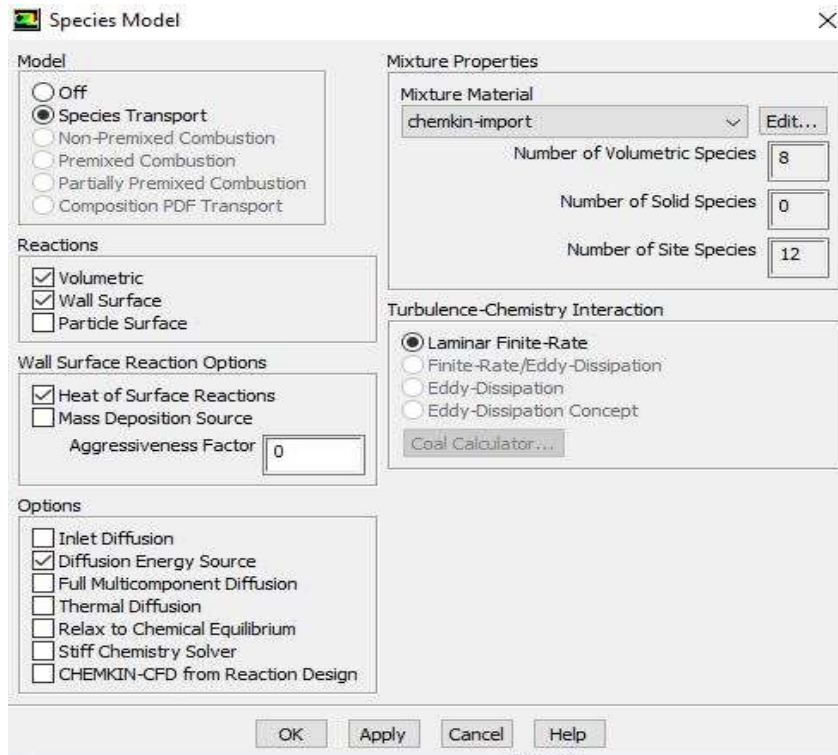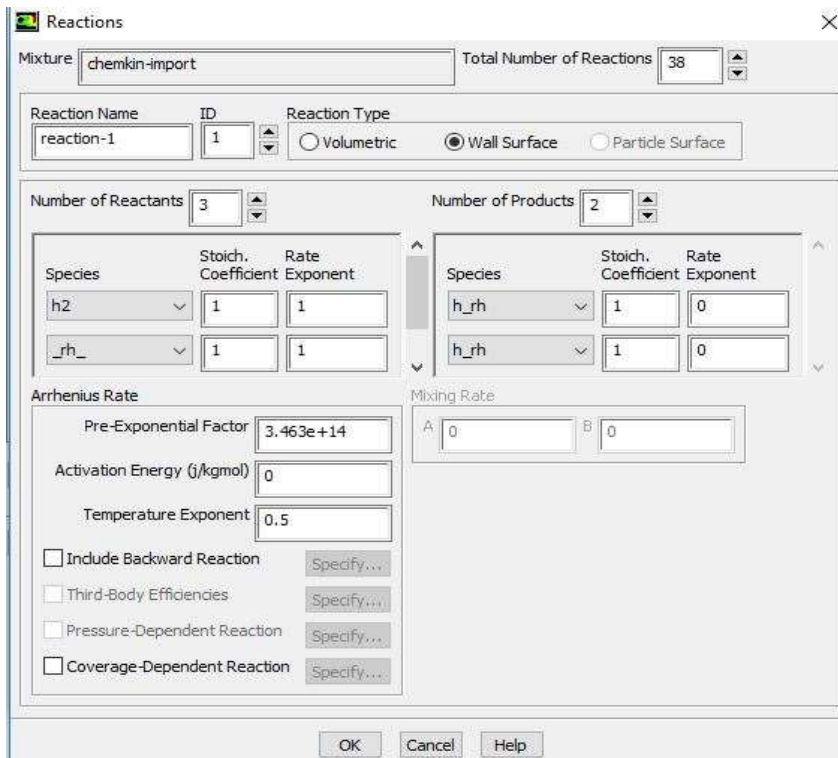
Figure 4 Reaction Models

Figure 5 Reaction Parameters

3.4 Convergence criteria

The commonly used absolute convergence criteria for the residuals of continuity, x-velocity, y-velocity, epsilon and species equation is .001 while the convergence criteria are 1e-04 for energy equation. For the convergence, the absolute convergence criteria need to be satisfied. Figure 6 shows the convergence of the solution for the required case that is being simulated for the Two-dimensional study of Catalytic combustion of Methane.
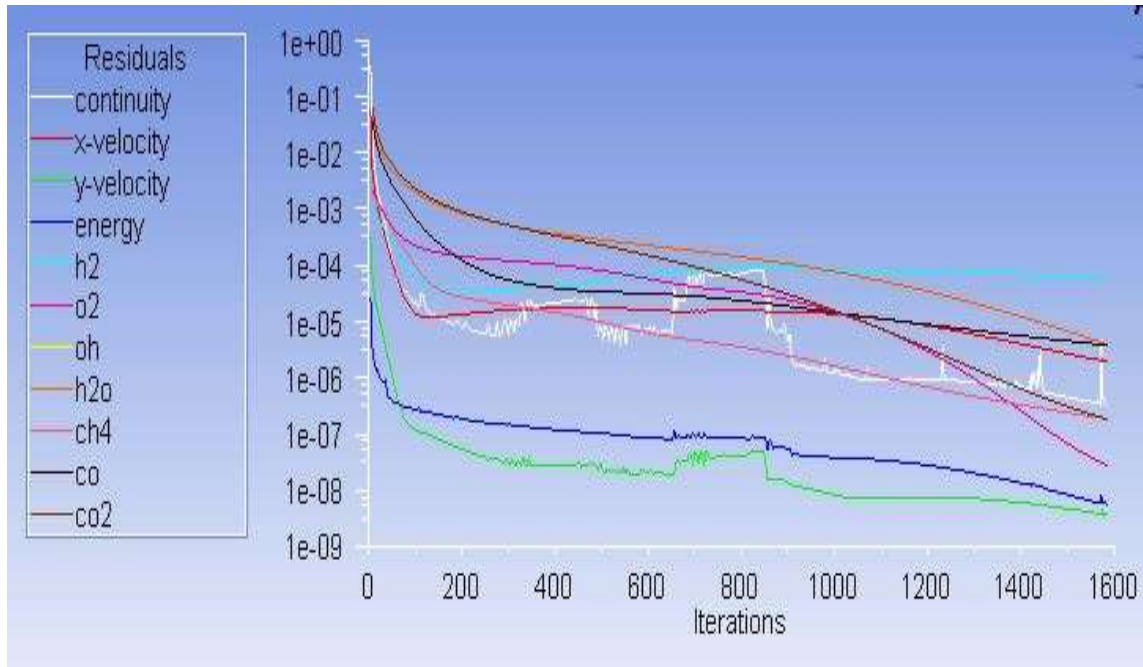

Figure 6 Scaled Residuals after 1600 iterations

3.5 Applications of Computational fluid dynamics modeling

CFD has different applications in different fields.

- In architectural field, it is used to design comfortable and safe environments
- It is used by vehicle's designers to improve aerodynamic features
- CFD is very helpful in the analysis of drug delivery
- Military equipment can be designed by using this technique
- Petroleum engineers used this technique to developed oil recovery strategies

3.6 CFD Modelling

The mathematical equations [29] that we use for the CFD modeling are as follows:

3.6.1 The equation of continuity

$$\frac{\partial(\rho u_j)}{\partial x_j} = 0 \tag{1}$$

In this equation, ρ is gas mixture density, u_j represents velocity of direction j, x_j denotes displacement of direction j.

3.6.2 Composition Equation

$$\rho u_j \frac{\partial Y_s}{\partial x_j} = \frac{\partial}{\partial x_j}\left(D\rho \frac{\partial Y_s}{\partial x_j}\right) + R_s \tag{2}$$

Here Y_s denotes the mass fraction of species s, Diffusion coefficient is represented by D and R_s describes the rate of generation. The rate of generation is explained as below,

$$R_s = \sum_{k=1}^{K_s} V'_{sk} K_k \prod_{i=1}^{N_g+N_s}[Y_i]^{V''_{ir}} \quad (i = 1,2,\dots,N_g + N_s) \tag{3}$$

Here K_s represents a total number of elementary surface reactions. N_g is the number of gas species and N_s is the number of surface species.

Arrhenius reaction source of the surface reaction is used to calculate Y_j as below,

$$K_r = A_r T^{\beta_r}\exp\left(-\frac{E_{ar}}{RT}\right) \prod_{S=1}^{N_S} \Theta_S^{\mu_{Sr}} \exp\left[\frac{-\varepsilon_{Sr}\Theta_S}{RT}\right] \tag{4}$$

In this equation, the Pre-exponential factor is represented by A_r, Temperature exponent is β_r, the activation energy of reaction r is represented by E_{ar} and surface coverage rate of species I is denoted by Θ_S.

The constant of adsorption reaction rate Krs is calculated as below,

$$K_{rs} = \left(\frac{2S_{O_S}}{2-S_{O_S}}\right)\frac{1}{(\Gamma)^\tau}\sqrt{\frac{RT}{2\pi M}} \tag{5}$$

Here S_{O_S} represents adsorption coefficient of adsorption species. Surface site density of the catalyst is represented by Γ.

3.6.3 Energy Equation

$$\rho u_j \frac{\partial h}{\partial x_j} = \frac{\partial}{\partial x_j}\left(\lambda \frac{\partial T}{\partial x_j}\right) + \frac{\partial}{\partial x_j}\left(\sum_S D\rho \frac{\partial Y_S}{\partial x_j} h_S\right) + q \tag{6}$$

Here h represents enthalpy, the heat of reaction is denoted by q and λ is used to represent thermal conductivity.

3.6.4 Ideal gas state

$$p = \rho RT \sum \frac{Y_S}{M_S} \tag{7}$$

20

Where R is universal gas constant, and molar mass is represented by M_S.

3.7 Simulation Setup

The physical process is done numerically by solving equations of the mathematical model in the computer system. This representation of equations is usually known as Numerical Simulation. This process has a tendency to produce results that are not achievable through other means. Numerical simulation usage is increasing day by day due to the increase in computer technology. By centralizing a computing capacity in a single system to enhance the performance of that system is regarded as the best way to solve complex problems that can occur in the field of physics and engineering. The evolution in the computer market has made the researcher think to find the new ways of solving complex problems by using computer systems. This can save a lot of time and cost as well. Different simulation tools are available in the market to solve a different set of complex reactions and problems. Computational fluid dynamics is that branch of mechanical science that tends to analyze and solve problems which involve fluid flow systems in chemical reactors. This is way CFD software pack is known as the best designing tool for different areas of reaction engineering as well. This thesis is being done for the numerically simulated combustion process in the presence of a platinum group metal as a catalyst. Two-dimensional (2D) and three-dimensional (3D) CFD analysis are being done in this research thesis.

Methane combustion is performed under catalytic overheated wall surfaces. Rhodium is used as the catalyst surface for this process of combustion of methane. The chemical reactions which involve catalytic activity taking place on the surface of the catalyst require modeling of a cylindrical channel of heated catalyst wall which is used as a surface phenomenon for the catalytic combustion of methane inside the combustion chamber [30].

For two-dimensional (2D) modeling of the reactor, the cylindrical channel was designed with the 2D axisymmetric solver. The first step of simulation was to create a geometry model which represents the desired flow. Gambit software was used to create the geometry and mesh involving catalyst channel. Two-dimensional CFD code was used for

this work. Catalyst cylinders were meshed using (Tet/Hybrid-TGrid). The reactor boundaries such as inlet, outlet and walls were resolved on this software. The geometry consisted of catalytic walls through which the fuel-air mixture is passed on at high temperature. The inlet temperature of the feed was set 300K and the wall temperature was set at 1290K. The three important parameters to evaluate the mesh quality are minimum orthogonal quality, maximum Ortho-Skew and maximum aspect ratio. Orthogonal quality ranges from 0 to 1, where values which are closer to 0 corresponds to low mesh quality. Similarly, Ortho Skew ranges from 0 to 1, where values closer to 1 are considered as the low mesh quality. The mesh generated for 2D had these values as 0.843787, 0.187859 and 5.38952 respectively. Table 2 presents the mesh characteristics of the 2D geometry such as minimum volume, maximum volume, total volume, no of elements, wedges, minimum face area and maximum face area. The total volume is a summation of volumes of all triangular cells present in geometry.

Table 2 Value of Different Mesh Properties

Mesh Properties	Values
Orthogonal quality (Minimum)	0.843787
Ortho Skew (Maximum)	0.187859
Aspect Ratio (Maximum)	5.38952
No of Nodes	13042
No of elements	6336
No of faces	13042
Wedges	6336
Minimum Volume (m^3)	3.818490e-09
Maximum Volume (m^3)	1.597526e-08
Total Volume (m^3)	5.400000e-05
Minimum Face area (m^2)	2.245272e-05
Maximum Face area (m^2)	1.724138e-04

A simulation involving catalytic combustion process was performed in Fluent 16.2. Species transport model was selected for the process. Wall surface reactions and heat of surface reactions were selected for the reaction type, and laminar finite-rate was selected for turbulence-chemistry interaction. Boundary conditions for inlet and wall were applied. The fluid regime, type of reactions either volumetric or surface type, kinetic and thermodynamic parameters of reactions, etc. were inserted. All the reactions considered in this work were supposed as the Surface type reactions. Gas mechanism and surface mechanism files were imported into the fluent for the reactions involved in the process. These files had the details of the surface chemistry and surface reactions which contributed to the catalytic combustion. The gas mechanism file had the details of the gaseous species involved in the process while surface mechanism file contributed by incorporating details of surface species and surface reactions in the process [31]. Volumetric reactions were not accounted in this research. These files were incorporated in the Ansys Fluent. The mesh generated consists of 6000 cells and 13000 nodes. Figure 7 shows the 2D geometry of the combustion chamber. The surface chemistry is explained in Table 3 which consists of the details of the surface reaction mechanism [32]. This table consists of the mechanism scheme of the reactions with associated rate expressions. This scheme assumes dissociative adsorption of methane CH_4 and oxygen O_2, formation of CO, CO_2, H_2, H_2O and desorption of products. All the steps in the reaction are reversible except methane adsorption and CO_2 desorption.
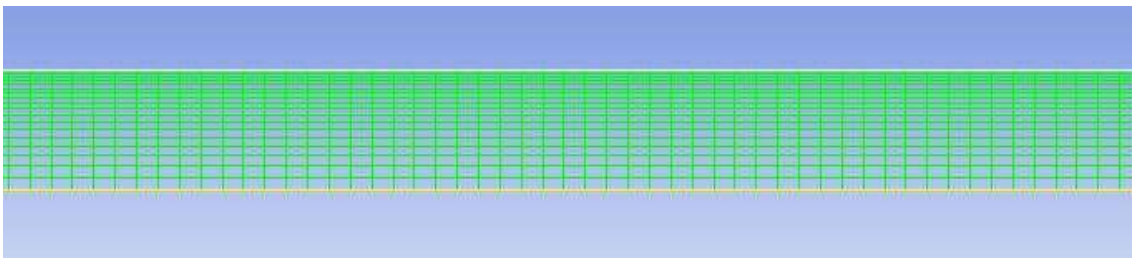

Figure 7 2D Mesh Generated

Table 3 Surface Reaction Mechanism

Reaction #	Reaction	A	E_a
1	$H_2 + 2Rh(s) \longrightarrow 2H(s)$	$1*10^{-2}$	s.c.
2	$O_2 + 2Rh(s) \longrightarrow 2O(s)$	$1*10^{-2}$	s.c.
3	$CH_4 + Rh(s) \longrightarrow CH_4(s)$	$8*10^{-3}$	s.c.
4	$H_2O + Rh(s) \longrightarrow H_2O(s)$	$1*10^{-1}$	s.c.
5	$CO_2 + Rh(s) \longrightarrow CO_2(s)$	$1*10^{-5}$	s.c.
6	$CO + Rh(s) \longrightarrow CO(s)$	$5*10^{-1}$	s.c.
7	$2H(s) \longrightarrow 2Rh(s) + H_2$	$3*10^{+21}$	77.8
8	$2O(s) \longrightarrow 2Rh(s) + O_2$	$1.3*10^{+22}$	355.2
9	$H_2O(s) \longrightarrow Rh(s) + H_2O$	$3*10^{+13}$	45
10	$CO(s) \longrightarrow Rh(s) + CO$	$3.5*10^{+13}$	133.4
11	$CO_2(s) \longrightarrow Rh(s) + CO_2$	$1*10^{+13}$	21.7
12	$CH_4(s) \longrightarrow Rh(s) + CH_4$	$1*10^{+13}$	25.1
13	$O(s) + H(s) \longrightarrow Rh(s) + OH(s)$	$5*10^{+22}$	83.7
14	$OH(s) + Rh(s) \longrightarrow O(s) + H(s)$	$3*10^{+20}$	37.7
15	$H(s) + OH(s) \longrightarrow Rh(s) + H_2O(s)$	$3*10^{+20}$	33.5
16	$Rh(s) + H_2O(s) \longrightarrow H(s) + OH(s)$	$5*10^{+22}$	104.7
17	$OH(s) + OH(s) \longrightarrow O(s) + H_2O(s)$	$3*10^{+21}$	100.8
18	$O(s) + H_2O(s) \longrightarrow OH(s) + OH(s)$	$3*10^{+21}$	171.8
19	$C(s) + O(s) \longrightarrow Rh(s) + CO(s)$	$3*10^{+22}$	97.9
20	$Rh(s) + CO(s) \longrightarrow C(s) + O(s)$	$2.5*10^{+21}$	169
21	$CO(s) + O(s) \longrightarrow Rh(s) + CO_2(s)$	$1.4*10^{+20}$	121.6
22	$Rh(s) + CO_2(s) \longrightarrow CO(s) + O(s)$	$3*10^{+21}$	115.3
23	$Rh(s) + CH_4 \longrightarrow H(s) + CH_3(s)$	$3.7*10^{+21}$	61
24	$H(s) + CH_3(s) \longrightarrow Rh(s) + CH_4(s)$	$3.7*10^{+21}$	51
25	$Rh(s) + CH_3(s) \longrightarrow CH_2(s) + H(s)$	$3.7*10^{+24}$	103
26	$CH_2(s) + H(s) \longrightarrow Rh(s) + CH_3(s)$	$3.7*10^{+21}$	44
27	$Rh(s) + CH_2(s) \longrightarrow CH(s) + H(s)$	$3.7*10^{+24}$	100
28	$CH(s) + H(s) \longrightarrow Rh(s) + CH_2(s)$	$3.7*10^{+21}$	68
29	$Rh(s) + CH(s) \longrightarrow C(s) + H(s)$	$3.7*10^{+21}$	21
30	$C(s) + H(s) \longrightarrow Rh(s) + CH_2(s)$	$3.7*10^{+21}$	172.8
31	$CH_4(s) + O(s) \longrightarrow CH_3(s) + OH(s)$	$1.7*10^{+24}$	80.3
32	$CH_3(s) + OH(s) \longrightarrow CH_4(s) + O(s)$	$3.7*10^{+21}$	24.3
33	$CH_3(s) + O(s) \longrightarrow CH_2(s) + OH(s)$	$3.7*10^{+24}$	120.1
34	$CH_2(s) + OH(s) \longrightarrow CH_3(s) + O(s)$	$3.7*10^{+21}$	15.1
35	$CH_2(s) + O(s) \longrightarrow CH(s) + OH(s)$	$3.7*10^{+24}$	158.4
36	$CH(s) + OH(s) \longrightarrow CH_2(s) + O(s)$	$3.7*10^{+21}$	36.4
37	$CH(s) + O(s) \longrightarrow C(s) + OH(s)$	$3.7*10^{+21}$	30.1
38	$C(s) + OH(s) \longrightarrow CH(s) + O(s)$	$3.7*10^{+21}$	145.5

The units of A are given in terms of [mol.cm.s] and of E_a in [kJ/mol].
s.c. = Initial Sticking Coefficient.

3.8 Numerical Methodology for 3D Simulation Setup

For three-dimensional modeling, following procedure was adopted for the simulation setup.

a) Geometry creation

b) Boundary Conditions

c) Solver Setting

d) Post Processing

3.8.1 Geometry creation

3D geometry was constructed for combustion model in the design modular. The dimension of the catalytic combustion model is taken from the previous work.
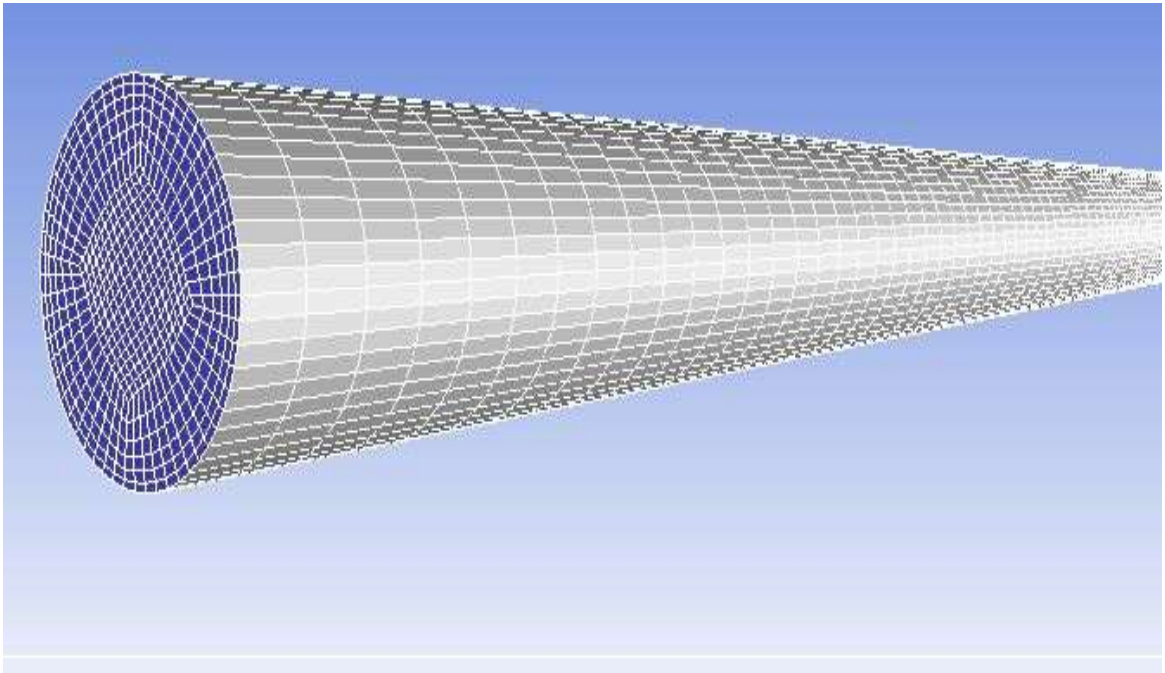
3.8.2 Meshing

Figure 8 3D Mesh Generated

When doing simulations in ANSYS, the solution of the problem depends strongly on the mesh quality. It is very necessary to have a reasonable mesh to solve the problem. The meshing of the computational domain is done in ANSYS ICEM CFD. ANSYS ICEM

CFD is a sophisticated tool for mesh creation. Figure 8 shows the 3D Mesh generated for the combustion chamber. The inlet of the mesh is shown in the below Figure 9.
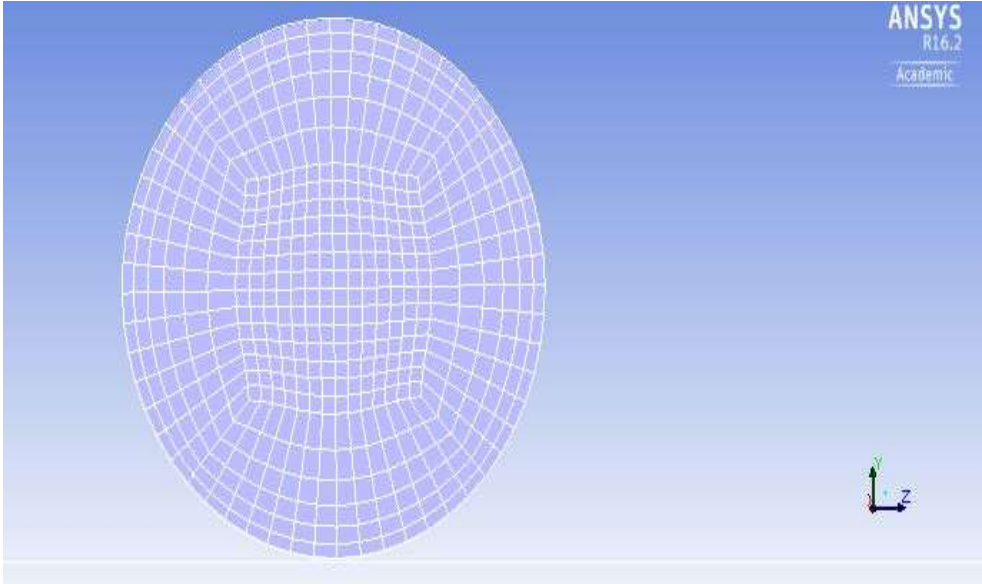
Figure 9 Mesh Inlet

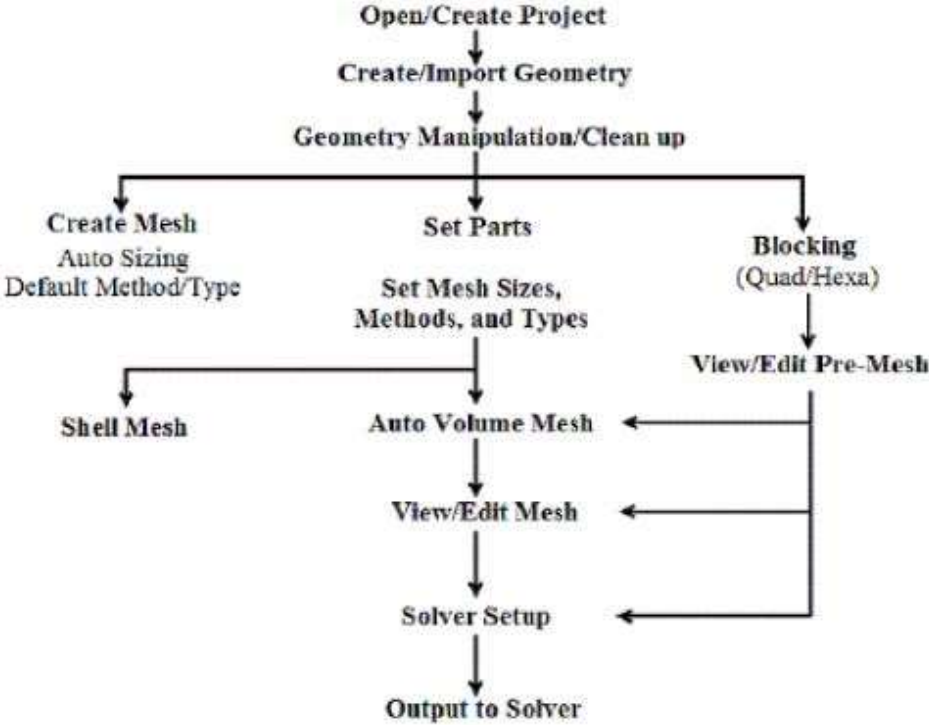The overall process of mesh generation is highlighted in Figure 10 below:

Figure 10 Mesh Generation Process

3.8.3 Steps of Creating Mesh

Following steps are performed for the mesh creation:

a) Geometry import to ICEM CFD

b) Blocking of the geometry

c) Splitting of the Blocks according to the requirement

d) Blocking associations are done

e) The setting of the edge parameters

f) Generating Pre-mesh

g) Checking quality

h) Setting output solver

The quality of the mesh created for the present model is above 0.6 which is in accordance with the mesh quality criteria defined by ICEM CFD.

3.8.4 Mesh Independence

In CFD analyses of any problem, the results of the problem are highly dependent on the mesh size and elements. The aim of mesh independence study is to check at what number of elements the solution becomes independent from the element size. In the following table 4, different values of the mesh properties of the 3D geometry are given.

Table 4 Properties of Mesh

Mesh Properties	Values
Orthogonal quality (Minimum)	8.09009e-01
Ortho Skew (Maximum)	1.90991e-01
Aspect Ratio (Maximum)	1.9777e+01
No of Nodes	77418
No of elements	72884
No of faces	223020
Wedges	72884

Minimum Volume (m^3)	1.387493e-13
Maximum Volume (m^3)	5.737389e-13
Total Volume (m^3)	2.347777e-08
Minimum Face area (m^2)	8.186211e-10
Maximum Face area (m^2)	1.724186e-08

3.8.5 Boundary Conditions

Boundary conditions specify the flow and thermal variables on the boundaries of the physical model. Boundary condition should be specified according to the conditions, as they are a critical component of ANSYS FLUENT simulations [33]. Boundary types in ANSYS FLUENT are of the following three types:

a) Flow boundaries

b) Wall, repeating and pole boundaries

c) Internal face boundaries

Boundary conditions were defined for the inlet feed of the reactors and the outlet of the reactors. Besides, a porous jump condition is applied to a model pressure drop within the reactor geometry. Temperature specifications for the inlet feed of reactor and mass fraction of components are described in the below Table 5.

Table 5 Boundary Conditions

Boundary Condition	Temperature (K)	Components Mass Fraction	
		CH$_4$	O$_2$
Inlet	298	0.05	0.23

3.9 CFD conservative equations

To differentiate between species, energy, continuity and momentum equations, Finite volume method with cell centered configuration is used. Finite volume basically points out the node at mesh which is being enclosed by small volumes. Conservative laws are

represented by the usage of computational control volumes. These laws are implemented on every control volume by the usage of different equations which may include species transport, energy conservative, continuity, and momentum equation.

3.10 Numerical Schemes

Individually separate and distinct environment is performed on integral nature of governing equations, which include momentum equation, energy equation, continuity equation, and species conservation by implementing Finite volume method on disorganized grid. Turbulence is dealt with the use of a semi empirical model which comprises of two equations. This model is known as standard k-epsilon model. This model is very simple and experimentally proven. SIMPLE (Semi-implicit Method for Pressure-Linked Equations) algorithm is used for pressure-velocity coupling. Separation of Correction of pressure and momentum equation is resolved indirectly while correction of velocity is performed indirectly. The evaluation of Green gauss cell-based gradient is done by the use of face values which are the arithmetic average of the values at the adjoining cell centers.

The development of model is started with the composition of geometry which is than introduce by the mesh preparation and boundary identification and zone cell conditions. ANSYS Fluent simulator is used to read and import the mesh. Then, properties of this mesh are introduced. For the analysis of temperature effect here, energy equation is enabled here because different up and down variations of temperature occur here due to reaction kinetics. The species transport model is enabled where reactions take place in bulk phase (volumetric reactions). To deal with turbulence, standard k-epsilon model is used. Finite rate/Eddy dissipation rate model is used in order to handle reactions involved in the process. Here, both rates are calculated, and the minimum rate is taken in account. User defined database is used to import reactions which are enabled in the porous zone into the ANSYS Fluent environment. Past literature is used to make a comparison of the results obtained through simulation process and the experimental process. The sequential procedure starting from mesh generation to convergence of the solution is shown in below Figure 11.
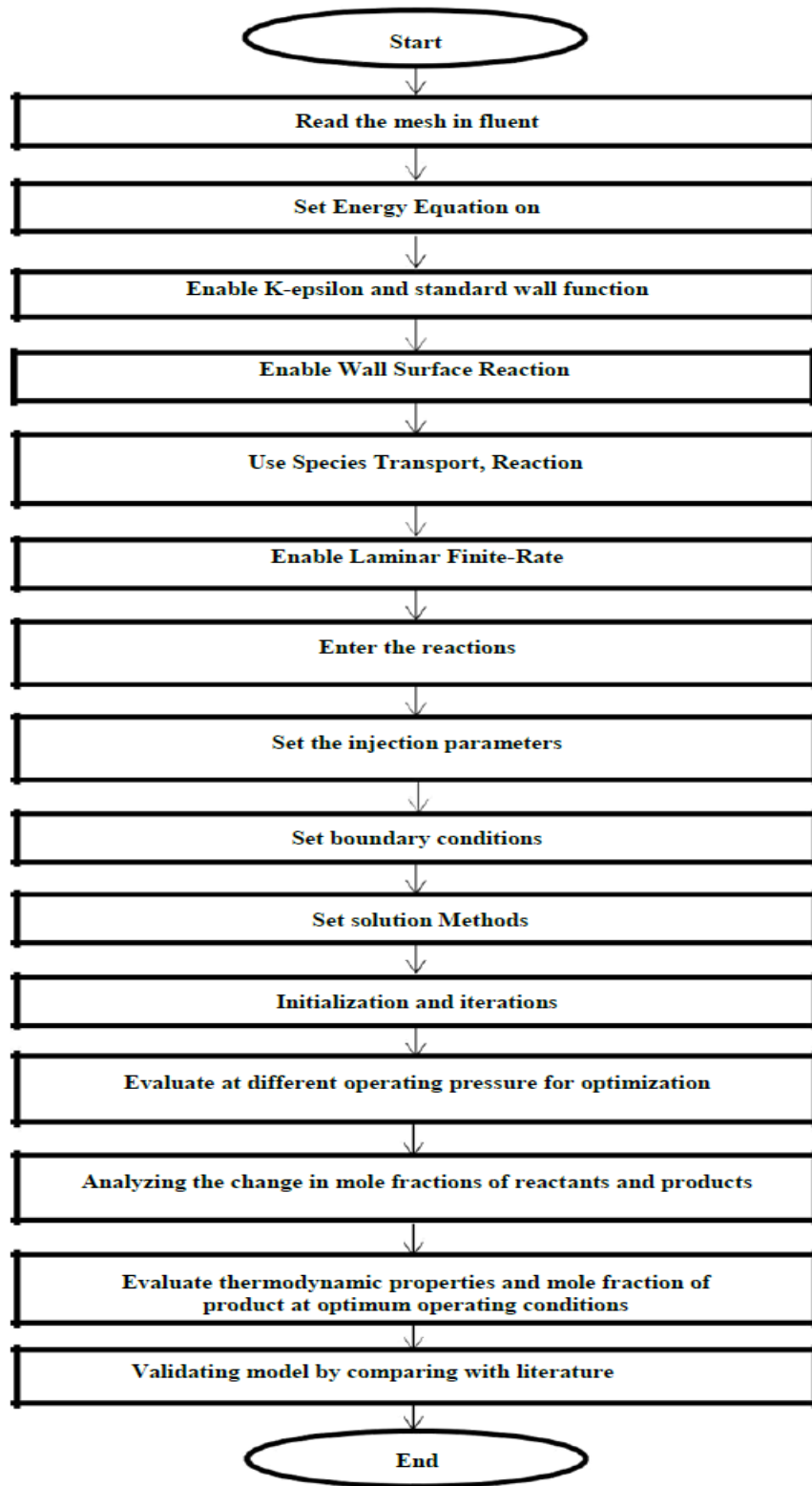
Figure 11 Schematic of Model Development Procedure

CHAPTER-4

Result and Discussion

The present work describes the methane combustion in the presence of surface catalytic activity. Simulation is performed to describe the behavior of different parameters involving combustion of methane under the influence of the surface catalyst. Results obtained from the simulation are discussed in detail in this section. Investigation of Mass fraction profiles of all the species involved in the reaction mechanism along with the temperature and pressure profiles obtain during the simulation process are discussed in detail. First of all, Two-Dimensional (2D) model is discussed by describing the results that are obtained from the simulation. Contours of Static Temperature obtained from simulation are shown in Figure 15. Calculations that are performed during iterations in the form of scaled residuals are graphically represented here as well. Mass fraction profiles of all the species are explained graphically and theoretically. Then Three-Dimensional (3D) model results are discussed. Again, here all the results that are obtained from the simulation are explained. Mass fraction profiles of all the species involved in the reaction mechanism of the combustion process are explained and represented in the three-dimensional (3D) view. Figures 15 describes the temperature profile of the two-dimensional model. Figure 12 represents the calculated iterations in the graphical manner. Figure 13 shows the convergence history along the iterations. Figure 14 describes the conversion of reactants and products along the position of the reactor. Figure 16,17 and 18 explains the mass fraction profiles of the reactants and products obtained through simulation.

Firstly, we discuss the results obtained from the two-dimensional (2D) model simulation. Combustion of methane involves the reactants Methane CH_4 and Oxygen O_2 and the process proceeds by exhausting reactants through the catalytic chamber to convert it into Carbon dioxide CO_2 and Water H_2O. The reaction is as follows:

$CH_4 + O_2 \rightarrow CO_2 + 2H_2O$
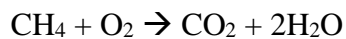
After inputting all the data in the model which is required to simulate the combustion process, the simulation was run, and the solution was converged at 184 iterations as we can observe in Figure 12. The scaled residuals obtained from the simulation after 1600 iterations are shown in Figure 6. The convergence history is shown in Figure 13. These graphs describe the iteration calculation which is performed to converge the data to see the results variations during the whole process. We can observe in these graphs that how the parameters are behaving as the process proceeds in the combustion chamber along the position of the catalytic reactor. Although it is a very simplified model but adequately predicts the behavior of mass fraction profiles of all the species which are involved in the reaction mechanism of the combustion process.

The contours of static temperature are shown in Figure 15. The inlet temperature of the combustion chamber at which the fuel/air entered the reactor was set at 300k. As, the reaction proceeded in the combustion chamber through the catalytic section of the chamber, an abrupt increase in temperature can be observed. The rise in temperature is because of the reactants reacting with catalytic wall surfaces of the combustion chamber which ignited the catalytic combustion reaction [34]. The contours of mass fraction profiles of methane CH_4 and oxygen O_2 are shown in Figure 16 and Figure 17. When fuel and air are allowed to enter combustion chamber at 300k, it reacts with the catalytic wall surfaces inside the combustion chamber. The catalytic wall surfaces upon reacting with reactants ignites the catalytic combustion reaction, and it raises the temperature of the chamber. Hence, the simulation predicts that the mass fraction profiles of methane and oxygen decrease as the temperature of the chamber rises as it passes through the catalytic wall surfaces of the chamber and the reactants start converting into products. As a result, it lowers down the amount of methane and oxygen in the reaction. The wall temperature of the chamber is 1290k, and hence reactants decreases as the reaction proceeds through the combustion chamber and the products are formed.

Methane and Oxygen conversion can be seen in the following graph represented in Figure 14. The point where the reactants enter the catalytic area is mentioned as 0mm. Along the reactor, when the reactants enter the catalytic area at low temperature, fast variation of temperature, velocity and transport coefficients of the reacting mixture occurs. This fluctuation is occurred because of the strong disturbance in the combustion chamber due

to an abrupt change in temperature, hence resulting in the conversion of the reactants into products. Along the position of the reactor, reactants are converted into the products.

The most significant product obtained from complete combustion of volatile organic compounds is Carbon dioxide CO_2. By this simulation results, it is predicted that there is an increase in the yield of carbon dioxide production as the temperature is increased under VOC combustion. Temperature is increased inside the chamber upon reaction of the fuel-air mixture with the catalytic surfaces. The catalyst ignites the catalytic combustion reaction and raises the temperature of the chamber. Contours of mass fraction of carbon dioxide are shown in Figure 18. The simulation describes that CO_2 amount increases as the reactants flow along the catalytic wall surfaces of the combustion chamber because VOCs combustion is occurring inside the chamber. The increase in temperature results in the increment of mass fractions of CO_2. Figure 19 shows the velocity vectors colored by velocity magnitude. The fluid velocity is less at the start and along the path of the upper wall section, but it is increased as the reaction is proceeding at the lower wall surface. Figure 19 clearly depicts that the fluid velocity is greater in the lower middle area of the reactor as compared to the upper region of the reactor.
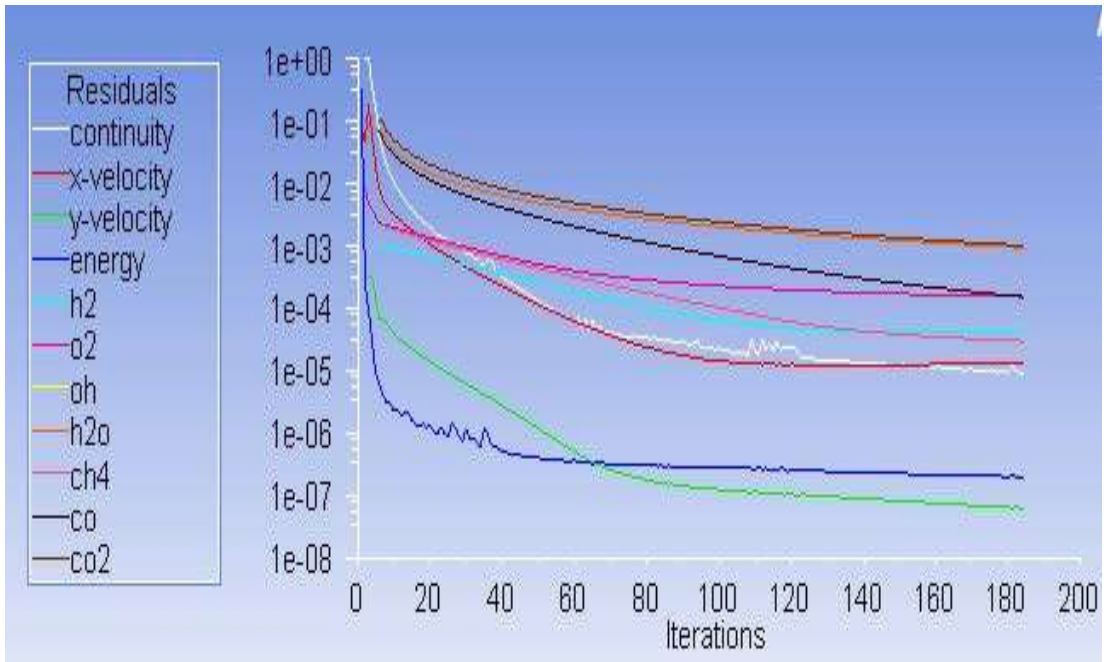
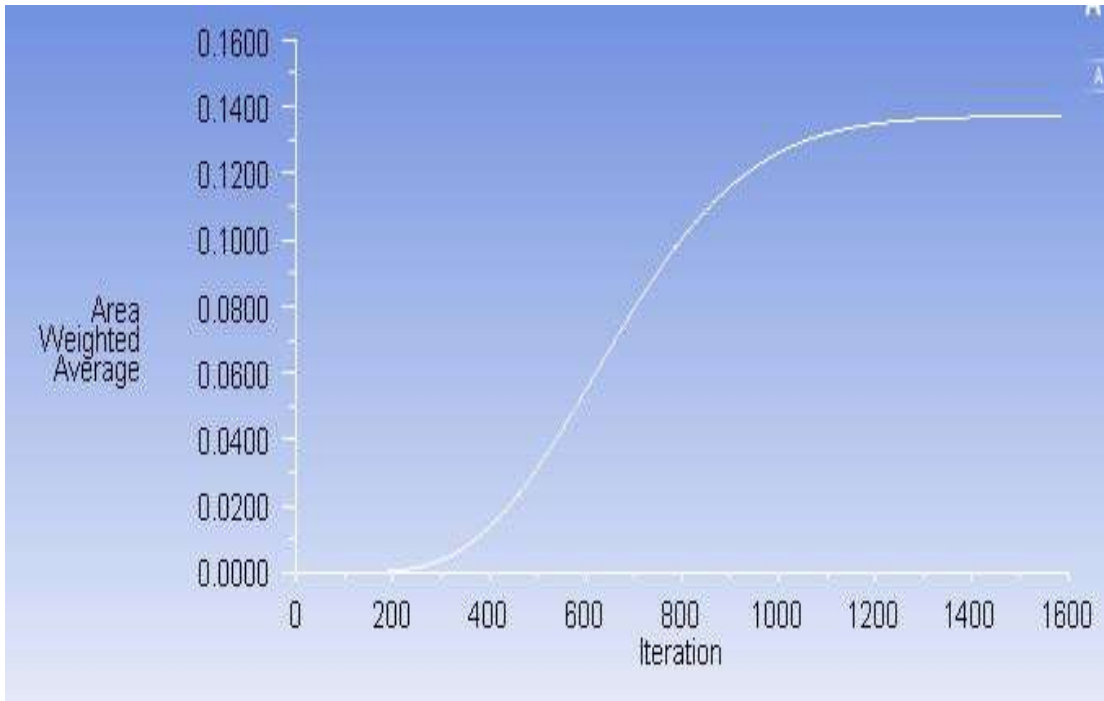Figure 12 Scaled Residuals after 200 iterations
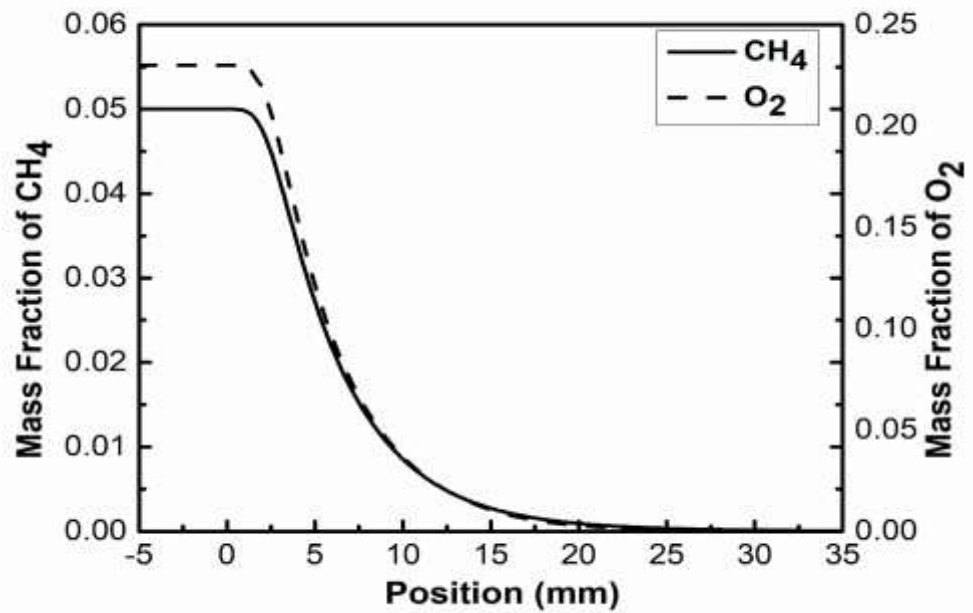

Figure 13 Convergence History
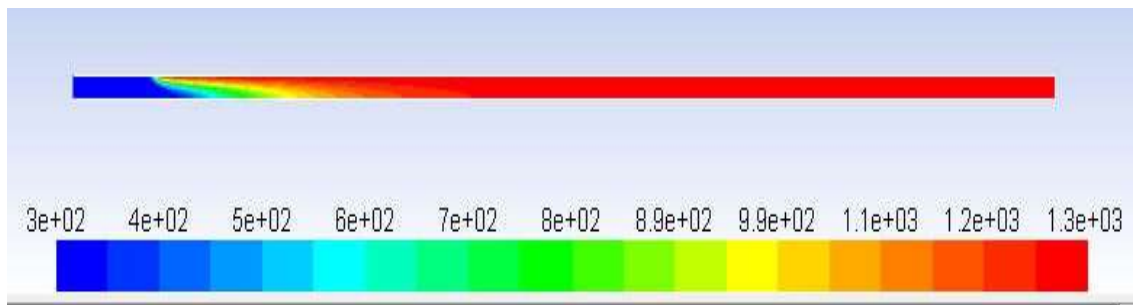
Figure 14 Conversion VS Position of Reactor
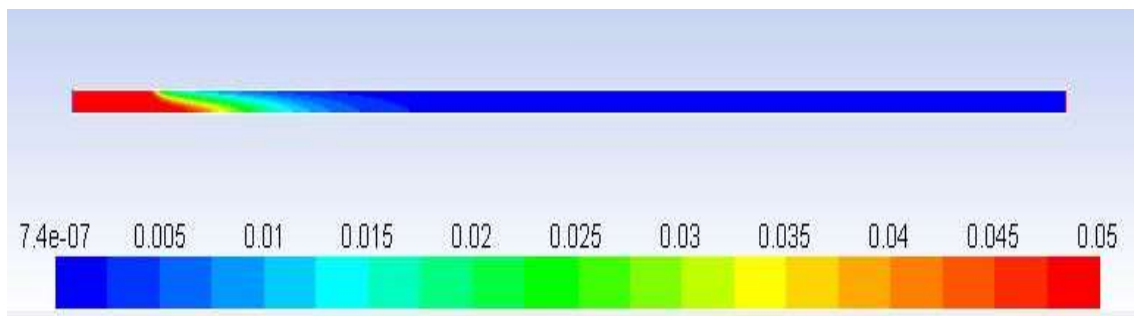

Figure 15 Contours of Static Temperature

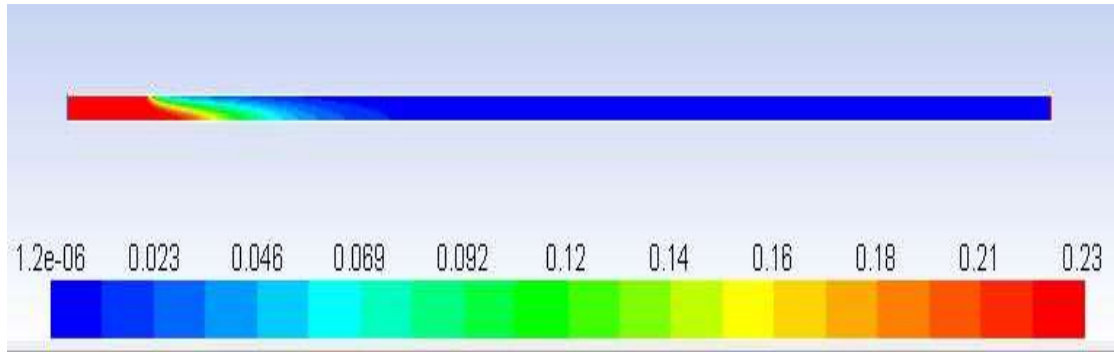Figure 16 Contours of Mass fraction of Methane CH4

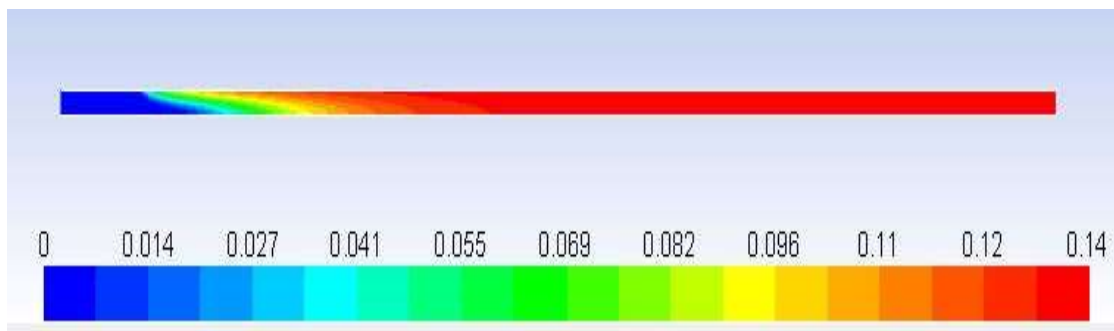Figure 17 Contours of Mass fraction of Oxygen O2
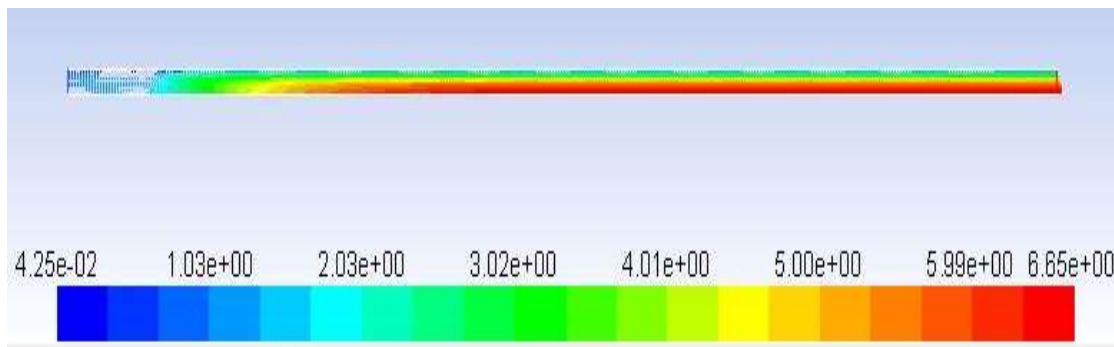

Figure 18 Contours of Mass fraction of Carbon dioxide CO2

Figure 19 Velocity Vectors Colored by Velocity Magnitude

Now, Results obtained from simulating the three-dimensional model will be discussed.

4.1 3D Results

3d results obtained from simulating catalytic combustion chamber are explained below:

This present work is done to explain further the results that were obtained through the 3D geometry of the reactor. Now, these results are interpreted in the three-dimensional reactor geometry. Simulation is run for the three-dimensional catalytic surface of the combustion chamber. Catalytic surface describes that the chamber has catalytic activity for the enhancement of the combustion process. Catalytic chamber increases the performance of the combustion phenomenon by igniting the fuel mixture inside the combustion chamber to produce better results with low energy requirement. Less undesirable components are produced in this process, and better production of desirable components are produced. Different fluid regimes of this combustion process are discussed in detail here. Mass fraction profiles of all the species that are involved in the catalytic combustion process are investigated here. Temperature profiles and pressure profiles obtained from simulation process are discussed as well. First of all, three-dimensional (3D) model was prepared for the simulation process. The simulation was run, and results were obtained. Here. Those results are discussed in detail. Contours of Temperature and pressure profiles obtained are shown in the Figure. Iterations are performed for the convergence of the solution. Scaled residuals obtained from converting the data are shown in the figure. All the mass fraction profiles of the species involved in the catalytic combustion process are described graphically and theoretically. Contours obtained are represented in a three-dimensional view in the following figures. Figure 27 consists of the Static pressure profile of the reaction process. Figure 28 tells us about the velocity vectors which are colored by velocity magnitude. Figure 26 represents the iterations that are calculated to converge the data of the simulation process in a graphically way. Figures 20-25 explains the mass fraction profiles of the reactant and products which are obtained by running the simulation.

Methane Combustion comprised Fuel-air mixture as the feed which passes through the catalytic combustion chamber to produce Carbon dioxide CO_2 and Water H_2O. The reaction is as follows:

$$CH_4 + O_2 \rightarrow CO_2 + 2H_2O$$

The simulation of the combustion process is run after inputting all the required parameters for the simulation. The solution was converged at about 240 iterations. The scaled residuals after 1600 iterations obtained from running the simulation are shown in Figure 6. These graphical representations describe the variations of different species involved in the combustion process. We can see the behaviors of different parameters as the process proceeds in the combustion chamber along the catalytic reactor position. Although it is a very simplified model but adequately predicts the behavior of mass fraction profiles of all the species which are involved in the reaction mechanism of the combustion process.

The temperature at the inlet of the combustion chamber where fuel/air entered the reactor was set at 300k. When, the reaction is proceeded in the combustion chamber through the catalytic section of the chamber, a sudden increment of temperature is observed. This abrupt increment of temperature is because of the reactants reacting with catalytic wall surfaces of the combustion chamber which ignited the catalytic combustion reaction. The contours of mass fraction profiles of methane CH_4 and oxygen O_2 are shown in Figure 20 and Figure 21. Methane and oxygen are entered in the combustion chamber at 300k resulting in the reaction with the catalytic wall surfaces inside the combustion chamber. The catalytic wall surfaces upon reacting with reactants ignites the catalytic combustion reaction, and it raises the temperature of the chamber. Hence, it is predicted by the simulation that the mass fraction profiles of methane and oxygen are decreased because of the rise in temperature inside the chamber as it passes through the catalytic wall surfaces of the chamber and the reactants start converting into products. As a result, it lowers down the amount of methane and oxygen in the reaction. The wall temperature of the chamber is 1290k, and hence reactants decreases as the reaction proceeds through the combustion chamber and the products are formed.

Methane and Oxygen conversion is presented in the graphical manner in the Figure 14. The point where the reactants enter the Catalytic area is mentioned as 0mm. Along the reactor, when the reactants enter the catalytic area at low temperature, fast variation of temperature, velocity and transport coefficients of the reacting mixture occurs. This fluctuation is occurred because of the strong disturbance in the combustion chamber due

to an abrupt change in temperature, hence resulting in the conversion of the reactants into products. Along the position of the reactor, reactants are converted into the products. Carbon dioxide CO_2 is the most important product obtained from complete combustion of volatile organic compounds. It is predicted by simulation analysis that there is an increase in the yield of carbon dioxide production as the temperature is increased under VOC combustion. Temperature is increased inside the chamber upon reaction of the fuel-air mixture with the catalytic surfaces. The catalyst ignites the catalytic combustion reaction and raises the temperature of the chamber. Contours of mass fraction of carbon dioxide are shown in Figure 22. The simulation describes that CO_2 amount increases as the reactants flow along the catalytic wall surfaces of the combustion chamber because VOCs combustion is occurring inside the chamber. The increase in temperature results in the increment of mass fractions of CO_2. Figure 23 consists of mass fraction profile of water. It is predicted by this simulation that amount of water is increased as the reaction is proceeded along the combustion chamber. Figure 24 and Figure 25 are presented to show the mass profiles for the Carbon Monoxide and Hydrogen. It can be observed in these two figures that the amount of CO and H_2 are in low quantity in the start but as the reaction is proceeded in the combustion chamber, the reactant methane is oxidized first to produce methylene radical. Further oxidation of this methylene radical produces formaldehyde. Similarly, reaction process is furtherly decomposing this formaldehyde in to carbon monoxide and hydrogen. Hence these two figures show some increase in the amount of CO and H_2 in the middle section of the tube but as the process is furthermore oxidized, this CO and H_2 are converted into Carbon dioxide and water, and during this process amount of CO and H_2 lowers down as it can be observed in the Figure 24 and 25. Figure 28 shows the velocity vectors colored by velocity magnitude. The fluid velocity is less at the start and along the path of the upper wall section, but it is increased as the reaction is proceeding at the lower wall surface. Figure 28 clearly depicts that the fluid velocity is greater in the lower middle area of the reactor as compared to the upper region of the reactor.
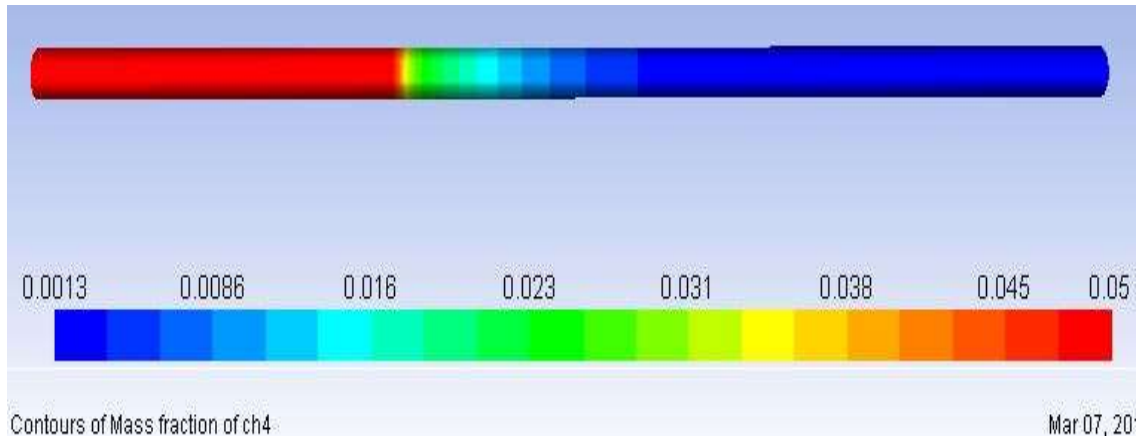
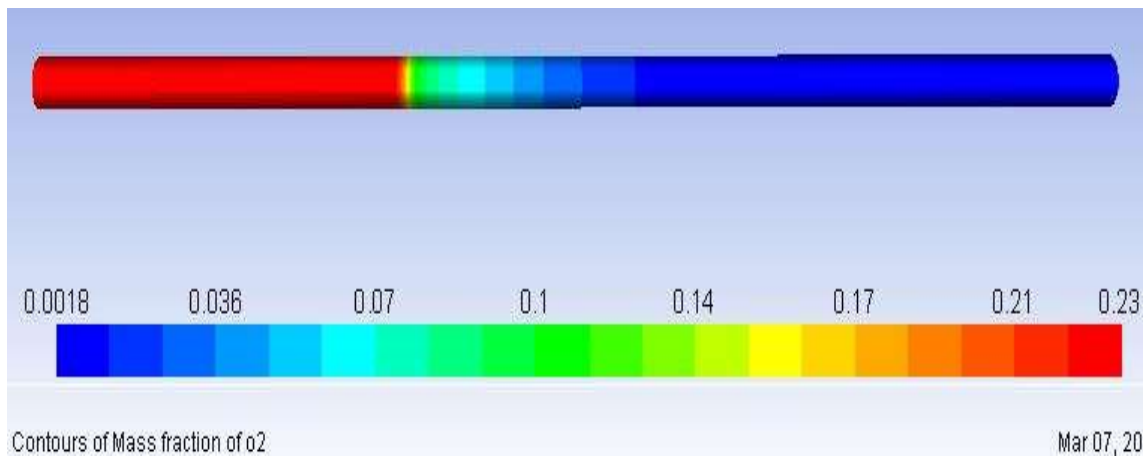Figure 20 Contours of Mass Fraction of Methane CH4 (3D)

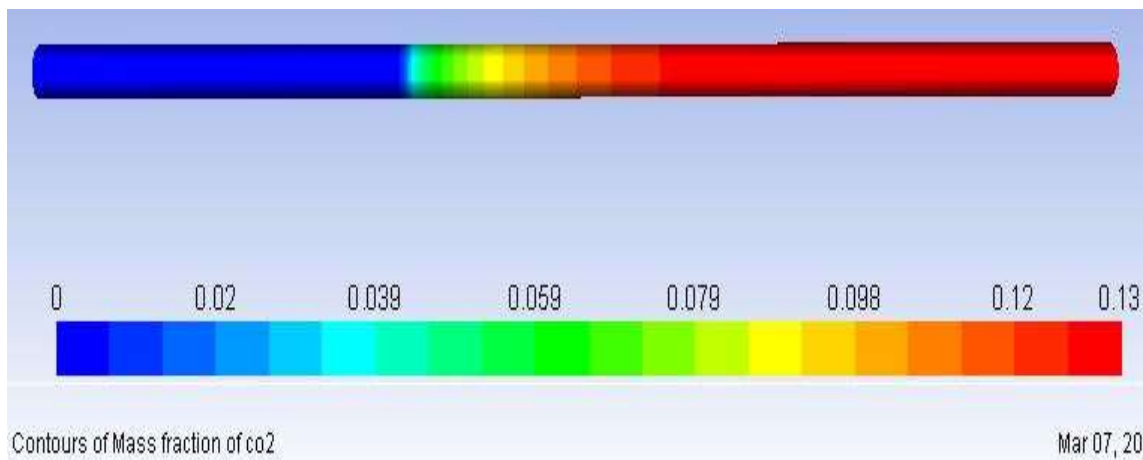Figure 21 Contours of Mass Fraction of Oxygen O2 (3D)

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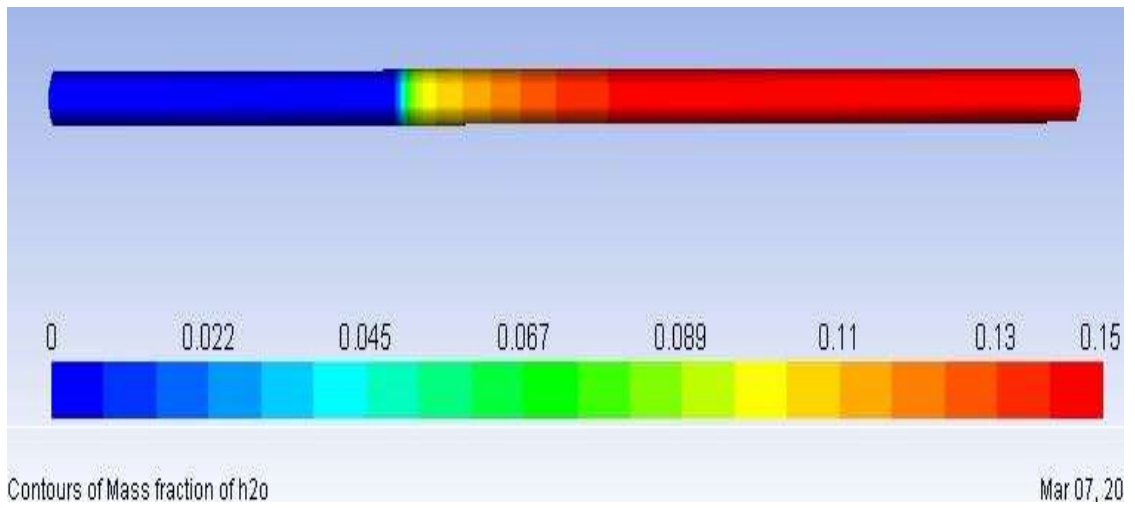Figure 22 Contours of Mass Fraction of Carbon Dioxide CO2 (3D)

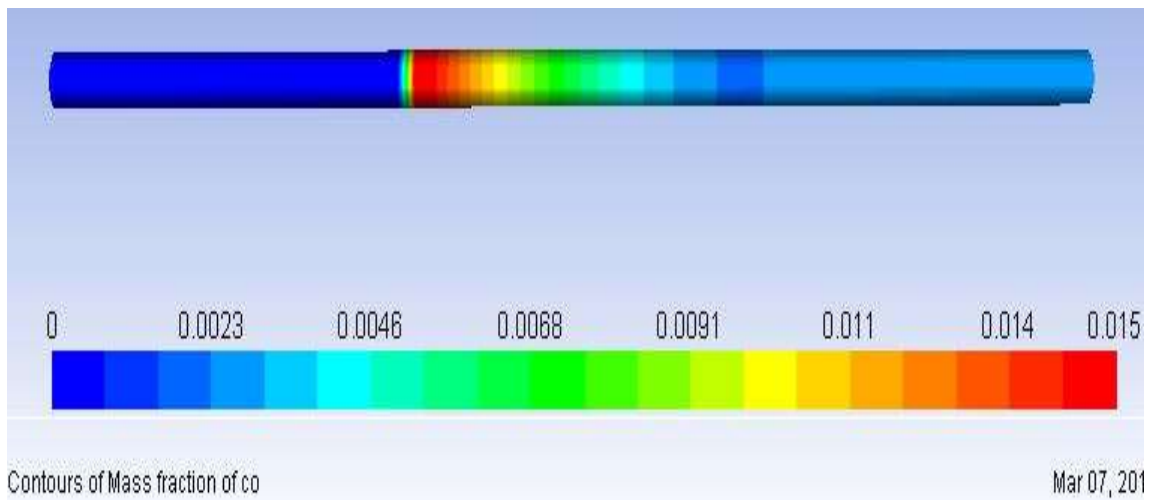Figure 23 Contours of Mass fraction of Water H2O (3D)

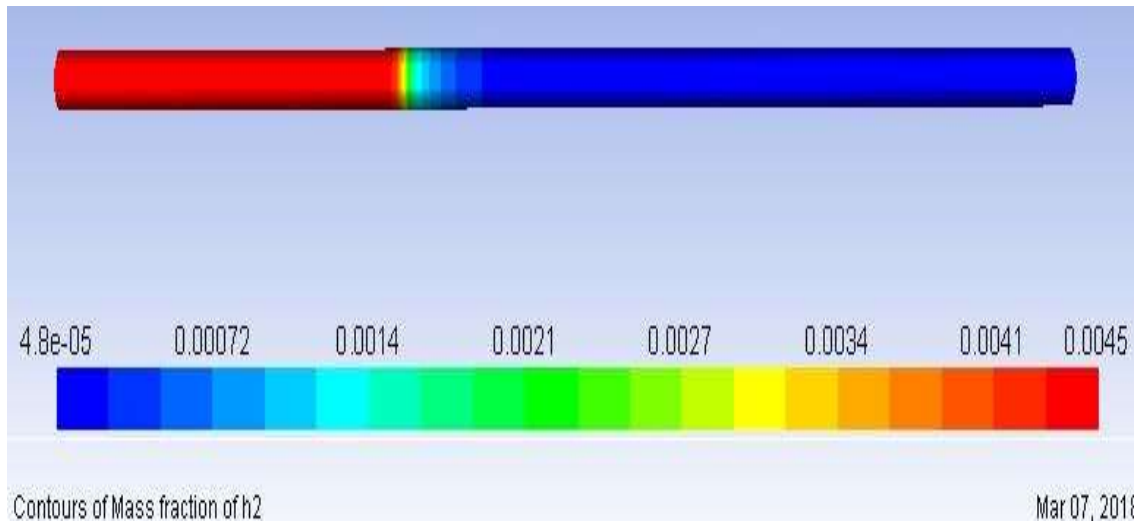Figure 24 Contours of Mass fraction of Carbon Monoxide CO (3D)

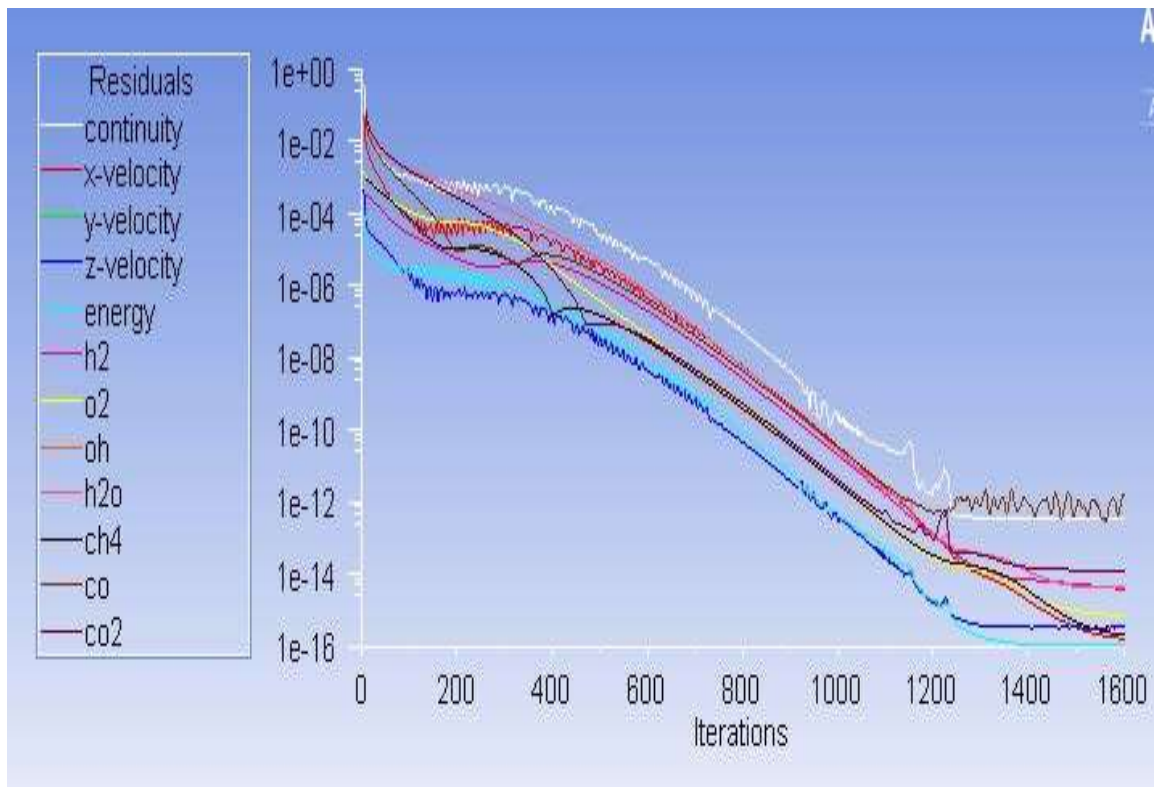Figure 25 Contours of Mass Fraction of Hydrogen H2 (3D)

Figure 26 Scaled Residuals after 1600 iterations (3D)

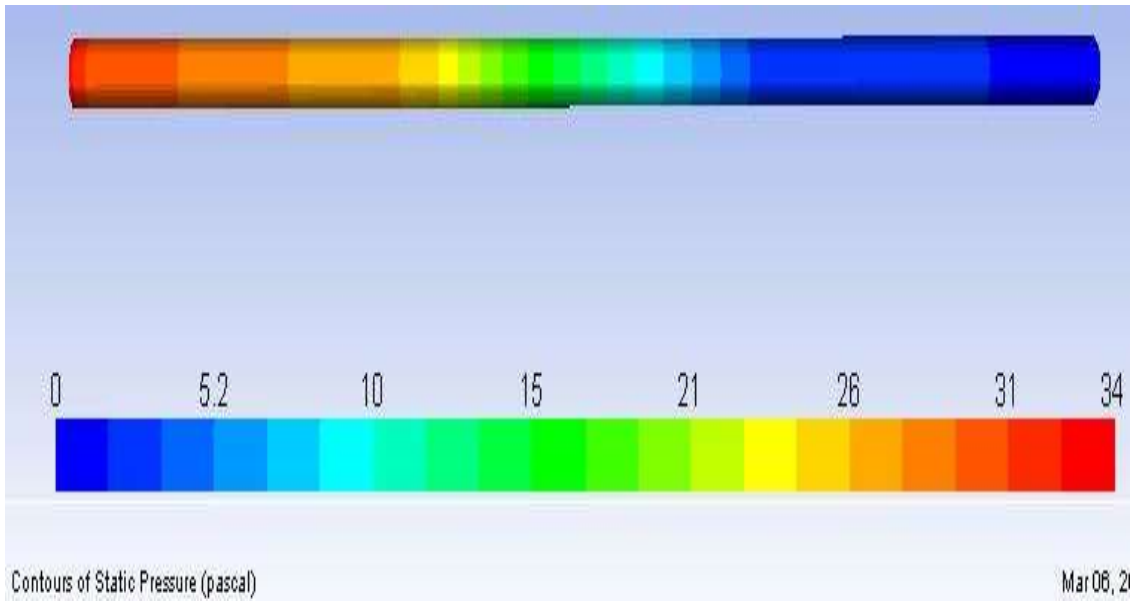Contours of Static Pressure (pascal)   Mar 06, 2

Figure 27 Contours of Static Pressure (3D)

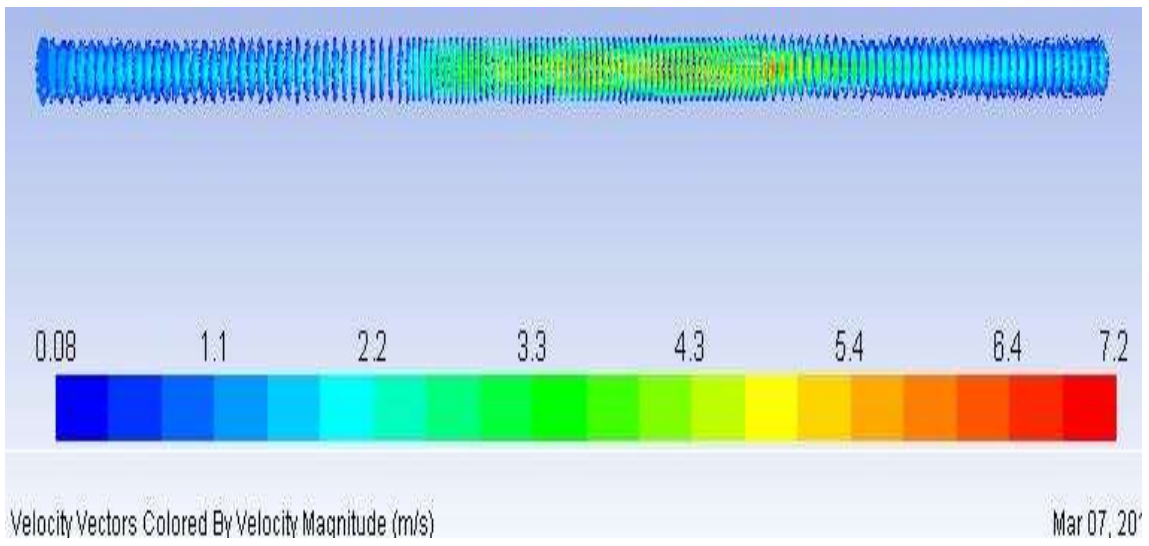Velocity Vectors Colored By Velocity Magnitude (m/s)   Mar 07, 20

Figure 28 Velocity Vectors by Velocity Magnitude (3D)

CHAPTER-5

Conclusions and Future Recommendations

A two-dimensional and three-dimensional cylindrical reactor has been made by using Ansys Gambit and Ansys ICEM comprising catalytic channel inside it for the catalytic combustion. Ansys Fluent has been used to predict the behaviour of the fluid regimes involving in the process of catalytic combustion. Incorporation of reaction mechanism for the catalytic combustion of methane in the software is done by creating a Chemkin mechanism file which consisted all the reactions involved in the methane combustion mechanism. The Chemkin file was imported into the software to conclude reaction mechanism. The simulation was performed on input data and it is concluded that the mass fraction of reactants decreased as the reaction proceeded through the catalytic channel of the combustion chamber. As a result, increase in product formation is observed. It was noticed that the presence of catalytic channel inside the combustion chamber ignited the combustion reaction. The catalytic activity was the reason to raise the temperature of the combustion chamber. Mass fraction profiles of the reactants and the products of combustion reaction are predicted in this study. This study recommended that the CFD simulation is the best software to predict the behaviour of chemical process mainly catalytic combustion. It is concluded through this research that CFD is the best software available for the prediction of surface reaction and related processes.

5.1 Future Recommendations

Future work should majorly focus on the following topics for the optimum prediction of fluid regimes of the combustion process and its behaviour inside the combustion chamber involving other hydrocarbons.

- Catalytic combustion of hydrocarbons and its simulation through Aspen Plus.
- Numerical Simulation analysis of the combustion of reforming process.
- Analysis of internal combustion engines through simulation using Computational Fluid Dynamics.
- CFD modelling and simulation of simultaneous removal of volatile organic compounds and sulphur particles generated during the combustion process.

References

[1] M.K. Hubbert, Energy from fossil fuels, Science, 109 (1949) 103-109.

[2] M.K. Hubbert, Nuclear energy and the fossil fuel, in: Drilling and production practice, American Petroleum Institute, 1956.

[3] L.F. Brown, A comparative study of fuels for on-board hydrogen production for fuel-cell-powered automobiles, International Journal of Hydrogen Energy, 26 (2001) 381-397.

[4] H. Rodhe, A comparison of the contribution of various gases to the greenhouse effect, Science, 248 (1990) 1217-1219.

[5] A. Michaelowa, C. Rolfe, Early Action to Reduce Greenhouse Gas Emissions Before the Commitment Period of the Kyoto Protocol: Advantages and Disadvantages, Environmental Management, 28 (2001) 281-292.

[6] D.t. Trimm, Catalytic combustion, Applied Catalysis, 7 (1983) 249-282.

[7] J.H. Lee, D.L. Trimm, Catalytic combustion of methane, Fuel processing technology, 42 (1995) 339-359.

[8] R. Carroni, V. Schmidt, T. Griffin, Catalytic combustion for power generation, Catalysis Today, 75 (2002) 287-295.

[9] R. Hayes, Catalytic solutions for fugitive methane emissions in the oil and gas sector, Chemical Engineering Science, 59 (2004) 4073-4080.

[10] R.M. Heck, R.J. Farrauto, Automobile exhaust catalysts, Applied Catalysis A: General, 221 (2001) 443-457.

[11] R. Anderson, K. Stein, J. Feenan, L. Hofer, Catalytic oxidation of methane, Industrial & Engineering Chemistry, 53 (1961) 809-812.

[12] D. Ferri, L. Forni, Methane combustion on some perovskite-like mixed oxides, Applied Catalysis B: Environmental, 16 (1998) 119-126.

[13] G. Veser, M. Ziauddin, L.D. Schmidt, Ignition in alkane oxidation on noble-metal catalysts, Catalysis Today, 47 (1999) 219-228.

[14] J. Kummer, Use of noble metals in automobile exhaust catalysts, The Journal of Physical Chemistry, 90 (1986) 4747-4752.

[15] D.L. Trimm, C.-W. Lam, The combustion of methane on platinum—alumina fibre catalysts—I: kinetics and mechanism, Chemical Engineering Science, 35 (1980) 1405-1413.

[16] M. Niwa, K. Awano, Y. Murakami, Activity of supported platinum catalysts for methane oxidation, Applied Catalysis, 7 (1983) 317-325.

[17] C. Cullis, B. Willatt, Oxidation of methane over supported precious metal catalysts, Journal of Catalysis, 83 (1983) 267-285.

[18] R.F. Hicks, H. Qi, M.L. Young, R.G. Lee, Structure sensitivity of methane oxidation over platinum and palladium, Journal of Catalysis, 122 (1990) 280-294.

[19] J. Veldsink, G. Versteeg, W.P.M. van Swaaij, Intrinsic kinetics of the oxidation of methane over an industrial copper (II) oxide catalyst on a γ-alumina support, The Chemical Engineering Journal and the Biochemical Engineering Journal, 57 (1995) 273-283.

[20] S. Dangi, M.A. Abraham, Kinetics and modeling of mixture effects during complete catalytic oxidation of benzene and methyl tert-butyl ether, Industrial & engineering chemistry research, 36 (1997) 1979-1988.

[21] S. Judd, The status of membrane bioreactor technology, Trends in biotechnology, 26 (2008) 109-116.

[22] R. Plascencia-Jatomea, F. Almazán-Ruiz, J. Gómez, E. Rivero, O. Monroy, I. González, Hydrodynamic study of a novel membrane aerated biofilm reactor (MABR): Tracer experiments and CFD simulation, Chemical Engineering Science, 138 (2015) 324-332.

[23] A.G. Dixon, M. Nijemeisland, CFD as a design tool for fixed-bed reactors, Industrial & engineering chemistry research, 40 (2001) 5246-5254.

[24] V.P. Zakharov, I.A. Zolotarskii, V.A. Kuzmin, CFD simulation of "gauze pad–honeycomb" catalytic system, Chemical Engineering Journal, 91 (2003) 249-255.

[25] R.J. Lopes, A.M. Silva, R.M. Quinta-Ferreira, Kinetic modeling and trickle-bed CFD studies in the catalytic wet oxidation of vanillic acid, Industrial & engineering chemistry research, 46 (2007) 8380-8387.

[26] R. Quiceno, J. Pérez-Ramírez, J. Warnatz, O. Deutschmann, Modeling the high-temperature catalytic partial oxidation of methane over platinum gauze: Detailed gas-phase and surface chemistries coupled with 3D flow field simulations, Applied Catalysis A: General, 303 (2006) 166-176.

[27] Y. Jiang, M.R. Khadilkar, M.H. Al-Dahhan, M.P. Dudukovic, CFD modeling of multiphase flow distribution in catalytic packed bed reactors: scale down issues, Catalysis Today, 66 (2001) 209-218.

[28] B. Blocken, T. Stathopoulos, J. Carmeliet, CFD simulation of the atmospheric boundary layer: wall function problems, Atmospheric environment, 41 (2007) 238-252.

[29] Y. Yan, W. Huang, W. Tang, L. Zhang, L. Li, J. Ran, Z. Yang, Numerical study on catalytic combustion and extinction characteristics of pre-mixed methane–air in micro flatbed channel under different parameters of operation and wall, Fuel, 180 (2016) 659-667.

[30] D. Hickman, L.D. Schmidt, Steps in CH4 oxidation on Pt and Rh surfaces: High-temperature reactor simulations, AIChE Journal, 39 (1993) 1164-1177.
[31] P. Kraus, R. Lindstedt, Microkinetic Mechanisms for Partial Oxidation of Methane over Platinum and Rhodium, The Journal of Physical Chemistry C, 121 (2017) 9442-9453.

[32] O. Deutschmann, R. Schwiedemoch, L.I. Maier, D. Chatterjee, Natural gas conversion in monolithic catalysts: interaction of chemical reactions and transport phenomena, in: Studies in Surface Science and Catalysis, Elsevier, 2001, pp. 251-258.
[33] A. Fluent, User's Guide, 2014.

[34] O. Deutschmann, R. Schmidt, F. Behrendt, J. Warnat, Numerical modeling of catalytic ignition, in: Symposium (international) on combustion, Elsevier, 1996, pp. 1747-1754.