

COMPARISON OF THE PERFORMANCES OF DIFFERENT CATALYTIC REACTOR
TYPES FOR THE WATER-GAS SHIFT REACTION USING COMPUTER
SIMULATIONS

by

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*Dedicated to my grandmother
and grandfather*

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ABSTRACT

COMPARISON OF THE PERFORMANCES OF DIFFERENT CATALYTIC REACTOR TYPES FOR THE WATER-GAS SHIFT REACTION USING COMPUTER SIMULATIONS

The low temperature water-gas shift reaction is mathematically modeled for packed-bed and monolith reactors by applying mass, energy and momentum balances at steady-state. One-dimensional pseudo-homogeneous and heterogeneous models are applied to the packed-bed reactor, while only one-dimensional pseudo-homogeneous model is applied to the monolith reactor. Kinetic rate expressions of the Cu-ZnO-Al₂O₃ and Pt-CeO₂-Al₂O₃ catalysts and the required data sets are taken from the literature. The modeling equations are developed on the basis of catalyst mass and the catalyst mass required to keep the downstream carbon monoxide concentration less than 1 mole per cent is calculated for desired methane conversion levels in a fuel processor feeding hydrogen to a 1.5 kW polymer electrolyte membrane fuel cell. The changes in temperature, pressure, methane conversion, carbon monoxide concentration in outlet and as well as molar flow rates of the components are simulated as a function of the calculated catalyst mass. The catalyst masses calculated by different mathematical models applied to the same type of the reactor are compared as well as the catalyst amounts calculated by using the same model for different types of reactors. The results of the water-gas shift reaction simulated over two different catalysts in the monolithic reactor are also compared.

ÖZET

FARKLI KATALİTİK REAKTÖR TİPLERİNİN SU-GAZI GEÇİŞ REAKSİYONU İÇİN PERFORMANSLARININ BİLGİSAYAR BENZETİMLERİ İLE KARŞILAŞTIRILMASI

Düşük sıcaklık su-gazı geçiş reaksiyonu, yatışkın durumda kütle, enerji ve momentum dengeleri kurularak sabit-yataklı ve monolit reaktörler için matematiksel olarak modellendi. Sabit-yataklı reaktörler için tek-boyutlu psödo-homojen ve heterojen modeller, monolit reaktörler için ise sadece psödo-homojen model uygulandı. Cu-ZnO-Al₂O₃ ve Pt-CeO₂-Al₂O₃ katalizörlerinin kinetik hız ifadeleri ve ilgili veri setleri kaynaklardan alınarak model eşitlikleri katalizör kütlesi temelinde geliştirildi ve reaktör çıkış gazındaki karbon monoksit derişiminin yüzde 1'in altında tutulması için gerekli katalizör kütlesi, 1,5 kW'lık polimer elektrolit membranlı yakıt piline hidrojen sağlayan yakıt işleme sistemindeki istenen metan dönüşme düzeyleri için hesaplandı. Sıcaklık, basınç, metan dönüşmesi, çıkış gazındaki karbon monoksit derişimi ve bileşenlerin molar debilerindeki değışiklikler hesaplanan katalizör kütlelerinin bir fonksiyonu olarak belirlendi. Aynı reaktör tipine uygulanan farklı matematiksel modeller sonucu elde edilen katalizör kütleleri ve aynı matematiksel modelin farklı reaktör tiplerine uygulanması sonucu elde edilen katalizör kütleleri kendi aralarında karşılaştırıldı. Düşük sıcaklık su-gazı geçiş reaksiyonunun monolit reaktörde modellenmesi iki farklı katalizör için yapılarak elde edilen sonuçlar karşılaştırıldı.

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LIST OF SYMBOLS / ABBREVIATIONS

A	Cross-sectional area of reactor	cm^2
A_m	Cross-sectional area of a single channel of monolith	cm^2
c	Total number of channels in a monolith	—
C_{CO}	Bulk concentration of CO	gmol cm^{-3}
C_{CO}^s	Surface concentration of CO	gmol cm^{-3}
CD_a	Collision diameter of H_2	A
CD_b	Average collision diameter of CO, CO_2 , CH_4 and/or N_2	A
CD_{ave}	Average collision diameter of bulk fluid	A
CI_{ave}	Collision integral for diffusion	—
Cp_i^{ig}	Heat capacity of species i	$\text{J gmol}^{-1}, \text{cal gmol}^{-1} \text{K}^{-1}$
Cp_f	Heat capacity of bulk fluid	$\text{J gmol}^{-1} \text{K}^{-1}$
D_{ab}	Diffusivity of bulk	$\text{cm}^2 \text{s}$
D_e	Effective diffusivity	$\text{cm}^2 \text{s}^{-1}$
D_h	Hydraulic diameter of monolith	cm
D_m	Diameter of the monolith reactor	cm
D_p	Equivalent diameter of the catalyst particle	cm
D_t	Diameter of the packed-bed reactor	cm
E	Activation energy of LTS reaction	J gmol^{-1}
F_{CO}	Molar flow rate of CO	gmol s^{-1}
F_i^0	Initial molar flow rate of species i	gmol s^{-1}
G	Superficial mass velocity	$\text{lb}_m \text{ft}^{-2} \text{h}^{-1}$
G_i^{ig}	Ideal gas Gibbs energy of species i	J gmol^{-1}
G_{Rxn}^{ig}	Ideal gas Gibbs energy of reaction LTS	J gmol^{-1}
GSA	Geometric surface area of monolith	$\text{cm}^2 \text{cm}^{-3}$
h_f	Heat transfer coefficient	$\text{J cm}^{-2} \text{s}^{-1} \text{K}^{-1}$
k	Temperature-dependent rate constant of the reaction	$\text{gmol gcat}^{-1} \text{s}^{-1} \text{atm}^{-2}$
k_f	Mass transfer coefficient	cm s^{-1}
K_{eq}	Equilibrium constant of the reaction	—
K_i	Temperature-dependent adsorption coefficient of species i	atm^{-1}

L	Length of one side of a square monolith channel	cm
L_m	Length of monolith reactor	cm
L_t	Length of packed-bed reactor	cm
LJ_a	Epsilon / kappa for H ₂	K
LJ_b	Epsilon / kappa for the mixture of CO, CO ₂ , CH ₄ and/or N ₂	K
LJ_{ave}	Epsilon / kappa for the gas mixture	K
m	Reaction order, which is 1 for LTS	—
M_a	Molecular mass of H ₂	g gmol ⁻¹
M_b	Average molecular mass of CO, CO ₂ , CH ₄ and/or N ₂	g gmol ⁻¹
M_{ave}	Average molar mass of bulk fluid	g gmol ⁻¹
M_i	Molecular mass of species i	g gmol ⁻¹
n	Number of cells per square inch of monolith surface area	cpsi
Nu	Nusselt number	—
OFA	Open frontal area of monolith	%
p_i	Partial pressure of species i	atm
P	Total pressure	atm
P^0	Initial pressure of bulk fluid	atm
Pr	Prandl number	—
r_i	Reaction rate of species i	gmol s ⁻¹ gcat ⁻¹
R	Gas constant	J gmol ⁻¹ K ⁻¹ , cal gmol ⁻¹ K ⁻¹
Re	Reynolds number	—
R_m	Fillet radius of a square monolith channel	cm
s	number of electrons involved in the reaction	—
Sc	Schmidt number	—
Sh	Sherwood number	—
t	Thickness of a square monolith channel	cm
T	Temperature	K
T^0	Initial temperature of bulk fluid	K
T_{ref}	Reference temperature	K
T_s	Surface temperature of catalyst	K
T^*	Dimensionless temperature	—
v	Average linear velocity of fluid	cm s ⁻¹
V	Volume of the catalyst bed, including the pores	cm ³

V_t	Total volumetric flow rate of bulk phase	$\text{cm}^3 \text{ s}^{-1}$
W	Total mass of the catalyst	g cat
W_c	Calculated mass of the catalyst per number of channels	g cat/channel
W_g	Given mass of the catalyst per number of channels	g cat/channel
W_e	Electrical work performed	J
y_i	Molar fraction of species i	—
ΔC	Change in concentration	gmol cm^{-3}
ΔG	Change in Gibbs free energy of the reaction	J
ΔH	Change in enthalpy of the reaction	J
ΔH_{Rxn}	Enthalpy of reaction	J gmol^{-1}
ΔP	Pressure drop along monolith	atm
ΔS	Isothermal entropy change of the reaction	J K^{-1}
ΔT	Change in temperature	K
ΔU_0	Voltage of the cell for thermodynamic equilibrium in the absence of a current flow	V
ΔU_{cell}	Cell voltage	V
β	Reversibility factor for rate equation	—
ε	Porosity of the catalyst bed	—
ε_r^{cell}	Thermodynamic efficiency of fuel cell	—
ε_V	Electrochemical efficiency of fuel cell	—
λ_i	Thermal conductivity of species i	$\text{J cm}^{-1} \text{ s}^{-1} \text{ K}^{-1}$
λ_f	Thermal conductivity of bulk fluid	$\text{J cm}^{-1} \text{ s}^{-1} \text{ K}^{-1}$
μ_i	Viscosity of species i	$\text{g cm}^{-1} \text{ s}^{-1}$
μ_f	Viscosity of gas mixture	$\text{g cm}^{-1} \text{ s}^{-1}$
ρ_s	Solid density of the catalyst	g cm^{-3}
ρ_b	Bulk density of the catalyst bed	g cm^{-3}
σ	Constriction factor	—
Φ_i	Dimensionless quantity	—
τ	Tortuosity	—

AFC	Alkaline fuel cell
ATR	Autothermal reforming
CHP	Combined heat and power
CH ₄	Methane
CO	Carbon monoxide
CO ₂	Carbon dioxide
DC	Direct current
DMFC	Direct methanol fuel cell
H ₂	Hydrogen
H ₂ O	Water / Steam
HTS	High temperature shift
ICE	Internal combustion engines
LPG	Liquefied petroleum gas
LTS	Low temperature shift
MCFC	Molten carbonate fuel cell
N ₂	Nitrogen
O ₂ /C	Oxygen:Carbon ratio
ODE	Ordinary differential equation
PAFC	Phosphoric acid fuel cell
PO	Partial oxidation
SOFC	Solid oxide fuel cell
SR	Steam reforming
S/C	Steam:Carbon ratio
S/G	Steam:Dry gas ratio
WGS	Water gas shift

1. INTRODUCTION

The recent dramatic growth in energy consumption is directly related to the rapid development in industrial and transportation sectors, improvements in living standards among residential sectors and the rapid increase in population. The emissions of enormously large amounts of gases from the combustion of the fossil fuels into the atmosphere have caused a rise in global concentrations of greenhouse gases, particularly carbon dioxide (CO_2). Greenhouse gas emissions can be controlled by some approaches such as major improvement in energy efficiency, the use of carbon-less (or carbon-free) energy, and the sequestration of carbon such as CO_2 storage in geologic formations [1].

Increasing concern about environmental consequences of fossil fuel consumption in electricity production and transport applications and the reality of limited reserves of fossil fuels that strengthen the dependence of countries on oil are two of the major factors which affect the development of fuel cells for transport applications, and for stationary and portable power generation. Using pure hydrogen (H_2), fuel cells only produce water (H_2O), thus locally eliminating all emissions otherwise caused by electricity production. [2]

The type of the fuel and the fuel cell depend on the application in which they are used. Methanol, gasoline, diesel may be utilized in transportation, while natural gas and propane are likely be used in stationary systems. In certain niche markets, the fuel can be ethanol, butane, or biomass-derived materials [3]. The alkaline fuel cell (AFC) technology has been used in space applications [1, 4], while the polymer electrolyte membrane fuel cell (PEMFC) is utilized primarily in residential combined heat and power (CHP) systems, transportation and portable applications [1-4]. The phosphoric acid fuel cell (PAFC) is used generally in CHP for decentralized stationary power systems. The molten carbonate fuel cell (MCFC) and the solid oxide fuel cell (SOFC) are used generally in central and stand-alone stationary CHP systems and transportation applications such as trains and boats. The application areas for the direct methanol fuel cell (DMFC) technology are the vehicle and small portable systems [2, 4].

Fuel processors are designed and developed to supply the H_2 rich gas mixture for the fuel cell depending on its requirements. There are several reactions to produce H_2 such as steam reforming (SR), catalytic or non-catalytic partial oxidation (PO) and autothermal reforming (ATR) in which SR and PO occur simultaneously in the same reactor. The SR is an endothermic reaction and steam reacts with the fuel to produce H_2 , carbon monoxide (CO) and CO_2 . On the other hand, the PO is an exothermic reaction, in which fuel reacts with a substoichiometric amount of oxygen (O_2) to produce H_2 , CO and CO_2 [3]. In ATR reactor, the SR reaction utilizes the heat generated by the PO reaction, which makes the ATR reactor a stand-alone process.

Since the CO amount of the downstream of these reactors is high for the low temperature fuel cells such as PEMFC, the water-gas shift (WGS) reaction is applied to the reformat gas to reduce the CO content to less than 1 per cent, which also increases the H_2 composition. The WGS reaction is slightly exothermic and generally takes place in two reactors to take advantage of kinetics and thermodynamics [5, 6]. The preferential oxidation reaction then takes place following the WGS reactors to reduce the CO content to 20–100 ppm since the Pt or Pt–Ru anodes of PEMFC are poisoned by CO [5, 6].

This study includes the mathematical modeling and steady-state simulation of the low temperature shift (LTS) reaction in packed-bed and monolith reactors by applying one-dimensional pseudo-homogeneous and heterogeneous models. Data sets and the kinetic rate equations of the catalysts are taken from the literature. The catalyst mass is calculated and the change in temperature, pressure and molar flow rates of components are simulated versus the calculated catalyst mass for each data set.

A literature survey is given in Chapter 2 about fuel cell technology, H_2 production and purification reactions. The types of the reactors and the mathematical models applied are presented in Chapter 3. Simulation results are presented and discussed in Chapter 4 by giving the related tables and figures. Finally conclusions about this study are given in Chapter 5, where some recommendations for future work are also made.

2. LITERATURE SURVEY

2.1. Fuel Cell Technology

Fuel cells are galvanic cells, in which the free energy of a chemical reaction is converted into electrical energy (via an electrical current). The principle of fuel cell was first discovered in 1839 by Sir William R. Grove, a British jurist and physicist, who used H_2 and O_2 as fuels catalyzed on platinum electrodes [1, 7], however it is written in another paper [2] that the principle was first discovered by Christian Friedrich Schönbein, a Professor at the University of Basle from 1829 to 1868, who was in close contact with Sir Grove, although the invention of fuel cells is attributed to Sir William Grove.

The fuel cells have similar basic structures that each of them consists of two electrodes, which are separated by the electrolyte and connected with an external circuit. In **Figure 2.1**, the fuel is oxidized electrochemically to positively charged ions at one of the electrodes, which is called anode, while O_2 molecules are reduced to oxide or hydroxide ions at the other electrode, which is called cathode. The electrolyte serves to transport either the positively or negatively charged ions from anode to cathode or vice versa. For PEMFCs, the H_2 flows over the anode, where the molecules are separated into electrons and positive ions, which can be also called protons. Protons enter the ionically conducting but electronically insulating electrolyte and are transported to the cathode, and the electrons flow through the outer circuit energizing an electric load [1, 2, 7].



At the cathode, the supplied O_2 reacts according to:



The oxygen ions recombine with protons migrating across the electrolyte to form H_2O , which is formed at the cathode [2].



Direct current (DC) electricity produced from the flow of electrons from the anode to the cathode is the main product of the fuel cell operation. Chemical activity and amount of fuels and the power loss inside the fuel cell stack affect the amount of the current available to the external circuit. The by-products of the fuel cell operation are heat, H_2O in the form of steam or liquid water, and CO_2 in the case of hydrocarbon fuel [1].

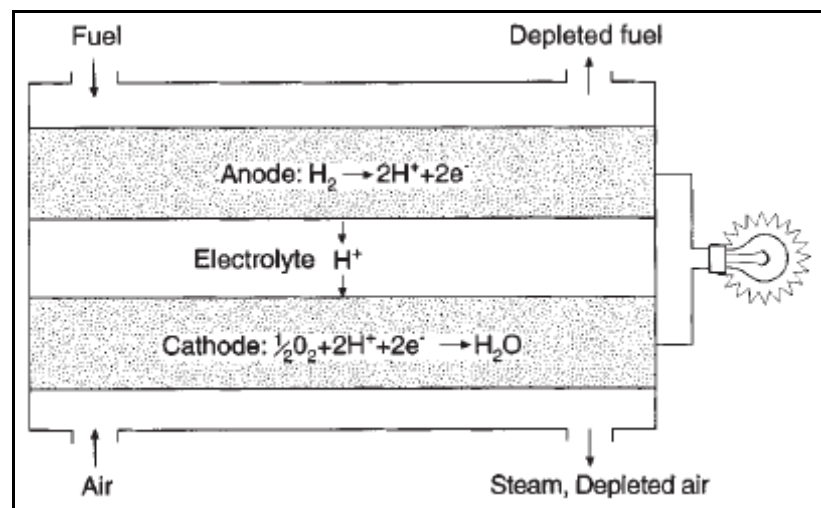


Figure 2.1. Fuel cell [7]

The anodes and cathodes of the fuel cells must be good electronic conductors and must have the required electrocatalytic properties for the desired reactions. In addition, the electrodes must have a porous structure to allow the fuel and oxidant gases to diffuse to the reaction sites. Also they must be mechanically strong enough to support the weight of the fuel cell stacks. The electrolyte must be chemically stable in H_2 and O_2 , and must have an ionic conductivity of at least 0.1 S/cm as well as it should be permeable to gas as low as possible [2, 7].

A fuel cell has advantages such as having no moving parts apart from the air and fuel blowers, which makes it more reliable, quiet operation with no vibration and being a clean

technology with no generation of gaseous pollutants [4, 7]. Other attractive characteristics of the fuel cells are high energy conversion efficiency of more than 40–50 per cent, which is higher than that of a coal fired power station or an internal combustion engine, very low chemical and acoustical pollution, fuel flexibility, cogeneration capability and rapid load response [4, 8]. It has a lower maintenance cost and a long operating life compared to an equivalent coal-fired power station or internal combustion engine. Also its modular compact design enables the modules to be added or removed to the required power in order to increase or decrease the power [4].

2.1.1. Fuel Cell Efficiency

The theoretical energy conversion efficiency is defined to compare fuel cells with other systems such as internal combustion engines (ICE). The efficiency of the fuel cell can be calculated from the ratio of Gibbs free energy to the enthalpy change of the electrochemical reaction, which is different depending on whether the product water is in vapor or in liquid state. Ideally, the free energy of the reaction can be completely converted into electrical energy and the thermodynamic efficiency is given by [1, 2, 7]:

$$\varepsilon_r^{cell} = \frac{W_e}{(-\Delta H)} = \frac{\Delta G}{\Delta H} = 1 - \frac{T \times \Delta S}{\Delta H} \quad (2.4)$$

The decrease in the efficiency by the losses due to electrode overpotentials and by the electrolyte resistance of the cell is expressed by the electrochemical efficiency. When fuel cells of different designs and components are desired to be compared by using the same reactions, the electrochemical efficiency gives more information about the fuel cells than the thermodynamic efficiency since it is directly related to the cell performance [2].

$$\varepsilon_v = \frac{\Delta U_{cell}}{\Delta U_0} \quad (2.5)$$

2.1.2. Types of Fuel Cells and their Applications

Fuel cells are usually classified by the electrolyte used in the cell except the DMFC, in which methanol is directly fed to the anode. They differ in the composition of the electrolyte and are in different stages of development. A second grouping can be done according to the operating temperature such as low-temperature and high-temperature fuel cells. The low-temperature fuel cells are the AFC, the PEMFC, the DMFC and the PAFC. The high-temperature fuel cells are the MCFC and the SOFC, which operate at temperatures between $600 \pm 1000^{\circ}\text{C}$. In all types of the fuel cells, separate reactions occur at the anode and the cathode depending on the input fuel and the electrolyte. An overview of the fuel cell types by giving detailed information about the anode and cathode reactions, and the charged ion is given in **Table 2.1** [1, 2, 9-11].

The AFC has the advantages of being less expensive, simple in design [1] and exhibiting the highest electrical efficiencies of all fuel cells but it works properly only with very pure gases which is considered a major restraint in most applications [2]. Also the alkaline electrolyte of the AFC reacts with CO_2 , which is present in reformed hydrocarbon fuels and air. The PEMFC, which has high power density as an advantage, and the PAFC, which has already commercialized, are compatible with CO_2 , but both are sensitive to CO (The PEFC is much more so than the PAFC), which is adsorbed onto the platinum catalyst and renders it inactive. Therefore, these three types of fuel cells require pure H_2 as fuel; and if the H_2 has been obtained by reforming a fuel such as natural gas, the H_2 -rich fuel stream must be purified before being introduced into the fuel cell. The MCFC and the SOFC can tolerate CO and can operate on hydrocarbon fuels with minimal fuel processing at high efficiency, but they operate at elevated temperatures, which may cause thermal stress failure. While sulfur poisoning is a common disadvantage for both the SOFC and the MCFC, problems such as electrolyte instability and corrosion may occur for the MCFC and the SOFC may suffer from coking. The DMFC has high power density and does not require any reforming process, but it has low efficiency, and methanol cross-over and poisoning byproduct may occur [4, 7]. Advantages and disadvantages of the different types of the fuel cells are given in **Table 2.2**.

Table 2.1. The features of different types of fuel cells, which are currently in use and development [2]

	AFC (Alkaline)	PEMFC (Polymer Electrolyte Membrane)	DMFC (Direct Methanol)	PAFC (Phosphoric Acid)	MCFC (Molten Carbonate)	SOFC (Solid Oxide)
<i>Operating temp. (°C)</i>	<100	60–120	60–120	160–220	600–800	800–1000 low temperature (500–600) possible
<i>Anode reaction</i>	$H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$	$H_2 \rightarrow 2H^+ + 2e^-$	$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$	$H_2 \rightarrow 2H^+ + 2e^-$	$H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$	$H_2 + O^{2-} \rightarrow H_2O + 2e^-$
<i>Cathode reaction</i>	$\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^-$	$\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O$	$\frac{3}{2} O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$	$\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O$	$\frac{1}{2} O_2 + CO_2 + 2e^- \rightarrow CO_3^{2-}$	$\frac{1}{2} O_2 + 2e^- \rightarrow O^{2-}$
<i>Applications</i>	Transportation Space Military Energy storage systems			Combined heat and power for decentralised stationary power systems	Combined heat and power for stationary decentralised systems and for transportation (trains, boats, ...)	
<i>Realised Power</i>	Small plants 5–150kW modular	Small plants 5–250 kW modular	Small plants 5 kW	Small – medium sized plants 50kW – 11MW	Small power plants 100–kW– 2 MW	Small power plants 100–250kW
<i>Charge Carrier in the Electrolyte</i>	OH^-	H^+	H^+	H^+	CO_3^{2-}	O^{2-}

The AFC technology has been used in space applications to take man to the moon with the Apollo missions since 1960s [1, 4]. The PEMFC is utilized primarily in residential combined heat and power (CHP) systems, transportation and portable applications [1-4]. The PAFC is used generally in CHP for decentralized stationary power systems. The MCFC and the SOFC are used generally in central and stand-alone stationary CHP systems and transportation applications such as trains and boats. The application areas for the DMFC technology are the vehicle and small portable systems [2, 4].

Table 2.2. Types of fuel cells [4]

Fuel cell	Temperature (°C)	Efficiency (%)	Application	Advantages	Disadvantages
Alkaline fuel cell (AFC)	50–90	50–70	Space application	High efficiency	Intolerant to CO ₂ in impure H ₂ and air, corrosion, expensive
Phosphoric acid fuel cell (PAFC)	175–220	40–45	Stand-alone & combined heat & power	Tolerant to impure H ₂ , commercial	Low power density, corrosion & sulfur poisoning
Molten carbonate fuel cell (MCFC)	600–650	50–60	Central, stand-alone & combined heat & power	High efficiency, near commercial	Electrolyte instability, corrosion & sulfur poisoning
Solid oxide fuel cell (SOFC)	800–1000	50–60	Central, stand-alone & combined heat & power	High efficiency & direct fossil fuel	High temperature, thermal stress failure, coking & sulfur poisoning
Polymer electrolyte membrane fuel cell (PEMFC)	60–100	40–50	Vehicle & portable	High power density, low temperature	Intolerant to CO in impure H ₂ and expensive
Direct methanol fuel cell (DMFC)	50–120	25–40	Vehicle & small portable	No reforming, high power density & low temperature	Low efficiency, methanol crossover & poisonous byproduct

2.2. Fuel Conversion

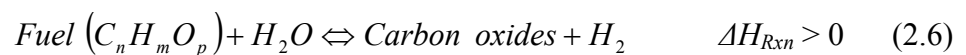
H₂ can be produced from natural gas at a refuelling station or from liquefied natural gas (LPG), gasoline or diesel on board a vehicle. Alcohols can also be converted to hydrogen and especially methanol can be an attractive fuel for small scale H₂ plants and automotive applications, but requires a new distribution and storage network [3, 12, 13]. Light distillate naphtha is also an alternative in areas, where the natural gas is not readily

available [13]. In certain niche markets, the fuel can be butane, or biomass-derived materials. All these fuels are hydrocarbons or oxygenates that need to be reformed [3].

The conversion of fuels to H_2 is carried out by one of the three major catalytic reactions; steam reforming (SR), partial oxidation (PO), and autothermal reforming (ATR).

2.2.1. Steam Reforming

SR is probably the most common method for producing H_2 in the chemical process industry. In this process, H_2O reacts with the fuel in the presence of a catalyst to produce H_2 , CO and CO_2 . An example is given for methane (CH_4).



Besides the SR reaction the WGS reaction also takes place separately as a side reaction by increasing the H_2 content while decreasing the amount of the CO.



The primary SR reaction is reversible and strongly endothermic, which causes the design of the reactor to be limited by heat transfer rather than by reaction kinetics. For CH_4 as a fuel, it is essential to operate at high temperatures, low pressures and relatively high Steam:Carbon (S/C) ratios. Consequently, the reactors are designed to promote heat exchange and tend to be large and heavy. Indirect heat transfer (across a wall) makes conventional steam reformers less attractive for the rapid start and dynamic response needed in automotive applications [3, 12, 13].

The SR reformers are well suited for long periods of steady-state operation and can deliver relatively high concentrations of H_2 (> 70 per cent on a dry basis). The CO and CO_2 are removed from the reformat gas stream by a variety of reactions and scrubbing techniques, such as the WGS reaction, methanation, CO_2 absorption in amine solutions, and pressure swing adsorption [3].

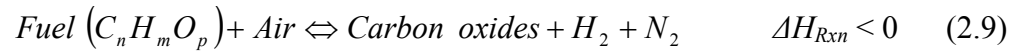
In general, the heavier the hydrocarbon fuel, the slower the reaction and the higher the risk of homogeneous reactions and coking. To avoid these problems, it may be necessary to introduce a prereformer in which heavier hydrocarbons are split into C_1 fragments (CH_4 and carbon oxides) at relatively low temperatures ($\sim 350\text{--}550^\circ\text{C}$). Subsequent secondary reforming produces H_2 at temperatures above $\sim 600^\circ\text{C}$ [12, 13]. Sufficient H_2O must also be added to minimize coking, although a choice of catalyst may reduce the amount of coke to be gasified [5].

The SR reactions are catalysed by Group 8-10 metals [14] and especially Ni is the preferred metal for industrial applications since Ni-based catalysts are the most cost-effective catalysts, although they are not the most efficient promoters. On the other hand, Rh-based catalysts are more efficient but more costly [5]. Co and noble metals are also active but more expensive. Attempts to use non-metallic or sulfur-resistant catalysts have had no commercial success because of the low activity. It has been shown that Ni and Ru catalysts may be able to convert CH_4 even at 300°C [14]. In the SR of methanol, although Pd catalysts are found to be highly active, Cu-based catalysts are preferred for the economical reasons [13]. Cu-Ni based catalysts are reported to be active below 300°C for ethanol SR [15]. Catalyst systems based on Co, Cu-Zn, Cu-Zn-Cr and noble metals supported on different carriers are also studied for SR of ethanol [16, 17].

2.2.2. Partial Oxidation

H_2 may also be produced by catalytic [18] or non-catalytic [19] PO reactions. In the PO reformers, the fuel reacts with a substoichiometric amount of O_2 or air as an O_2 source

to produce H_2 , CO , and CO_2 [3]. Nitrogen (N_2) acts as an inert in the reaction in case of air fed to the PO reactor.



Both catalytic and non-catalytic oxidation processes are exothermic and result in heat generation, high temperatures and short residence times (milliseconds). The heat generated increases the gas temperature to over $1000^\circ C$ by ensuring the required conditions for the SR reaction to occur relatively easy if an appropriate amount of H_2O is added into this gas mixture [3, 12].

The PO reaction is almost thermo-neutral and has a low net energy demand. The reaction is ideally kinetically controlled due to the short contact times and being much faster than the equilibrating SR and shift reactions [13]. Although the PO reaction produces advantageous $CO:H_2$ ratios for further processing of synthesis gas, the $CO:H_2$ ratio of 2 is less than the optimum value in case of fuel cells. The advantages of the PO reaction are the small size of the reactor, the rapid response to changes, and possible absence of coking problems, while the fact that fuel and air must be premixed becomes a disadvantage. However, the advantages of the small reactor and of rapid response make PO a process worth consideration. [5]

Total oxidation may be required to heat the systems and / or may occur as a side reaction to produce CO_2 and H_2O [3, 12].

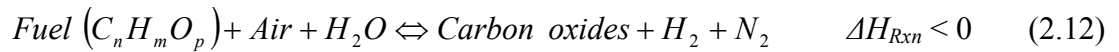


For natural gas conversion, the preferred catalysts are based on Ni and in particular Rh, which ensures 90 per cent selectivity at conversion beyond 90 per cent [13]. The PO of CH_4 over Rh-washcoated monoliths reaches high conversion and high selectivity of almost 90 per cent at very low contact times at $\sim 1000^\circ C$. Coke formation is avoided under these

conditions, but the role of the catalyst and the importance of pore structure in the washcoat are established [5]. Ni-based catalysts with alkaline and rare earth oxide supports in the pellet form are used in the PO of pure CH₄ and 91 per cent CH₄ conversion is obtained at 800°C with 95 per cent selectivity to H₂ [20, 21].

2.2.3. Autothermal Reforming

Autothermal reformers combine the heat effects of the PO and the SR reactions by feeding the fuel, H₂O, and air together into the same reactor:



The ATR is a catalytic reaction, in which relative extents of the SR and the PO reactions are controlled by the appropriate S/C and oxygen to carbon (O₂/C) ratios depending on the heat demand of the particular fuel. The fuel is partly oxidized by generating heat and increasing the temperature and then the SR reaction absorbs part of the heat by limiting the maximum temperature in the reactor, which makes the ATR a slightly exothermic stand-alone process. Thus the product gas composition can be adjusted thermodynamically by the pressure, exit temperature, S/C and O₂/C ratios [3, 5, 13].

The relatively lower-temperature process of the ATR reaction provides many benefits, especially for automotive applications, such as favoring the WGS reaction (2.8), which increases the selectivity for CO₂ and H₂, requirement of less thermal integration, consumption of less fuel during start-up and a wider choice of materials for construction, which can lower manufacturing costs [3].

Selection of the ATR catalyst is very important to achieve the desired conversion and product selectivity [5]. The use of Cu-Zn-Al ternary oxides [22] and Pd-ZnO catalysts [23] for the production of H₂ from methanol are studied. Pd-ZnO may not be the best catalyst due to some alloy formation at higher temperatures, but Pd-catalysts seem to offer a real alternative [23]. On Ni-based catalysts, the reaction appears to proceed via total oxidation

coupled to SR, except at very low O_2 partial pressures [24]. The conversion of CH_4 to H_2 using Pt to promote oxidation and Ni to promote SR is studied in depth. The use of two beds of catalyst, of mixed oxidation and SR catalyst, and of a Ni catalyst on which Pt is deposited is considered. Rh and Ru are found to be more active than Ni for reforming CH_4 and produced less carbon [5].

2.3. Water Gas Shift Reaction

High temperature fuel cells such as MCFCs and SOFCs are tolerant to CO in the reformat gas, while the CO content should be decreased to 20–100 ppm for lower temperature fuel cells such as PEMFCs since the Pt or Pt–Ru anodes of PEMFCs are poisoned by CO, which strongly chemisorbs on the active sites, where the dissociation/oxidation of H_2 can take place by decreasing the fuel cell performance [5, 6]. Thus, the WGS reaction (2.8) becomes a very critical step in fuel processors for low temperature fuel cells in reducing the CO per cent. In addition, a mole of H_2 is produced for every mole of CO that is converted in the WGS reaction, which increases the fuel cell efficiency.

In most fuel processor designs the WGS reaction must deliver a CO concentration of less than 1 per cent to the selective CO oxidation reactor. Any further reduction in CO concentration eases the load on the CO oxidizer. Temperature, water concentration and methods of reforming must be considered, when designing a WGS reactor system and catalysts [6].

2.3.1. Thermodynamic Aspects

Due to the exothermic nature of the WGS reaction, higher CO conversions are favored at lower temperatures. The WGS equilibrium constant is nearly 80 times greater,

when the temperature is decreased from 600 to 200°C. The WGS equilibrium constants at various temperatures are summarized in **Table 2.3**.

The H₂O content has a strong positive influence in converting the CO and its flow rate can be varied by controlling the amount added at the reformer or by injecting H₂O before or between stages of the WGS reactors. In contrast, the CO, CO₂ and H₂ concentrations are more dependent on the reformer operation, which in turn determines the thermodynamic limitations. The effect of temperature and H₂O concentration on the equilibrium CO concentration is shown in **Figure 2.2** for a HTS reactor [6].

Table 2.3. WGS equilibrium constants [6]

Temperature (°C)	Equilibrium constant, K _p
93.3	4523.00
148.9	783.60
204.4	206.80
260.0	72.75
315.6	31.44
371.1	15.89
426.7	9.030
482.2	5.610
537.8	3.749
593.3	2.653
648.9	1.966
704.4	1.512

Single stage WGS is desired but difficult to accomplish due to the adiabatic temperature rise. To account for the increasing temperature, the inlet temperature to the catalyst must be relatively low, where existing catalysts may reach kinetic limitations. Two stages of WGS are traditionally used to take advantage of kinetics and thermodynamics. By operating a HTS catalyst at higher temperatures the favorable kinetics can be exploited and the volume of the catalyst can be minimized. By cooling the syngas between the HTS and LTS stages an active catalyst can take advantage of the thermodynamic equilibrium at

low temperature. A two-stage WGS configuration can produce an exit CO concentration of much less than 1 per cent [6].

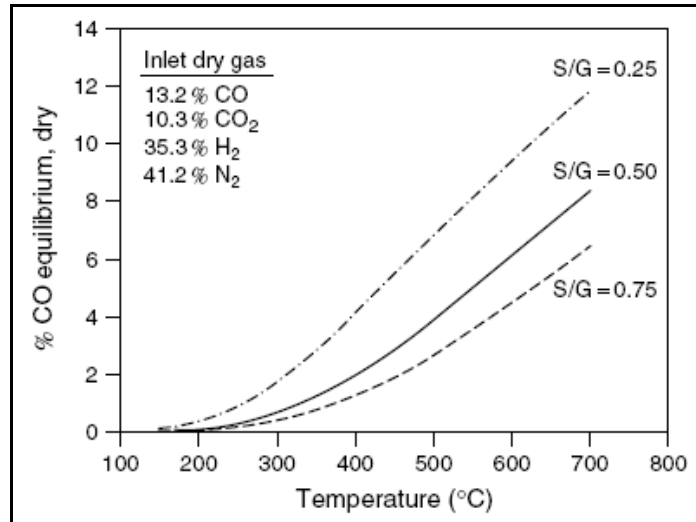


Figure 2.2. CO equilibrium of HTS gas from ATR reformer at various Steam: Dry gas (S/G) ratios [6]

The method of producing the syngas affects the WGS equilibrium. ATR produces a syngas with lower H_2 concentration due to the dilution of N_2 as compared to SR. The lower H_2 concentration improves the equilibrium CO conversion whereas the high H_2 concentration expected with SR lowers the WGS reaction equilibrium conversion. In **Figure 2.3**, the equilibrium CO is shown as a function of H_2 content at constant CO and CO_2 concentrations for the LTS reactor [6]. The effect of H_2 concentration is not as significant as the S/G ratio, but must be considered when trying to maximize efficiency and minimize the volume of the WGS reactor.

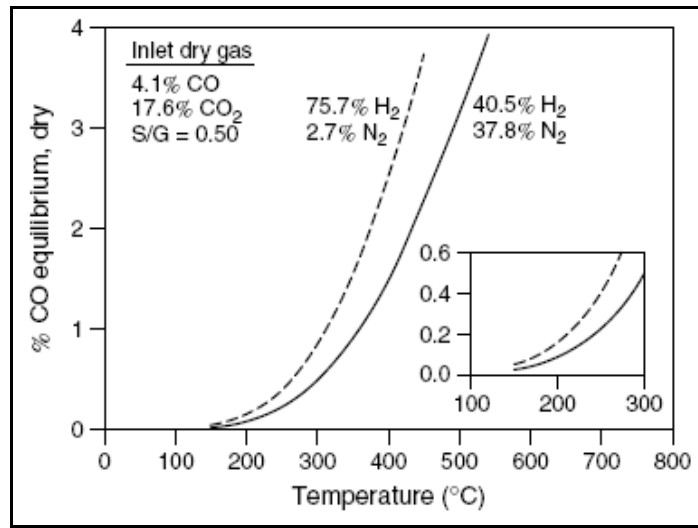


Figure 2.3. CO equilibrium of LTS gas from ATR versus SR for CH₄: effect of H₂ [6].

Since the WGS reaction is equimolar the effect of pressure is minimal considering the pressure range used for fuel processing. By increasing the pressure from 3 to 30 atm there is negligible effect on the thermodynamic CO conversion (**Table 2.4**). But if the pressure is increased to 300 atm, the equilibrium CO concentration is lower. However it is not practical to increase the pressure to take advantage of the slightly higher equilibrium CO conversion.

Table 2.4. Effect of pressure on equilibrium CO concentrations (inlet dry gas: 13.2% CO, 10.3% CO₂, 35.3% H₂, 41.2% N₂, S/G = 0.5) [6]

Temperature (°C)	P = 3 atm (% CO)	P = 30 atm (% CO)	P = 300 atm (% CO)
200	0.12	0.12	0.07
300	0.68	0.65	0.48
400	1.98	1.94	1.61
500	3.93	3.88	3.46
600	6.15	6.10	5.68
700	8.38	8.34	7.95

From a thermodynamic perspective, the efficiency of the WGS reaction is maximized at low temperature, high H₂O and a low H₂ concentration. However under

some conditions the catalysts available today are kinetically limited at the low temperatures needed for high CO conversion, while striving to minimize reactor volumes.

2.3.2. Catalysts

The desired requirements of the WGS catalysts used to produce H₂ for the fuel cells are very different from the industrial applications as seen in **Table 2.5**. Industrial WGS catalysts are designed to operate at steady-state conditions for a long time without any interruption, while fuel processor WGS catalysts are exposed to many start-up / shut-down cycles [6].

Table 2.5. WGS catalyst requirements for mobile and stationary applications [6]

WGS catalyst attribute	Mobile application	Stationary application
Volume reduction	Critical, < 0.11 kW ⁻¹	Not as constrained
Weight reduction	Critical, < 0.1 kg kW ⁻¹	Not as constrained
Cost	Critical, < \$ 1 kW ⁻¹	Not as critical
Rapid response	Critical, < 15 s	Load following
Non-pyrophoric	Important	Eliminate purging
Attrition resistance	Critical	No constraint
Selectivity	Critical	Important
No reduction required	Critical	Important
Oxidation tolerant	Critical	Important
Condensation tolerant	Important	Important
Poison tolerant	Desired	Desired
Pressure drop	Important	Important

Reformate gas enters the HTS reactor at about 350–450°C to reduce the CO concentration to ~ 3–4 per cent [25]. Conventional HTS catalysts are based on iron–chromium oxides and have the advantages of low cost, long life, and are reasonably resistant to sulphur, but they are not active below ~ 350°C. Recent studies have proved that

chromium oxides can also catalyze the reaction but are less significant than iron. The possibility of increasing the activity of $\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3$ catalysts by promotion has recently been studied and small amount of precious metals are found to increase the rate of the forward reaction significantly under reforming conditions. Pt promoted urania catalysts are found to be almost as efficient as promoted $\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3$ catalysts suggesting that the rate of decomposition of H_2O can be important. However, catalytic activity drops away quickly as temperature is reduced [12].

Although the promoted catalysts are more efficient, they are still less active than Cu-based catalysts at temperatures below $\sim 300^\circ\text{C}$. As a result, the CO concentration can be reduced in the HTS reactor to 3–4 per cent, but it is still too high for the fuel cells, so the LTS reaction is required to reduce CO still further [12].

Cu-Zn-based catalysts are used for the LTS reaction in industrial applications [6, 12], but they are not proper for vehicles since their temperature stability is poor above $\sim 300^\circ\text{C}$ and they are pyrophoric if exposed to air [25]. Constant cycling in vehicle use may cause condensation of water, which also irreversibly deactivates the Cu-based catalysts. As a result, Cu-based catalysts are more suitable for stationary applications rather than for mobile use, while precious metal-based catalysts are preferred for transportation applications [12].

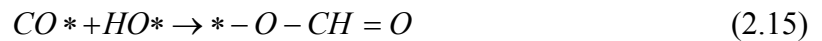
The disadvantages of Cu-based catalysts can be overcome by using precious metals, but then high cost becomes a problem. They are active over the temperature range $250\text{--}300^\circ\text{C}$ and thermally stable to above 400°C . They also have the advantage that they can be coated on the walls of a monolith, which saves space and increases the mechanical ruggedness [26, 27].

Pd-ceria, Ni-ceria, Fe-ceria, Co-ceria, ceria and Pd-ceria are studied for the WGS reaction and Pd-ceria and Ni-ceria are found to be more active than Fe-ceria, Co-ceria and Pd-ceria [28]. Precious metal-based catalysts have the advantage of greater thermal stability than Cu-Zn systems and are relatively resistant to deactivation. They have the disadvantage of not being significantly active below about 250°C , which limits the reduction of CO.

Interest has focused on Au-based catalysts since they are reported to catalyze WGS at lower temperatures [29]. Catalytic activity is high only when the Au is widely dispersed. The LTS over Au- α Fe₂O₃ shows that the catalysts are active at even 160°C. ZrO₂ is found to be the best additive to Au-Fe₂O₃-MO_x for the stabilization of the Au [12].

2.3.3. Mechanisms and Kinetics

Different mechanisms have been proposed for the WGS reaction. According to one of these mechanisms [30, 31], the WGS reaction proceeds via the formation of an adsorbed formate group, which decomposes to H₂ and CO (* is an active metal site). The rate-determining step is found to be the decomposition of the formate and the rate of the formate decomposition can be increased by increasing the H₂O partial pressure [30].



Several other groups have suggested that a redox mechanism is predominant that is a bi-functional process, where the adsorbed CO on the precious metal or mixed metal oxide is oxidized by the support and H₂O fills the support oxygen vacancy [6, 32, 33]:





Recent studies [12] have suggested that the process involves interaction of two *OH groups:



The HTS reaction on Fe-Cr catalyst is reported to proceed via the regenerative mechanism [34]. The question of the LTS reaction mechanism over Cu-based catalysts is still debated today. The catalyst composition, catalyst precursors, its resulting surface properties as well as the reaction conditions obviously play a decisive role. Most authors propose the redox mechanism [35-37], while in another study [38], good evidence is reported that formate-based mechanism is important.

The kinetics of the WGS reaction under typical reforming conditions is summarized in **Table 2.6**. For Pt-ceria catalysts, the rate of migration of oxygen to metal-support interface may be the rate-determining step [33]. However, the different apparent activation energy for the reaction promoted by different metals supported on iron–chromium suggests that this is not the case for this system. The bulk of the evidence suggests that the decomposition of H_2O is rate determining [12]. Strong inhibition is observed in the forward reaction by CO_2 and H_2O for Cu-Zn catalyst [38]. Neither ceria nor zinc oxide shows a promotional effect. Reduction of surface oxygen by adsorbed CO is determined as the rate-limiting step in kinetic modeling.

Table 2.6. Kinetics of the WGS reaction [12]

Catalyst	Power rate law	Temperature range (°C)	Ref.
Fe-Cr Fe-Cr (promoted)	$K \times (CO)^{0.9} \times (H_2O)^{0.25} \times (CO_2)^{-0.6} (H_2)^0 \times (1 - \beta)$	300-450	12
Cu-Zn	$K \times (CO)^{0.8} \times (H_2O)^{0.8} \times (CO_2)^{-0.9} (H_2)^{-0.9} \times (1 - \beta)$	200-310	38
Precious metal/ceria	$K \times (CO)^0 \times (H_2O)^{0.5} \times (CO_2)^{-0.5} (H_2)^{-1} \times (1 - \beta)$	200-250	28

The kinetics of the WGS reaction are studied over Pd-ceria, Ni-ceria, Fe-ceria, Co-ceria, ceria and Pd-ceria catalysts and the reaction mechanism is found to include the oxidation of the reduced ceria by water, which is followed by the oxygen transfer to the metal to react with adsorbed CO [28]. Bunluesin et al. find similar conclusion for the ceria supported Pt, Pd and Rh catalysts [32].

In contrast, Shido et al. [39] suggest that the WGS reaction on the Rh-ceria proceeds via decomposition of formate intermediates. Jabobs et al. [40] also reach similar conclusions for the study, in which Pt-thoria is found to be more active than Pt-ceria due to higher active site densities per g of catalyst for the thoria support.

3. MODELING OF PACKED-BED AND MONOLITH REACTORS

The LTS reaction is modeled in a packed-bed reactor and in a monolith reactor separately. One-dimensional pseudo-homogeneous and / or heterogeneous models are applied along with Langmuir–Hinshelwood–Hougen–Watson type and power law type rate equations. The mathematical models developed and their numerical solution procedures are given in this chapter.

3.1. Modeling of Packed-Bed Reactors

A packed-bed reactor can be modeled in various ways depending on the required degree of sophistication of the process. In modeling and design of the packed-bed reactors, the considerations given in **Figure 3.1** should be determined first.

The models are separated in two main groups such as pseudo-homogeneous model and heterogeneous model. In the pseudo-homogeneous models, the solid phase of the catalyst is neglected and only the bulk phase is considered. On the other hand, in the heterogeneous models, the presence of the catalyst is accounted as a separate phase and the conservation equations are written for both solid phase and fluid phase separately. If only the transport in axial direction is assumed by applying plug-flow, the model becomes one-dimensional. When also the radial gradients have to be accounted for, the model should be applied as two-dimensional [41]. If there is no change per time in the reaction, the modeling equations are written in the steady-state mode, but for dynamic modes such start-up or shut down periods, time derivative should be added to the model.

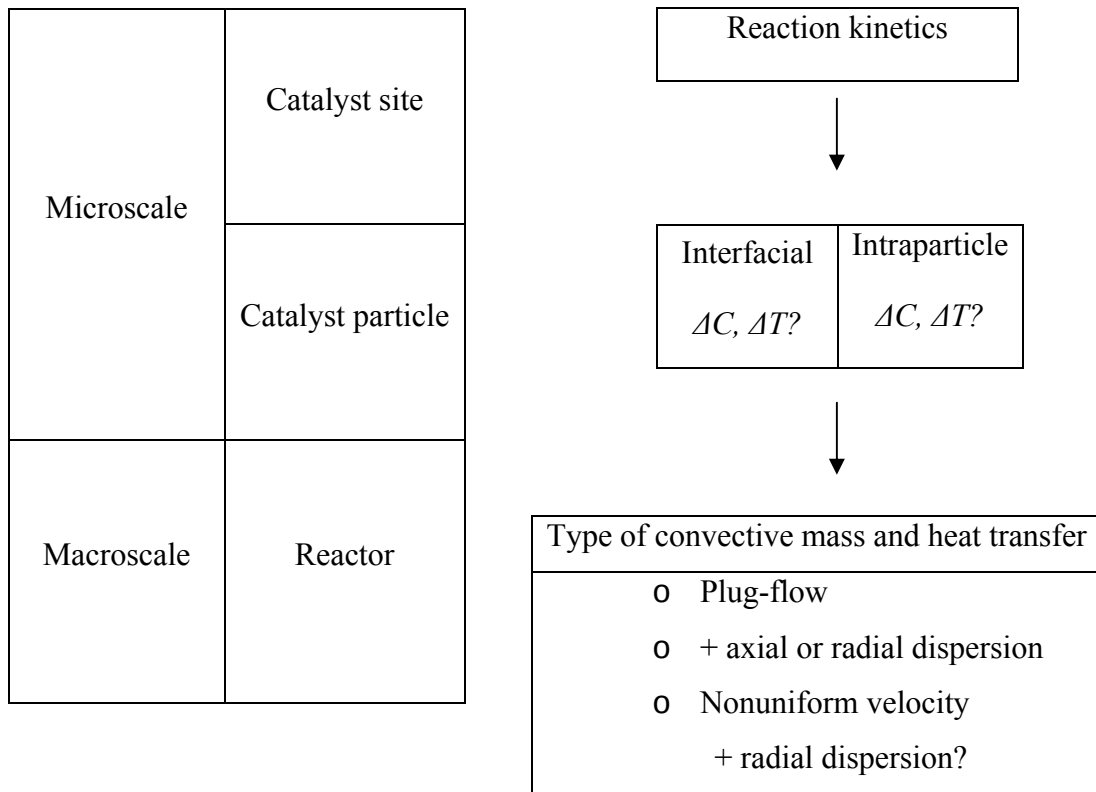


Figure 3.1. Aspects to be considered in the modeling of packed-bed reactors [41]

3.1.1. Pseudo-Homogeneous Model

One-dimensional pseudo-homogeneous model is the basic model, in which concentration and temperature gradients are assumed to occur only in the axial direction. The only transport mechanism is the overall flow, which is considered to be plug-flow. Mass diffusion and heat conduction in the axial direction are neglected for this study.

The conservation equations of mass, energy and momentum in the axial direction, which are referred to the catalyst mass, for the steady-state and a single reaction carried out in a cylindrical tube are given below, respectively [42]. In the mass balance, the reaction is assumed to occur in the bulk phase homogeneously over the whole reactor and the intrinsic kinetics is considered due to the lack of external and internal transport effects. In the energy balance, heat is generated in the bulk due to the mildly exothermic nature of the

LTS reaction in an adiabatic reactor. Ergun equation is applied to determine the pressure drop along the catalyst bed for the momentum balance.

$$\left. \frac{dF}{dW} \right|_{co} = -r_{co}(T) \quad (3.1)$$

$$\frac{dT}{dW} = \frac{(r_{co}(T)) \times (-\Delta H_{Rxn}(T))}{\sum_i F_i \times C_{p_i}(T)} \quad (3.2)$$

$$\frac{dP}{dW} = -\frac{G}{\rho_b \times g_c \times D_p} \times \left(\frac{1-\varepsilon}{\varepsilon^3} \right) \times \left[\frac{150 \times (1-\varepsilon) \times \mu_f}{D_p} + (1.75 \times G) \right] \quad (3.3)$$

In Ergun Equation, g_c is equal to $32.174 \text{ lb}_m \text{ ft s}^{-2} \text{ lb}_f^{-1}$ and the unit of the total pressure, P is $\text{lb}_f \text{ ft}^{-2}$ and the catalyst bulk density, ρ_b is $\text{lb}_m \text{ ft}^{-3}$. The required unit conversion is done to obtain the pressure gradient in atm g cat^{-1} .

3.1.2. Heterogeneous Model

In heterogeneous models, the mass and energy conservation equations are written for the solid phase and the fluid phase separately. For one-dimensional heterogeneous model, only the concentration and temperature gradients in the axial direction are considered. Mass diffusion and heat conduction in the axial direction are neglected for this study.

The conservation equations of mass, energy and momentum in the axial direction, which are referred to the catalyst mass, for the steady-state and a single reaction carried out in a cylindrical tube are given below for the two phases, respectively. Since no external and internal mass transport effects are considered in this study, the conservation equation of mass is the same. The conservation equation of energy for the fluid phase (**Figure 3.2**) is changed due to the addition of the external heat transport effects by bringing a new

variable of surface temperature of the catalyst, T_s forward besides the bulk temperature [43, 44]. This equation does not deal with the heat generated through the reaction, while it only accounts for the external heat transport from the catalyst surface to the bulk fluid. In this case, the heat generated is described by a nonlinear algebraic equation written for the solid phase. For the momentum balance, Ergun equation (Equation 3.3) is again applied for the determination of the pressure drop along the catalyst bed.

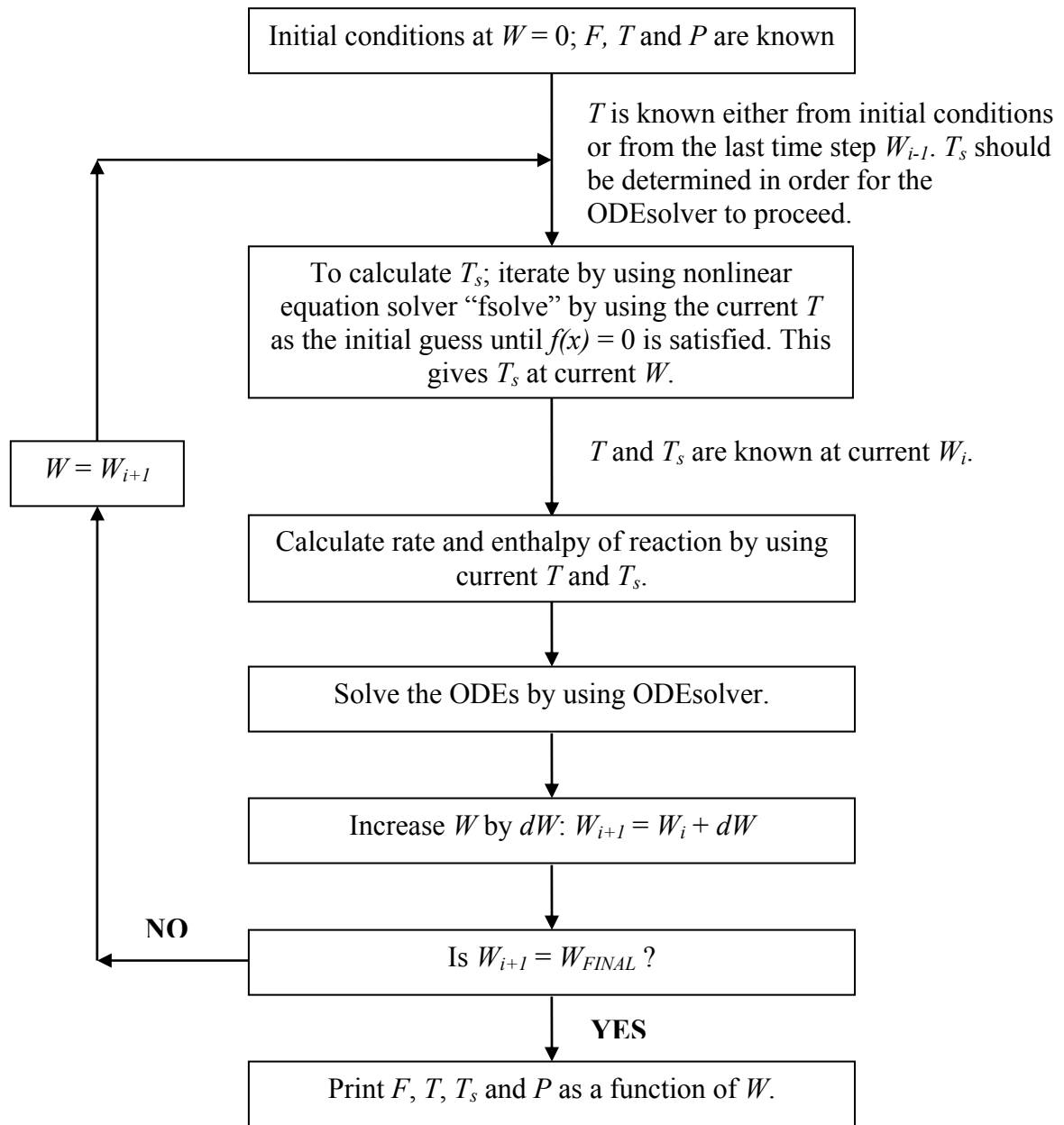


Figure 3.2. Flowchart for the application of heterogeneous model to packed-bed reactor

Equations for the fluid phase:

$$\left. \frac{dF}{dW} \right|_{CO} = -r_{CO}(T) \quad (3.1)$$

$$\frac{dT}{dW} = \frac{h_f(T) \times (T_s - T)}{\sum_i F_i \times Cp_i(T)} \quad (3.4)$$

Energy balance equation for the solid phase:

$$h_f(T) \times (T_s - T) = -\Delta H_{Rxn}(T_s) \times r_{CO}(T_s) \quad (3.5)$$

In the literature, several criteria are presented to determine whether external and internal mass transfer and external heat transfer between the bulk fluid and the catalyst can be neglected [42]. According to the Mears' Criterion, when

$$\frac{-r_{CO} \times \rho_b \times (D_p/2) \times m}{k_f \times C_{CO}} < 0.15 \quad (3.6)$$

external mass transfer effects can be neglected, which means that the bulk concentration and the concentration on the external surface of the catalyst of a species is equal to each other. Mears also proposed that when

$$\left| \frac{(-r_{CO}) \times \rho_b \times (-\Delta H_{Rxn}) \times (D_p/2) \times E}{h_f \times T^2 \times R} \right| < 0.15 \quad (3.7)$$

external heat transfer effects can be neglected, which means that the bulk fluid temperature is the same as the temperature at the external surface of the catalyst. According to the Weisz–Prater Criterion, internal mass transfer effects can be neglected, when

$$\frac{-r_{CO} \times \rho_b \times (D_p/2)^2}{D_e \times C_{CO}^s} \leq 1.0 \quad (3.8)$$

which means that there are no diffusion limitations and so no concentration gradient can occur within the catalyst.

3.2. Modeling of Monolith Reactors

In monolithic reactors, external mass transfer occurs from the bulk gas flow in the channels to the channel wall and then diffusion takes place through the porous washcoat on the channel wall, where reaction occurs simultaneously. Inside the gas phase, convective and diffusive transport of mass, momentum and energy occur in both axial and radial directions, while convective transport can be neglected inside the porous washcoat as well as momentum diffusion. Diffusive mass transport may play a significant role on conversion. Energy balance of solid phase is affected by heat conduction as well as radiation and chemical reaction [45].

Flow regime in the monolith reactors is usually laminar flow with a Reynolds number generally smaller than 500. The length of the entrance zone is usually neglected since it is typically less than 10 per cent of the reactor length [46]. A uniform gas distribution over the channels at the inlet is very important for the activity of the catalytic monolith. Assumption of identical boundary conditions due to the uniform distribution of gas across the inlet cross-section of the monolith makes “a single channel” a representative of the whole monolith [45, 46].

3.2.1. Pseudo-Homogeneous Model

One-dimensional pseudo-homogeneous model is applied to model the LTS reaction in “a single channel” of a catalytic monolith reactor in this study by neglecting the

monolith catalyst as the solid phase. Uniform distribution of conserved quantities across the inlet face of the monolith is assumed. Concentration and temperature gradients in the radial direction are not considered. Diffusive heat and mass balances in bulk fluid phase are small, when compared to convection and so they are neglected in this study.

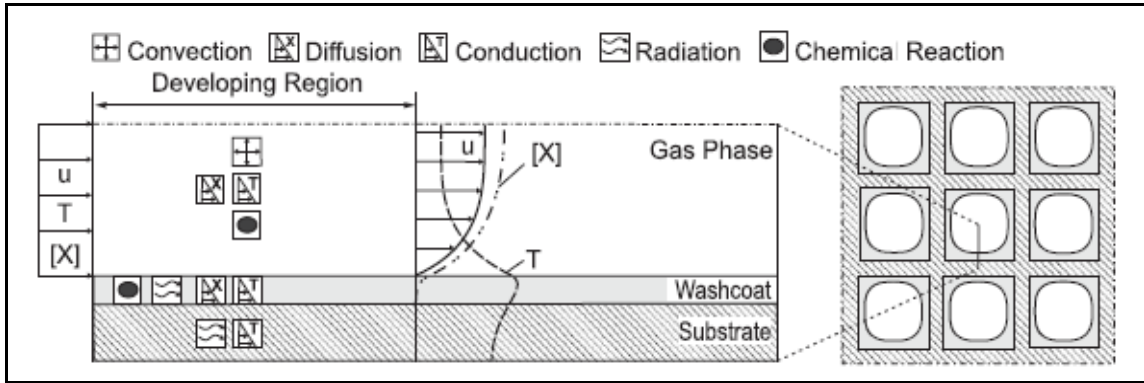


Figure 3.3. A monolith channel indicating the physical and chemical phenomena in gas phase, washcoat and substrate [45]

The conservation equations of mass and energy in the axial direction, which are referred to the catalyst mass, for the steady-state and a single reaction carried out in a single channel of a monolith reactor are given below, respectively. For the mass balance, mass transfer only exists by the reaction, which is assumed to occur homogeneously. The energy balance accounts for the heat generated by the mildly exothermic reaction in adiabatic conditions.

$$\left. \frac{dF}{dW} \right|_{co} = -r_{co}(T) \quad (3.1)$$

$$\frac{dT}{dW} = \frac{(r_{co}(T)) \times (-\Delta H_{Rxn}(T))}{\sum_i F_i \times C_{p_i}(T)} \quad (3.2)$$

Pressure drop along the monolith reactor can be calculated by the equation 3.10 with the required unit conversion to obtain the pressure in atm and it is originally derived for laminar flow in an empty tube [47]. In the case of the monolith reactor, the diameter of the tube is replaced by the hydraulic diameter of the single channel of the monolith. Also in

the calculation of the linear velocity, open frontal area of the monolith has to be considered due to the presence of the channels. In this study, the pressure is assumed to be constant over the monolith reactor since pressure drop is very small and has negligible effect on the conversion, which is the general situation for monolith reactors presented in the literature [45, 46].

$$v = \frac{V_t}{A \times OFA} \quad (3.9)$$

$$\Delta P = \frac{32 \times \mu_f \times v \times L_m}{D_h^2} \times \left(\frac{10 \text{ g/cm.s}}{1 \text{ Pa.s}} \right) \times \left(\frac{1 \text{ Pa}}{1.01325 \times 10^5 \text{ atm}} \right) \quad (3.10)$$

The equations of the mass and energy balances can also be written referring to the monolith length by directly multiplying with the bulk catalyst density and the cross-sectional area of a single channel.

$$A_m = \pi \times \frac{D_h^2}{4} \quad (3.11)$$

$$\left. \frac{dF}{dz} \right|_{CO} = -r_{CO}(T) \times \rho_b \times A_m \quad (3.12)$$

$$\frac{dT}{dz} = \frac{(r_{CO}(T)) \times (-\Delta H_{Rxn}(T))}{\sum_i F_i \times Cp_i(T)} \times \rho_b \times A_m \quad (3.13)$$

3.3. Numerical Solution Methods

The conservation equations of mass, energy and pressure, which are developed for the packed-bed and the monolith reactors, are first order ordinary differential equations (ODE) and are solved by using an appropriate ODE solver function such as ode45 or ode15s of MATLABTM numerical computation software for the boundary conditions given below:

$$at \ W = 0; \quad T = T^0; \quad P = P^0; \quad F_i = F_i^0 \quad (3.14)$$

ode45 ODE solver function is based on an explicit Runge-Kutta (4,5) formula, the Dormand-Prince pair. In general, ode45 is the best function to apply as a first try for most problems. When ode45 fails or is very inefficient, as well as the problem is stiff or solving a differential–algebraic problem, ode15s ODE solver function is tried, which is a variable order solver based on the numerical differentiation formulas [48, 49]. In the code written for Amadeo data set, ode45 is used, while ode15s is used for the rest.

The energy balance equation for the solid phase, which is developed for the heterogeneous model applied to the packed-bed reactor, has to be solved simultaneously with ODEs to calculate the surface temperature of the catalyst iteratively for an initial guess by nonlinear regression methods using fsolve function of MATLABTM numerical computation software.

4. RESULTS AND DISCUSSION

Low temperature water-gas shift reaction is studied in packed-bed and monolith reactors by applying pseudo-homogeneous and heterogeneous models separately.

4.1. Packed-Bed Reactor

4.1.1. Pseudo-Homogeneous Model

MATLAB codes are written for the simulations of the LTS reaction in an adiabatic packed-bed reactor by applying one-dimensional pseudo-homogeneous model, in which both external and internal mass and heat transport resistances are neglected. The hypothesis of plug flow is assumed. Three separate data sets (Data Set 1, 2, and 3) taken from Amadeo et al. [50], Francesconi et al [43] and Tan [51], respectively, are used in the simulations.

4.1.1.1. Data Set 1 and Langmuir-Hinshelwood Kinetic Model: In the study of Amadeo et al. [50], the kinetics of the LTS reaction was studied over a commercial Cu-ZnO-Al₂O₃ catalyst in an adiabatic packed-bed reactor and a Langmuir-Hinshelwood kinetic expression, which considers the adsorption of the four components of the reaction, was obtained. This kinetic expression and its parameters, given below in Equations 4.1–4.8, are used in the present simulations by applying the inlet conditions of the LTS reactor given in **Table 4.1**.

$$K_{eq} = \exp\left(\frac{-G_{Rxn}^{ig}}{R \times T}\right) \quad (4.1)$$

$$k = 0.92 \times \exp\left(\frac{-454.3}{T}\right) \quad (4.2)$$

$$K_{CO} = 2.2 \times e^{(101.5/T)} \quad (4.3)$$

$$K_{H_2O} = 0.4 \times e^{(158.3/T)} \quad (4.4)$$

$$K_{CO_2} = 0.0047 \times e^{(2737.9/T)} \quad (4.5)$$

$$K_{H_2} = 0.05 \times e^{(1596.1/T)} \quad (4.6)$$

$$\beta = \frac{P_{CO_2} \times P_{H_2}}{K_{eq} \times p_{CO} \times p_{H_2O}} \quad (4.7)$$

$$r_{CO} = \frac{k \times p_{CO} \times p_{H_2O} \times (1 - \beta)}{(1 + K_{CO} \times p_{CO} + K_{H_2O} \times p_{H_2O} + K_{CO_2} \times p_{CO_2} + K_{H_2} \times p_{H_2})^2} \times \frac{1}{60} \quad (4.8)$$

$$r_{H_2O} = r_{CO} \quad (4.9)$$

$$r_{CO_2} = -r_{CO} \quad (4.10)$$

$$r_{H_2} = -r_{CO} \quad (4.11)$$

Table 4.1. Inlet conditions for the LTS reaction [50]

Temperature (K)	Pressure (atm)	Steam feed flow rate (gmol s ⁻¹)	Dry-gas feed flow rate (gmol s ⁻¹)	Dry-gas composition (vol. %)			
				CO	CO ₂	H ₂	CH ₄
480	16.78	0.20800	0.33900	3.20	18.20	76.80	1.80

The conversion of CO, the outlet temperature and the composition of the product gas leaving the LTS reactor are simulated in MATLAB environment by using Equations 3.1–3.3 of the pseudo-homogeneous packed-bed reactor model, Equations 4.1–4.11 given above, and the inlet conditions of **Table 4.1**. The results obtained in this study are given in **Table 4.2** for 195.0 g of catalyst, which is found to be sufficient for attaining the desired CO level at the desired fractional CO conversion of 0.84. These values are also compared with those given in the paper and the per cent errors are calculated. The closeness of the simulation results indicates that both the mathematical model used and the code written are successful in describing and simulating the LTS reactor under these conditions. The corresponding temperature, molar flow rates of the components, CO level and CO conversion profiles are plotted in **Figure 4.1–Figure 4.4**.

Table 4.2. The properties of the product gas leaving the LTS reactor
(Data Set 1, L-H pseudo-homogeneous model)

	Present Study	Amadeo et al. [50]	Difference%
y CO %	0.313	0.308	1.63
y H ₂ O %	36.355	35.889	1.30
y CO ₂ %	12.950	12.688	2.07
y H ₂ %	49.267	49.513	0.50
y CH ₄ %	1.115	1.116	0.03
T (K)	499.80	502.00	0.44
Conversion	0.842	0.845	0.30

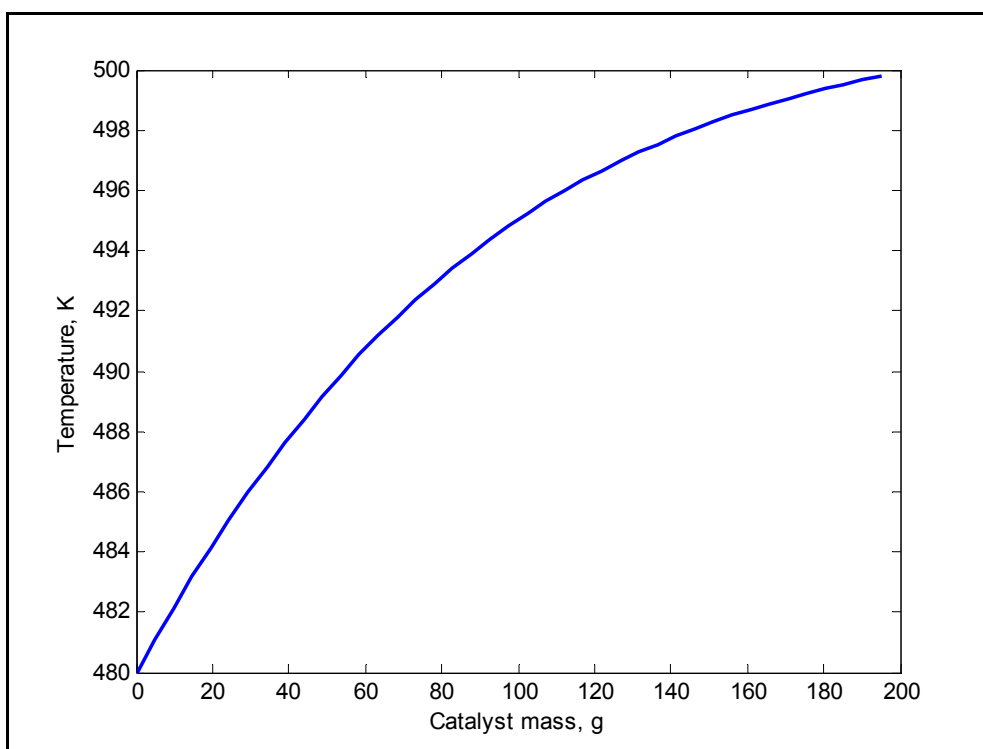


Figure 4.1. Temperature of bulk gas (K) versus catalyst mass (g)
(Data Set 1, L-H pseudo-homogeneous model)

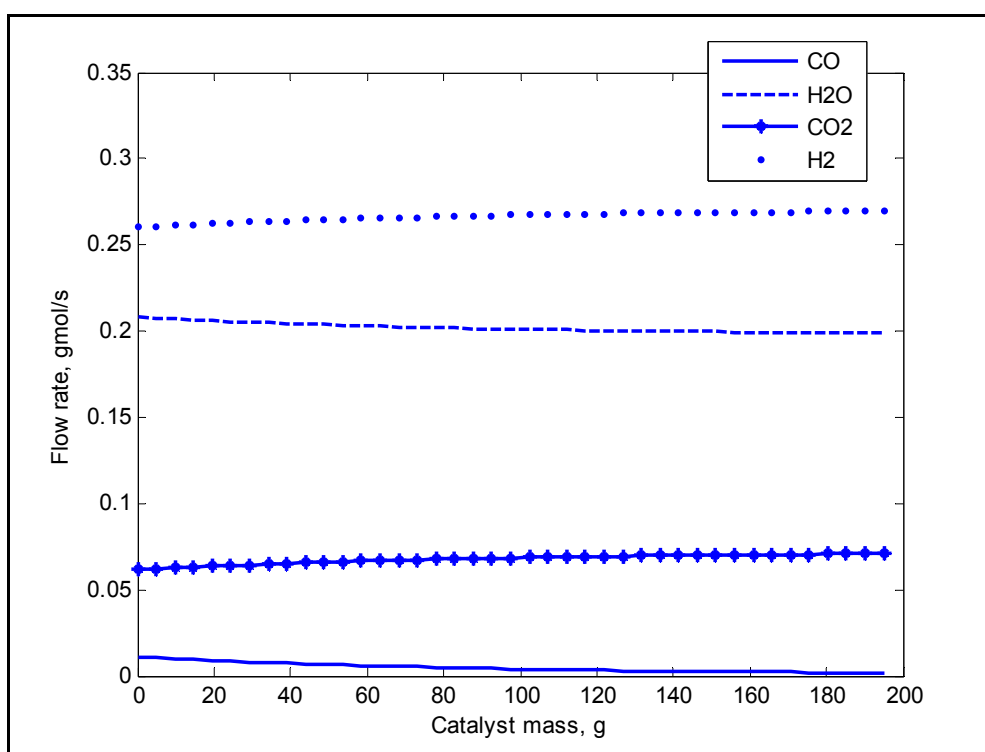


Figure 4.2. Flow rate of components in the bulk gas (gmol s⁻¹) versus catalyst mass (g)
(Data Set 1, L-H pseudo-homogeneous model)

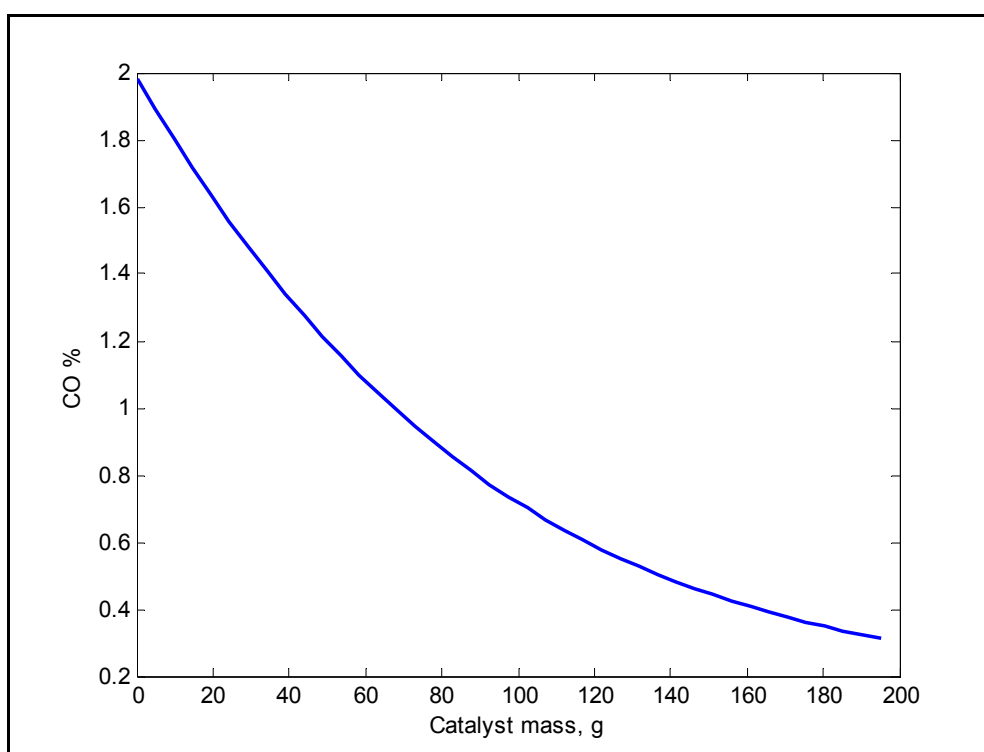


Figure 4.3. CO per cent of the bulk gas (wet-base) versus catalyst mass (g)
(Data Set 1, L-H pseudo-homogeneous model)

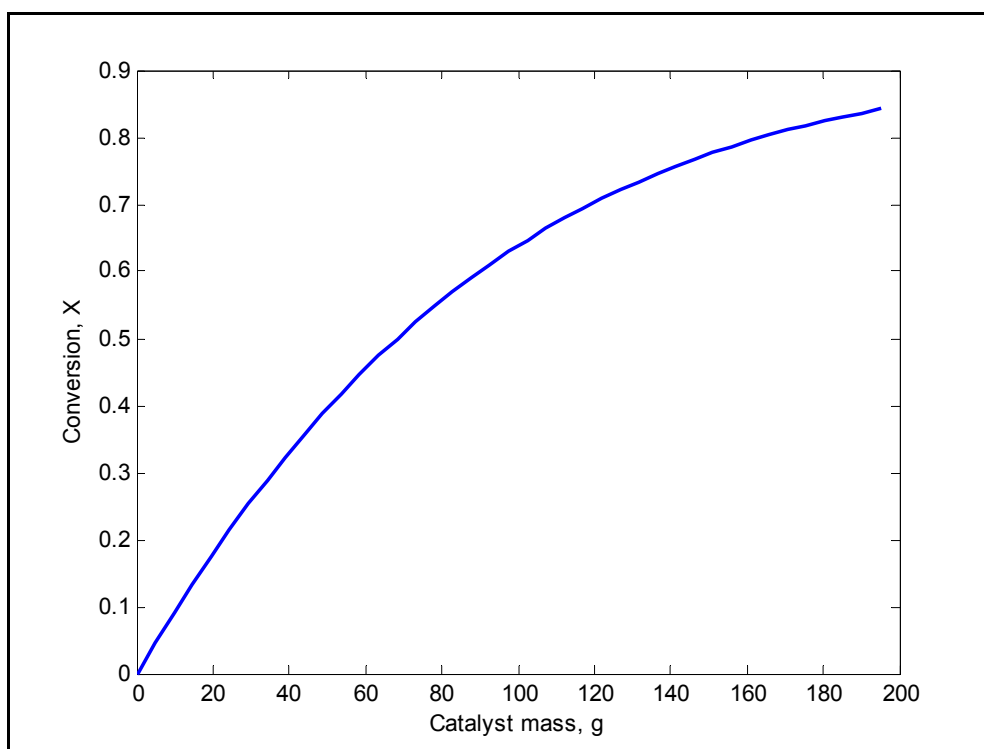


Figure 4.4. Conversion of CO versus catalyst mass (g)
(Data Set 1, L-H pseudo-homogeneous model)

4.1.1.2. Data Set 2 and Power Function Kinetic Model: In the study reported by Francesconi et al. [43], the WGS reactor design was analyzed as a part of the ethanol processor producing H_2 for PEMFC applications, in which a one-dimensional heterogeneous model was used to obtain the optimum values for reactor and catalyst dimensions. A power function kinetic expression for the commercial Cu-ZnO-Al₂O₃ catalyst [52], which is expressed in Equations 4.12–4.13, is used in the simulations by using the inlet conditions given in Table 4.3 for the LTS reactor.

$$K_{eq} = \exp((-4577.8/T) - 4.33) \quad (4.12)$$

$$r_{CO} = 82.2 \times \exp\left(-\frac{47400}{R \times T}\right) \times \left(p_{CO} \times p_{H_2O} - \frac{p_{CO_2} \times p_{H_2}}{K_{eq}}\right) \quad (4.13)$$

$$r_{H_2O} = r_{CO} \quad (4.14)$$

$$r_{CO_2} = -r_{CO} \quad (4.15)$$

$$r_{H_2} = -r_{CO} \quad (4.16)$$

$$r_{CH_4} = 0 \quad (4.17)$$

Table 4.3. Inlet conditions of the LTS reactor [43]

Temperature (K)	Pressure (atm)	Steam feed flow (gmol s ⁻¹)	Dry-gas feed flow (gmol s ⁻¹)	Dry-gas composition (vol. %)			
				CO	CO ₂	H ₂	CH ₄
400.25	1.000	0.00733	0.01567	11.70	16.13	63.83	8.33

The optimum values of the dimensions of a single-stage adiabatic WGS reactor, and the catalyst requisites are given in the paper for CO output levels of 0.30, 0.70 and 1.00

mole per cent (wet-base) separately. The molar flow rates used are based on the assumption that $33.3 \text{ gmol h}^{-1} \text{ H}_2$ is required per kW of PEMFC power. The set of conditions corresponding to 0.30 per cent CO output given in **Table 4.4** is selected for conducting the simulations of the present study, because more information has been given. Since neither solid nor bulk catalyst density is reported, the solid catalyst density for Cu-ZnO-Al₂O₃ is taken as 1.863 g cm^{-3} as reported in other work on alumina-supported catalysts [51]. The mass of catalyst in the given bed volume is calculated by using the Equations 4.18–4.20 [42, 43].

Table 4.4. Optimization results for a single-stage adiabatic WGS reactor [43]

CO output (%) (wet-base)	0.30
L_t (cm)	36.50
D_t (cm)	7.20
V (cm³)	1460
D_p (cm)	0.05

$$\varepsilon = 0.38 + 0.073 \times \left[1 - \frac{(D_t/D_p - 2)^2}{(D_t/D_p)^2} \right] \quad (4.18)$$

$$\rho_b = \rho_s \times (1 - \varepsilon) \quad (4.19)$$

$$W = \rho_b \times V \quad (4.20)$$

In the present study, CO conversion, reactor temperature, pressure and composition of product gas leaving the LTS reactor are simulated in the MATLAB environment by using Equations 3.1–3.3 of the pseudo-homogeneous packed-bed reactor model, Equations 4.12–4.17 given above, and the inlet conditions of Table 4.3. The simulation results for 1680.9 g of catalyst and their comparison with the values given by Francesconi et al. [43] are given in **Table 4.5**. The reactor dimensions required and the catalyst properties are taken directly from **Table 4.4**. As indicated by **Table 4.5**, only the mole fraction or per

cent values of CO and H₂ in the product gas, the CO conversion and the outlet temperature are given in the paper. Therefore, the rest of the results can not be compared.

The mole fraction of H₂ calculated by simulation is very close to the value reported in the paper, while that of CO deviates considerably from the given value by about 14 per cent. However, both results are acceptable as they are under the one mole percent CO constraint at reactor exit. The outlet temperature values are also satisfactory. The comparison in **Table 4.5** shows that the use of a pseudo-homogeneous reactor model gives results similar to a heterogeneous model, since the LTS reaction is only mildly exothermic and the external heat transfer resistances are not appreciable. The pressure of the bulk gas drops from 1 atm to 0.964 atm at the outlet of the reactor due to the catalyst packing as the main reason. The corresponding temperature, molar flow rates of the components, CO level in the downstream, CO conversion, pressure and pressure drop profiles are plotted in **Figure 4.5–Figure 4.10**.

Table 4.5. The properties of the product gas leaving the LTS reactor
(Data Set 2, power-function pseudo-homogeneous model)

	Present Study	Francesconi et al. [43]	Difference%
y CO %	0.259	0.300	13.82
y H₂O %	24.172	-	-
y CO₂ %	18.703	-	-
y H₂ %	51.191	52.000	1.56
y CH₄ %	5.676	-	-
T (K)	489.49	493.15	0.74
P (atm)	0.964	-	-
Conversion	0.968	0.960	0.79

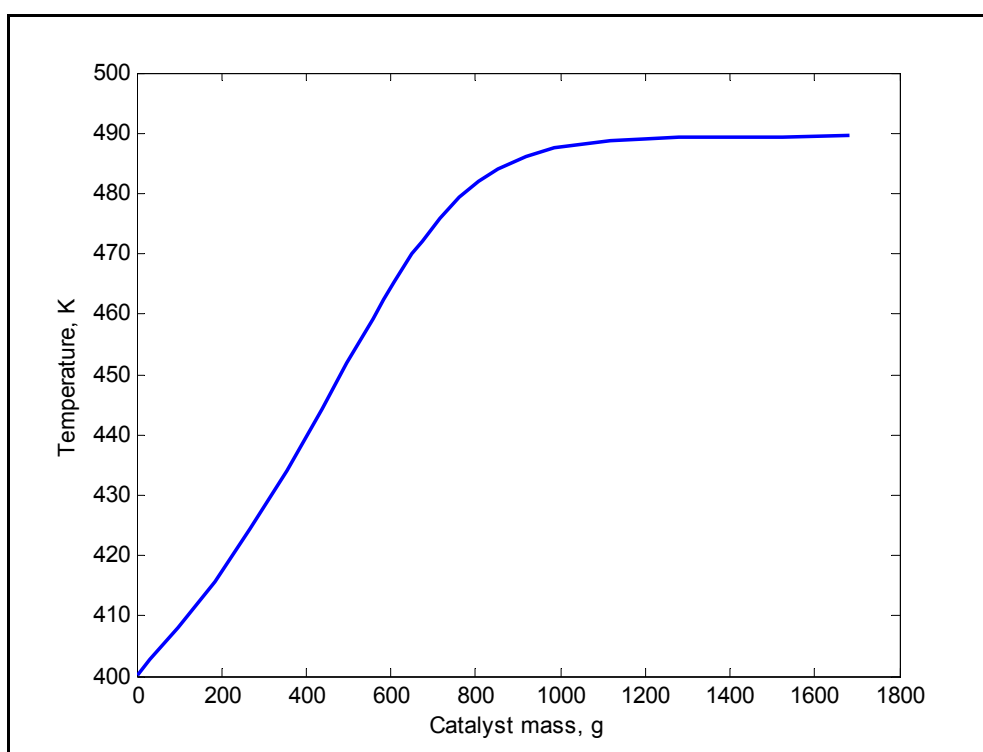


Figure 4.5. Temperature of bulk gas (K) versus catalyst mass (g)
(Data Set 2, power-function pseudo-homogeneous model)

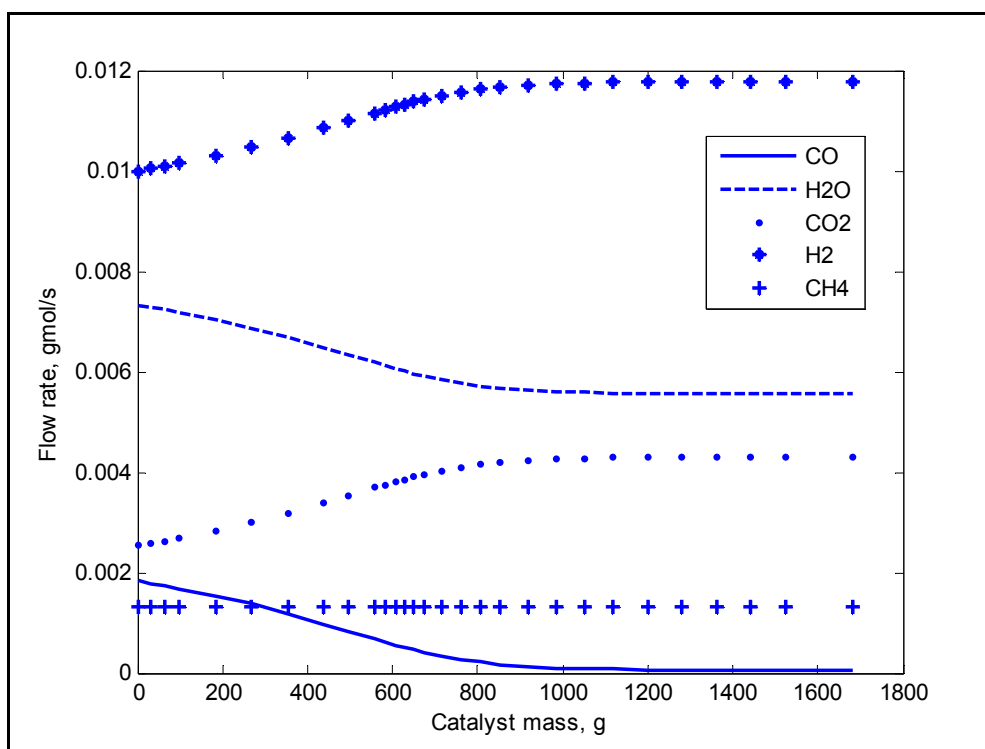


Figure 4.6. Flow rate of components in the bulk gas (gmol s^{-1}) versus catalyst mass (g)
(Data Set 2, power-function pseudo-homogeneous model)

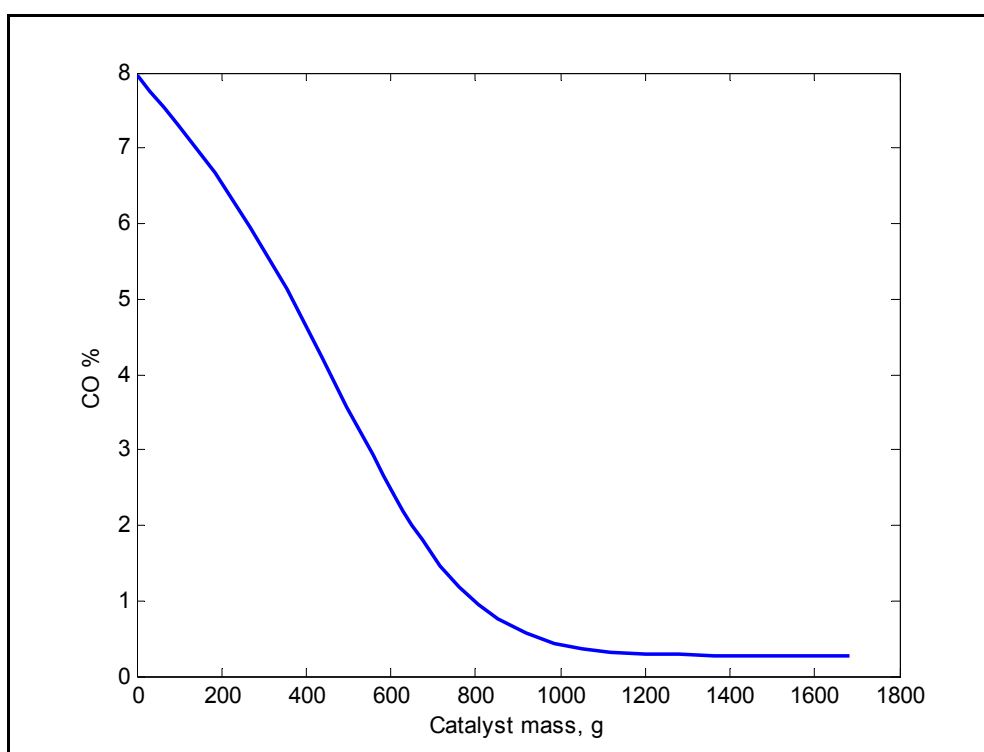


Figure 4.7. CO per cent of the bulk gas versus catalyst mass (g)
(Data Set 2, power-function pseudo-homogeneous model)

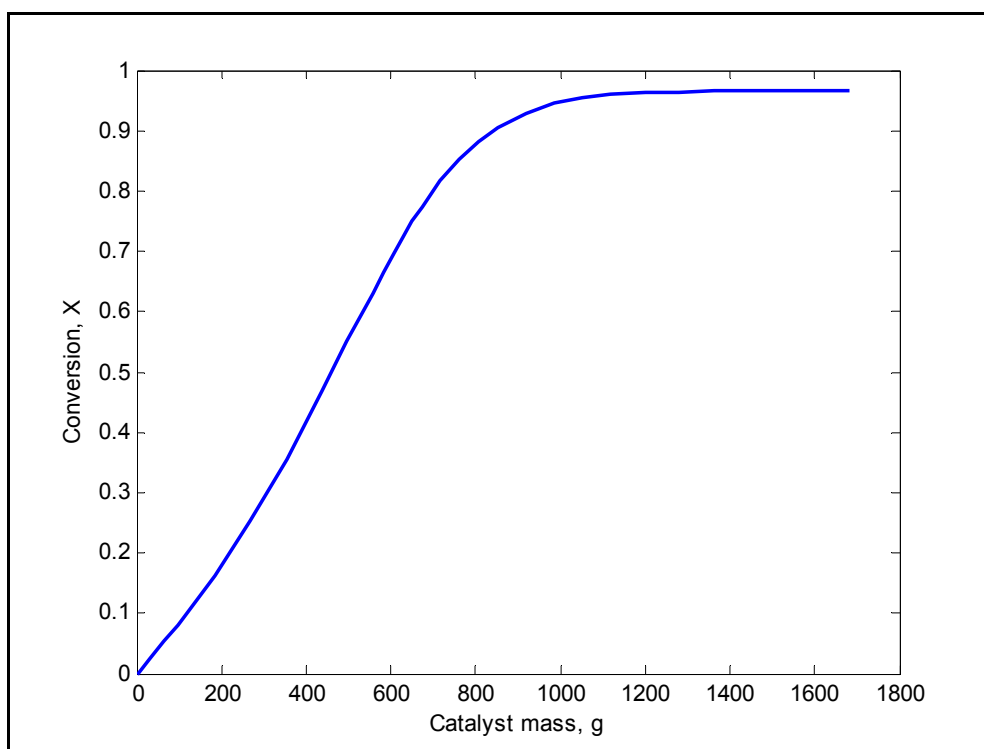


Figure 4.8. Conversion of CO versus catalyst mass (g)
(Data Set 2, power-function pseudo-homogeneous model)

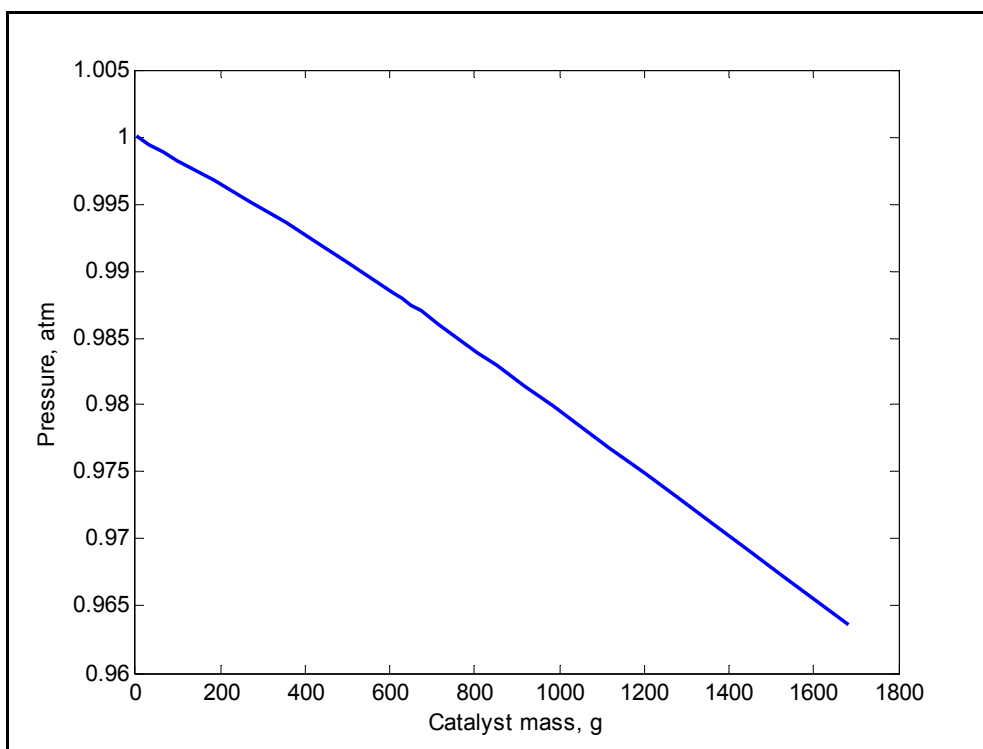


Figure 4.9. Pressure of the bulk gas (atm) versus catalyst mass (g)
(Data Set 2, power-function pseudo-homogeneous model)

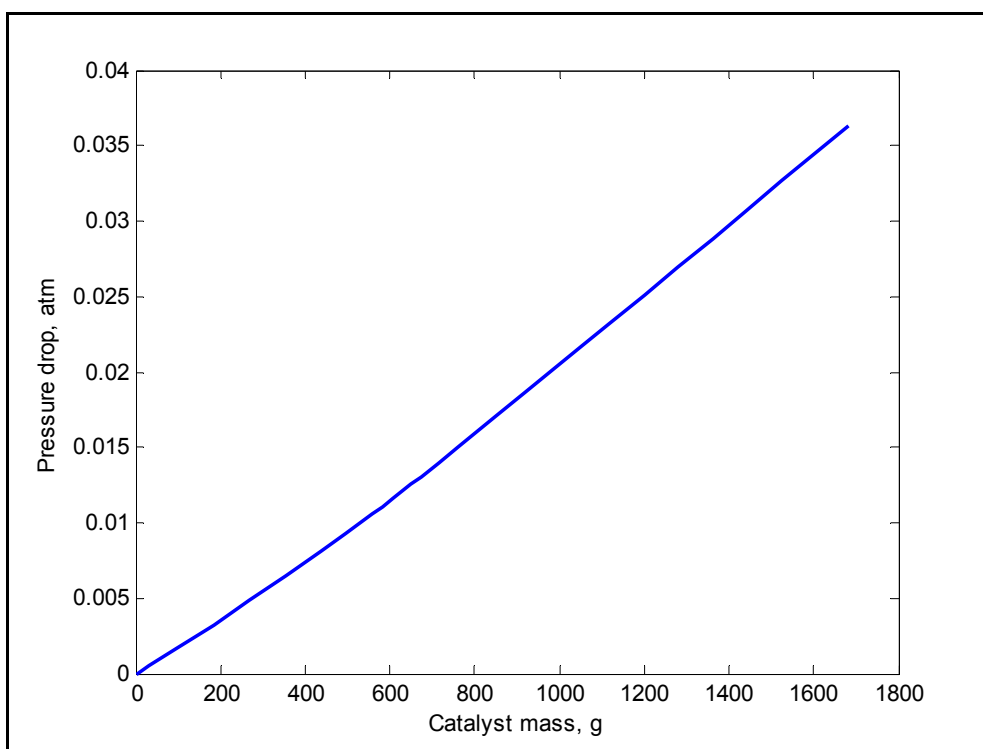


Figure 4.10. Pressure drop (atm) along catalyst bed versus catalyst mass (g)
(Data Set 2, power-function pseudo-homogeneous model)

4.1.1.3. Data Set 3 and Power Function Kinetic Model: The computational study by Tan [51] considers the pseudo-homogeneous model of an adiabatic packed-bed reactor for the LTS reaction over Cu-ZnO-Al₂O₃ catalyst in a fuel processor consisting of a methane ATR reactor located before and a selective CO oxidation reactor located after the LTS converter. The methane processor was designed for feeding H₂ to a PEMFC with 1.5 kW power rating, and the component flow rates were calculated on the basis of a H₂ requirement of 37–41 gmol h⁻¹ per kW. The rate expression given in section 4.1.1.2, i.e. Equations 4.12–4.13 and the inlet conditions given in **Table 4.6** were used in the simulations. The reactor dimensions and the catalyst properties calculated by Tan [51] for obtaining 0.76 per cent CO in the downstream of the LTS reactor are given in **Table 4.7**. In the present work, these data are utilized to simulate and calculate the CO conversion for the same amount of catalyst in the MATLAB environment by using Equations 3.1–3.3 of the pseudo-homogeneous packed-bed reactor model and Equations 4.12–4.17 given in section 4.1.1.2.

Table 4.6. Inlet conditions for the LTS reactor [51]

Temperature (K)	Pressure (atm)	Steam feed flow (gmol s ⁻¹)	Dry-gas feed flow (gmol s ⁻¹)	Dry-gas composition (vol. %)				
				CO	CO ₂	H ₂	CH ₄	N ₂
473	0.987	0.01258	0.04905	4.66	8.40	33.08	8.04	45.82

Table 4.7. Optimization results for an adiabatic LTS reactor [51]

CO output (per cent) (wet-base)	0.76
L_t (cm)	25.60
D_t (cm)	6.00
D_p (cm)	0.10
W (g cat)	650
ρ_b (g cm⁻³)	1.863

The results of MATLAB simulations and their comparison with the values reported by Tan [51] as well as the per cent differences are given in **Table 4.8** for the same catalyst

mass. As seen from **Table 4.8**, the CO conversion calculated by the simulation for the catalyst amount of 650 g is 7.95 per cent lower, which affects the composition of the product gas and the outlet temperature; also, a higher outlet pressure is predicted than the level reported by Tan [51]. This is likely to arise from small differences between the two codes in both of which the major constraint is to achieve a CO level of less than 1 mole per cent. Since catalyst mass is sensitive to CO conversion level, the incremental increase in the catalyst mass necessary for increasing fractional CO conversion from 0.733 to 0.80 is considerable. The corresponding temperature, molar flow rates of the components, CO level in the downstream, CO conversion and pressure profiles are plotted in **Figure 4.11–Figure 4.15** respectively for 650 g of catalyst.

Table 4.8. The properties of the product gas leaving the LTS reactor
(W = 650 g, Data Set 3, power-function pseudo-homogeneous model)

	Present Study	Tan [51]	Difference %
y CO %	0.992	0.759	30.63
y H₂O %	17.689	17.498	1.09
y CO₂ %	9.403	9.393	0.11
y H₂ %	29.048	29.363	1.07
y CH₄ %	6.401	6.419	0.27
y N₂ %	36.468	36.568	0.27
T (K)	504.71	510.00	1.04
P (atm)	0.9502	0.7797	21.87
Conversion	0.733	0.796	7.95

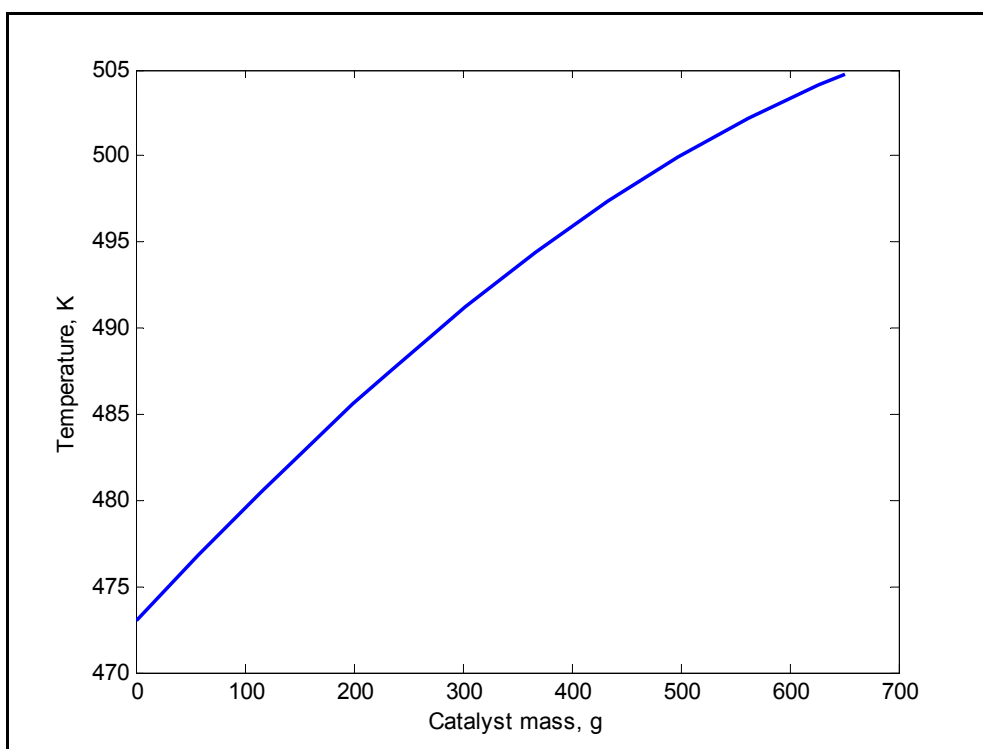


Figure 4.11. Temperature of bulk gas (K) versus catalyst mass (g)
(W = 650 g, Data Set 3, power-function pseudo-homogeneous model)

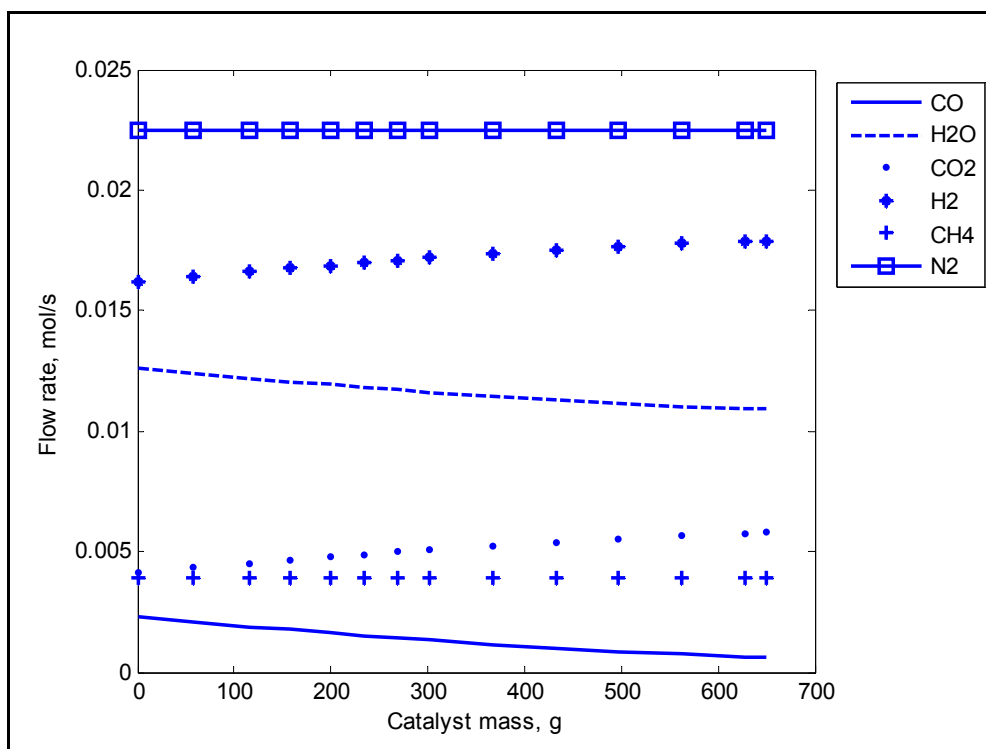


Figure 4.12. Flow rate of components in the bulk gas (gmol s^{-1}) versus catalyst mass (g)
(W = 650 g, Data Set 3, power-function pseudo-homogeneous model)

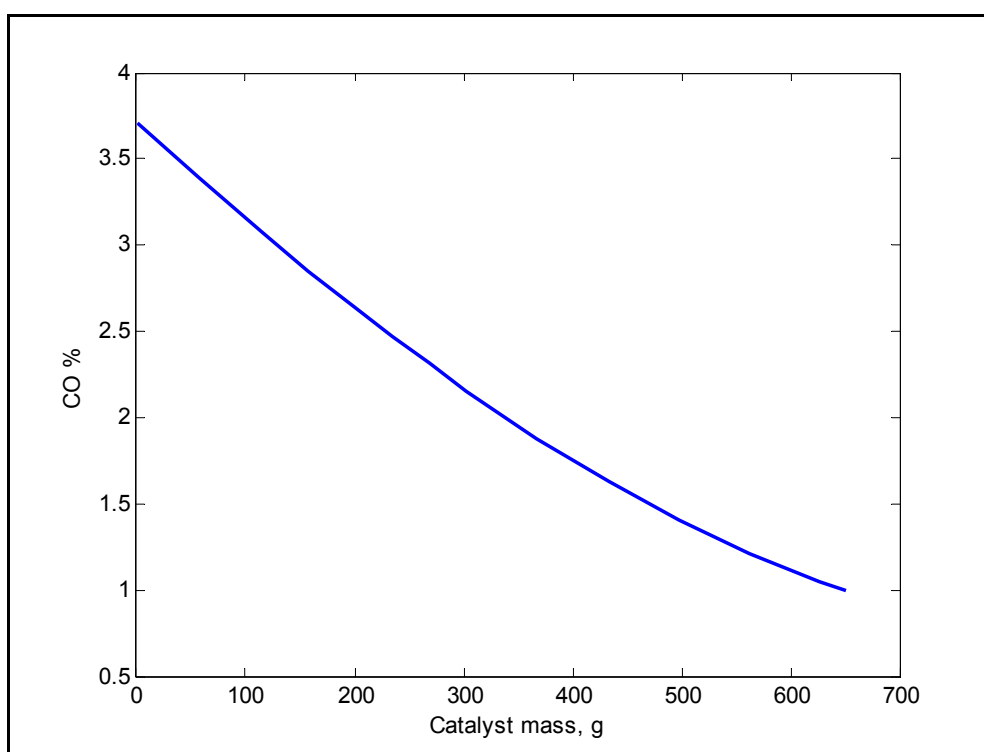


Figure 4.13. CO per cent of the bulk gas versus catalyst mass (g)
($W = 650$ g, Data Set 3, power-function pseudo-homogeneous model)

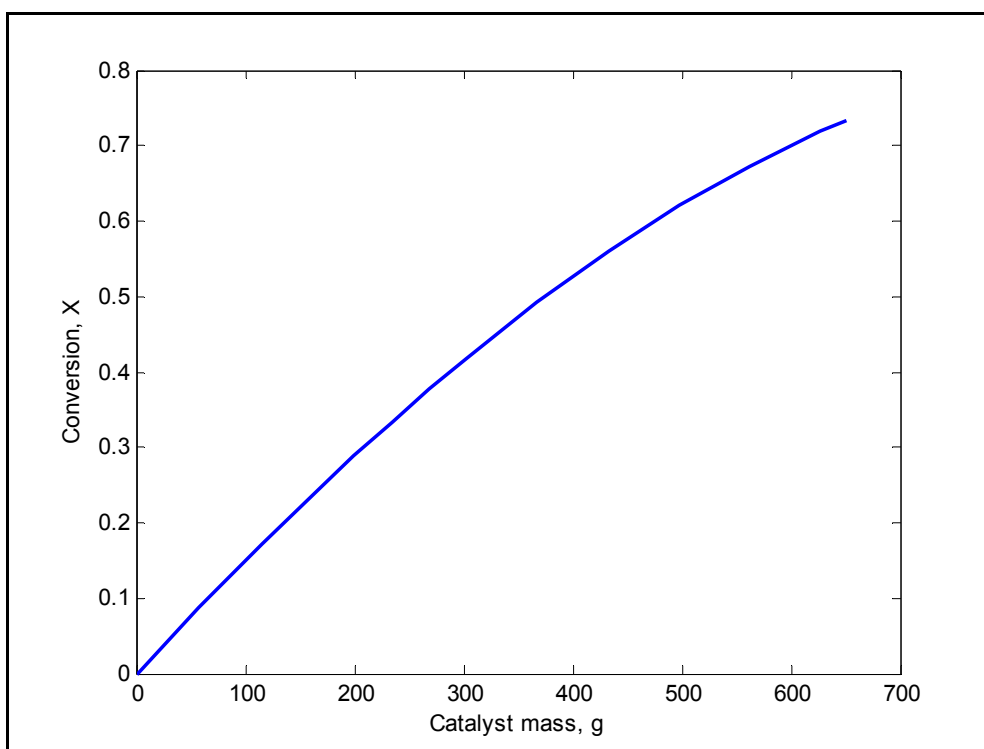


Figure 4.14. Conversion of CO versus catalyst mass (g)
($W = 650$ g, Data Set 3, power-function pseudo-homogeneous model)

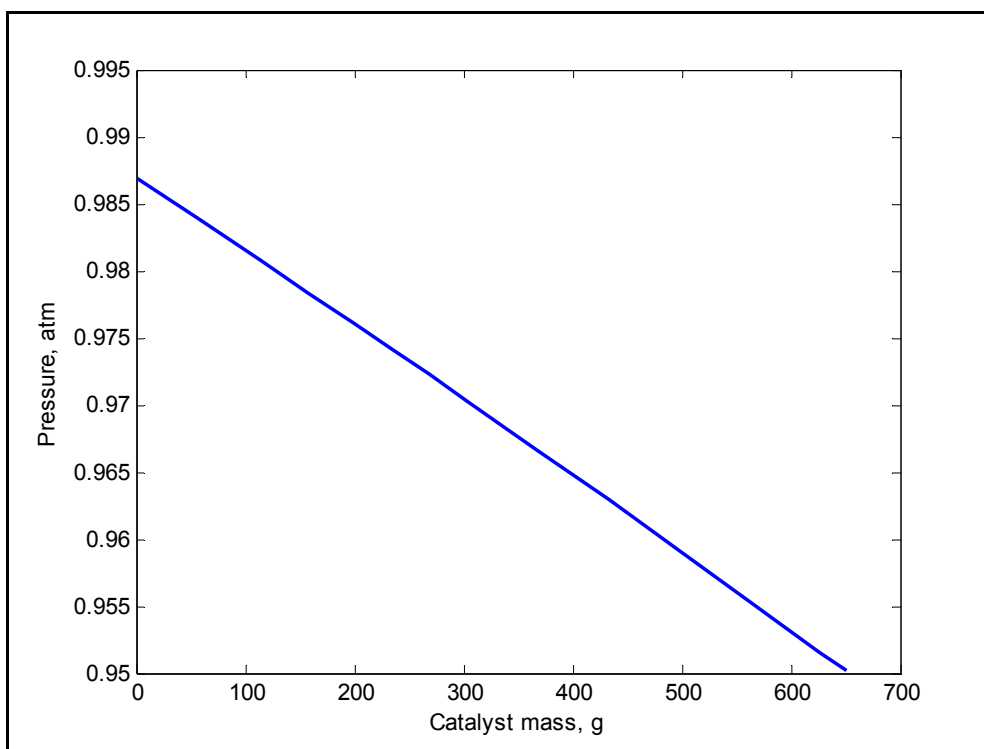


Figure 4.15. Pressure of the bulk gas (atm) versus catalyst mass (g)
($W = 650$ g, Data Set 3, power-function pseudo-homogeneous model)

As a next step, the amount of catalyst required to reach the same conversion of 0.80 is calculated and a catalyst mass of 770 g is found, which is approximately 19 per cent higher than 650 g. According to the comparative results given in **Table 4.9**, the composition and the outlet temperature of the product gas are very close to those obtained by Tan [51], while the per cent difference of the outlet pressure decreases by only 1 per cent.

4.1.2. Heterogeneous Model

External heat transfer effects are taken into consideration in the heterogeneous model, while internal heat transfer effects as well as external and internal mass transfer are neglected. All other assumptions are the same as in section 4.1.1. Heterogeneous reactor model is applied to two data sets, namely, Data Set 2 and 3 [43, 51].

Table 4.9. The properties of the product gas leaving the LTS reactor
(CO conversion = 0.80, Data Set 3, power-function pseudo-homogeneous model)

	Present Study	Tan [51]	Difference %
y CO %	0.756	0.759	0.43
y H₂O %	17.453	17.498	0.26
y CO₂ %	9.639	9.393	2.62
y H₂ %	29.284	29.363	0.27
y CH₄ %	6.401	6.419	0.27
y N₂ %	36.468	36.568	0.27
T (K)	507.42	510.00	0.51
P (atm)	0.9431	0.7797	20.95
W (g)	770.00	650.00	18.46

4.1.2.1. Data Set 2 and Power Function Kinetic Model: Francesconi et al. [43] have considered both internal and external mass and heat transfer effects in their work whereas in the present study only external heat transfer effects are included in the calculations, and simulations are conducted using Equations 3.1, 3.3–3.5 and 4.12–4.17 as well as the catalyst and reactor geometries given in **Table 4.4**. Comparative results are given in **Table 4.10**. It can be said that the H₂ mole fraction in the product gas, outlet temperature and CO conversion values obtained in the simulation are very close to the values given in the paper [43], while a difference of around 14 per cent is obtained in the CO mole fraction of the product gas. The pressure of the bulk gas decreases from 1 atm to 0.9636 atm at the reactor outlet, which can be explained by the presence of catalyst packing as the main reason. The corresponding temperature, molar flow rates of the components, CO level in the downstream, CO conversion and pressure profiles are plotted in **Figure 4.16–Figure 4.15** respectively.

Table 4.10. The properties of the product gas leaving the LTS reactor
(Data Set 2, power-function heterogeneous model)

	Present Study	Francesconi et al. [43]	Difference %
y CO %	0.259	0.300	13.77
y H₂O %	24.172	-	-
y CO₂ %	18.703	-	-
y H₂ %	51.191	52.000	1.56
y CH₄ %	5.676	-	-
T (K)	489.53	493.15	0.73
P (atm)	0.9636	-	-
Conversion	0.968	0.960	0.79

External heat and mass transfer and internal mass transfer are calculated to be negligible when Mears' Criteria for external mass and heat transfer, and Weisz–Prater Criterion for internal mass transfer are considered [42].

Table 4.11. Criteria for external mass and heat transfer, internal mass transfer
(Data Set 2, power-function heterogeneous model)

External heat transfer (Mears' Criterion)	1.55×10^{-6}	negligible
External mass transfer (Mears' Criterion)	1.58×10^{-5}	negligible
Internal mass transfer (Weisz–Prater Criterion)	4.26×10^{-4}	negligible

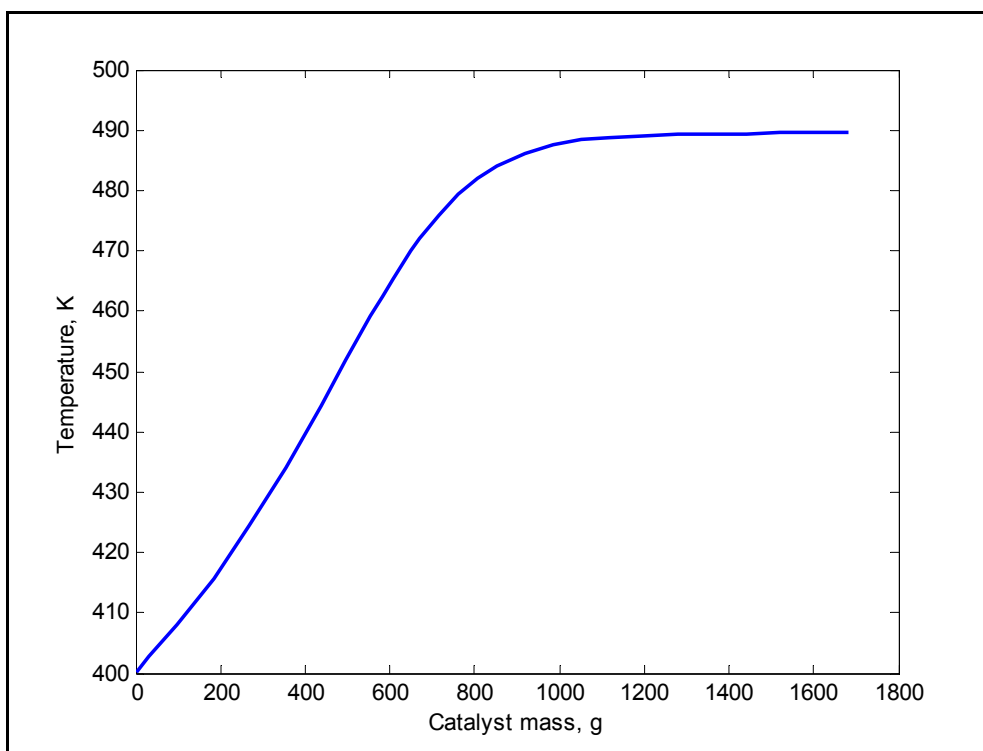


Figure 4.16. Temperature of bulk gas (K) versus catalyst mass (g)
(Data Set 2, power-function heterogeneous model)

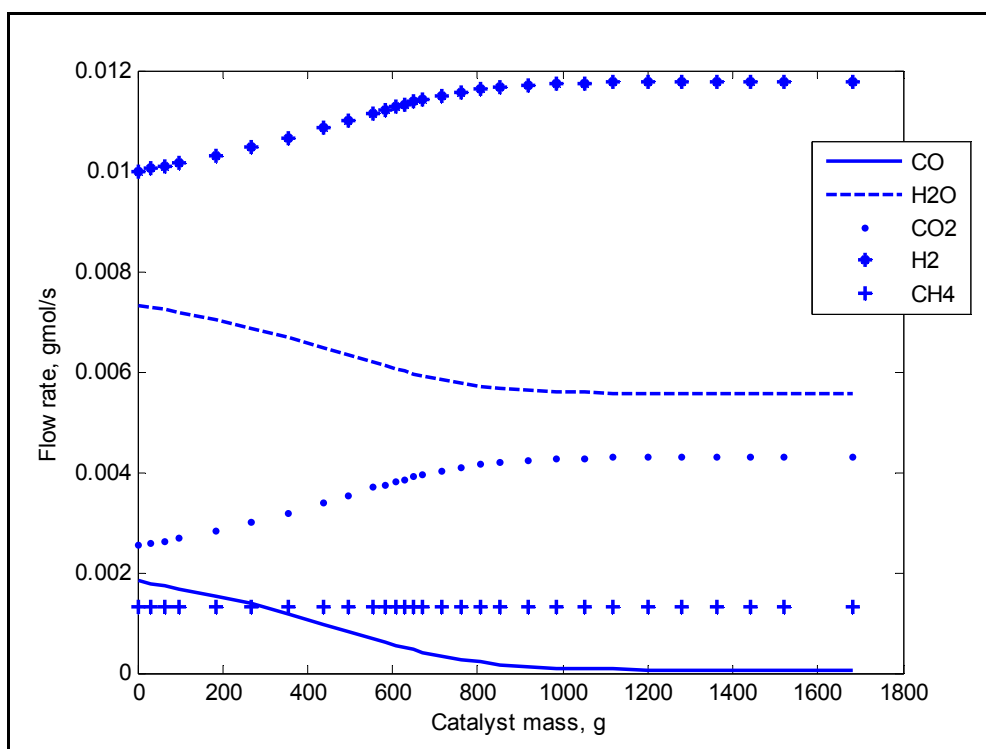


Figure 4.17. Flow rate of components in bulk gas (gmol s^{-1}) versus catalyst mass (g)
(Data Set 2, power-function heterogeneous model)

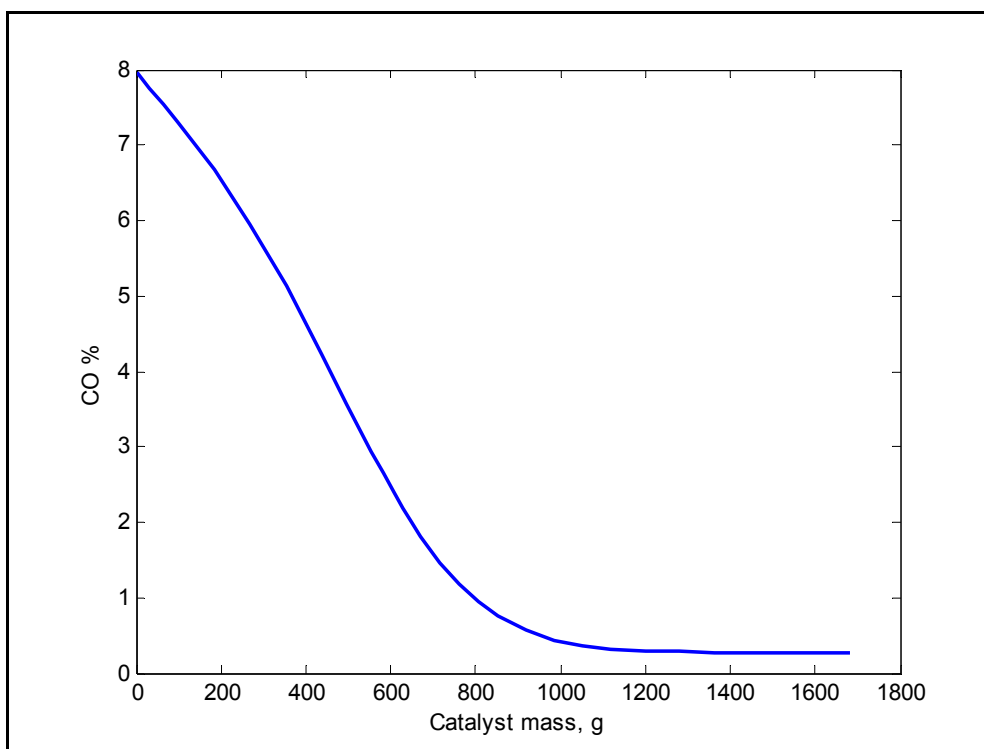


Figure 4.18. CO per cent of the bulk gas versus catalyst mass (g)
(Data Set 2, power-function heterogeneous model)

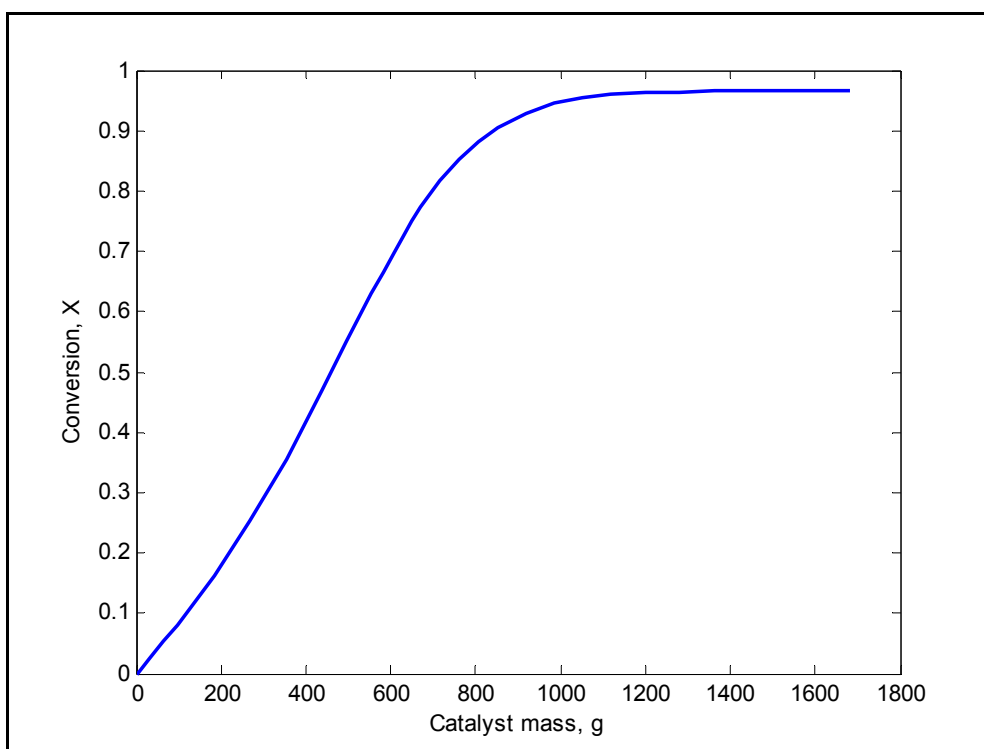


Figure 4.19. Conversion of CO versus catalyst mass (g)
(Data Set 2, power-function heterogeneous model)

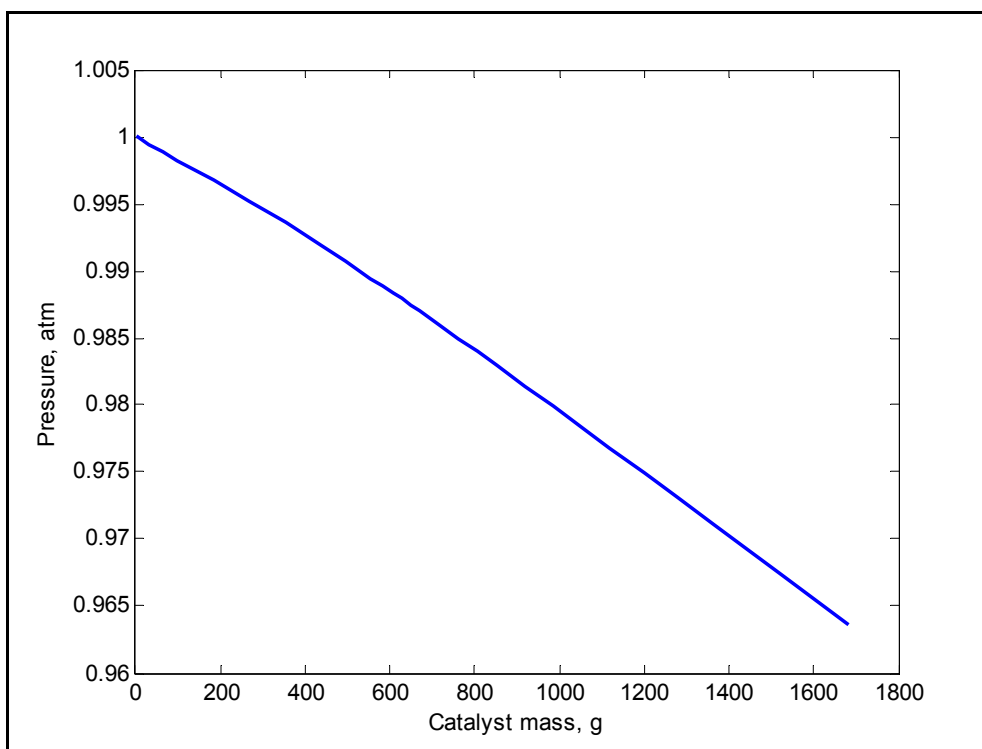


Figure 4.20. Pressure along the catalyst bed (atm) versus catalyst mass (g)
(Data Set 2, power-function heterogeneous model)

4.1.2.2. Data Set 3 and Power Function Kinetic Model: For Data Set 3, the simulations are conducted using Equations 3.1, 3.3–3.5 and 4.12–4.17 as well as the catalyst and reactor geometries given in **Figure 4.7**. The results of the pseudo-homogeneous model applied previously [51] are also compared with those obtained in the present study with the heterogeneous model including external heat transfer resistances (**Table 4.12**).

The calculated values are very close to each other except the 2.63 per cent difference in CO_2 mole fraction in the product gas. The outlet pressure calculated is 21 per cent higher than the value given by Tan [51]. The corresponding temperature, molar flow rates of the components, CO level in the downstream, CO conversion and pressure profiles are plotted in **Figure 4.21–Figure 4.25** respectively.

Table 4.12. The properties of the product gas leaving the LTS reactor
(Data Set 3, power-function heterogeneous model)

	Present Study	Tan [51]	Difference %
y CO %	0.755	0.759	0.54
y H₂O %	17.452	17.498	0.26
y CO₂ %	9.640	9.393	2.63
y H₂ %	29.284	29.363	0.27
y CH₄ %	6.401	6.419	0.27
y N₂ %	36.468	36.568	0.27
T (K)	507.48	510.00	0.49
P (atm)	0.9430	0.7797	20.95
Conversion	0.796	0.796	0.07

These results are supported by **Table 4.13**, which indicates that external heat and mass transfer and internal mass transfer are negligible when Mears' Criteria and Weisz–Prater Criterion are considered [42].

Table 4.13. Criteria for external mass and heat transfer, internal mass transfer
(Data Set 3, power-function heterogeneous model)

External heat transfer (Mears' Criterion)	9.00×10^{-4}	negligible
External mass transfer (Mears' Criterion)	$- 2.60 \times 10^{-3}$	negligible
Internal mass transfer (Weisz–Prater Criterion)	$- 1.39 \times 10^{-1}$	negligible

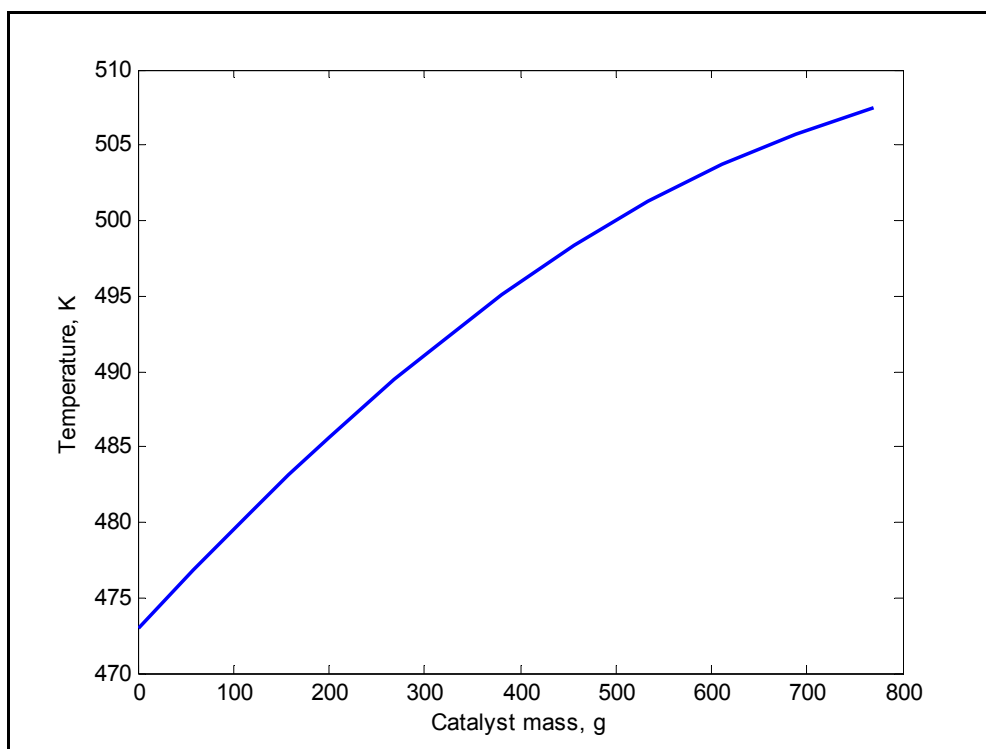


Figure 4.21. Temperature of bulk gas (K) versus catalyst mass (g)
(Data Set 3, power-function heterogeneous model)

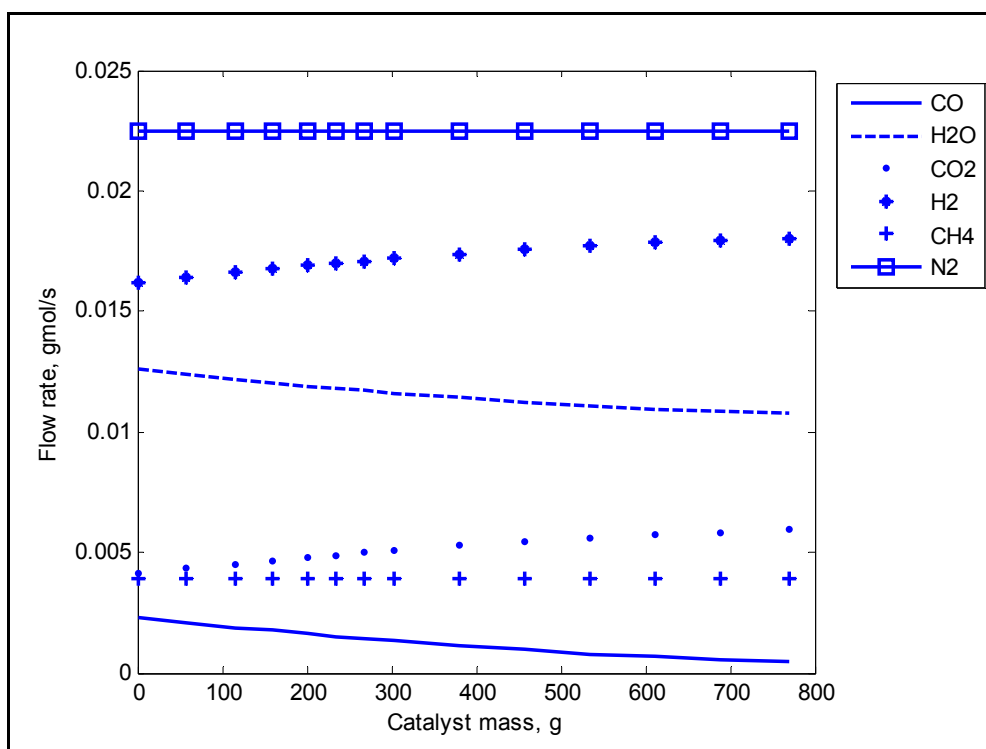


Figure 4.22. Flow rate of components in bulk gas (gmol s^{-1}) versus catalyst mass (g)
(Data Set 3, power-function heterogeneous model)

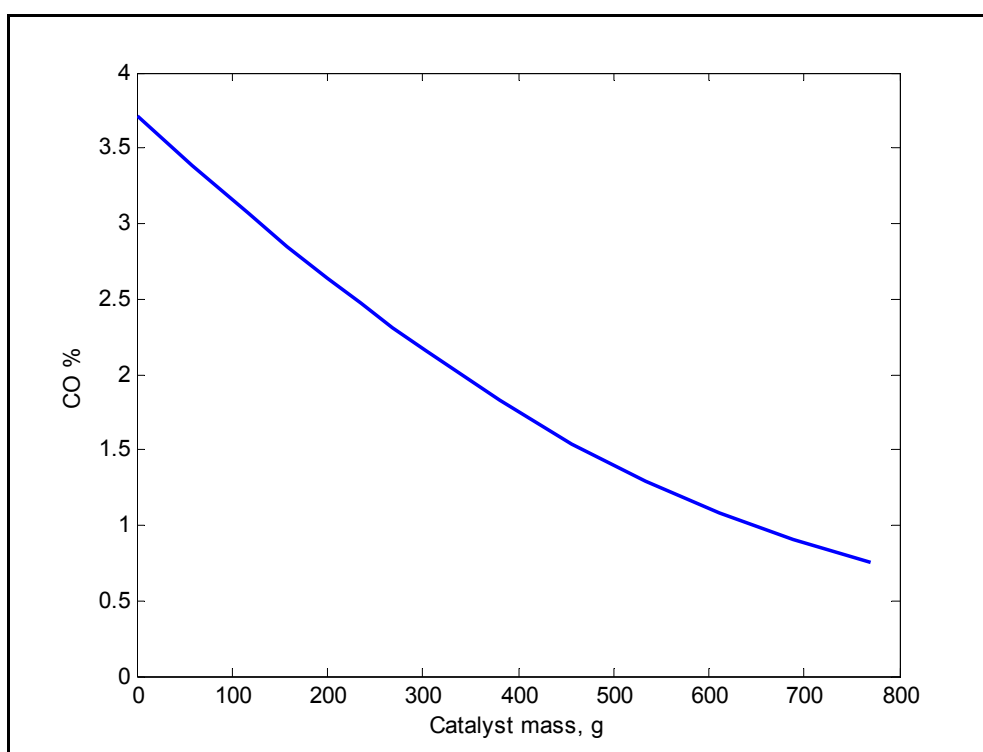


Figure 4.23. CO per cent of the bulk gas versus catalyst mass (g)
(Data Set 3, power-function heterogeneous model)

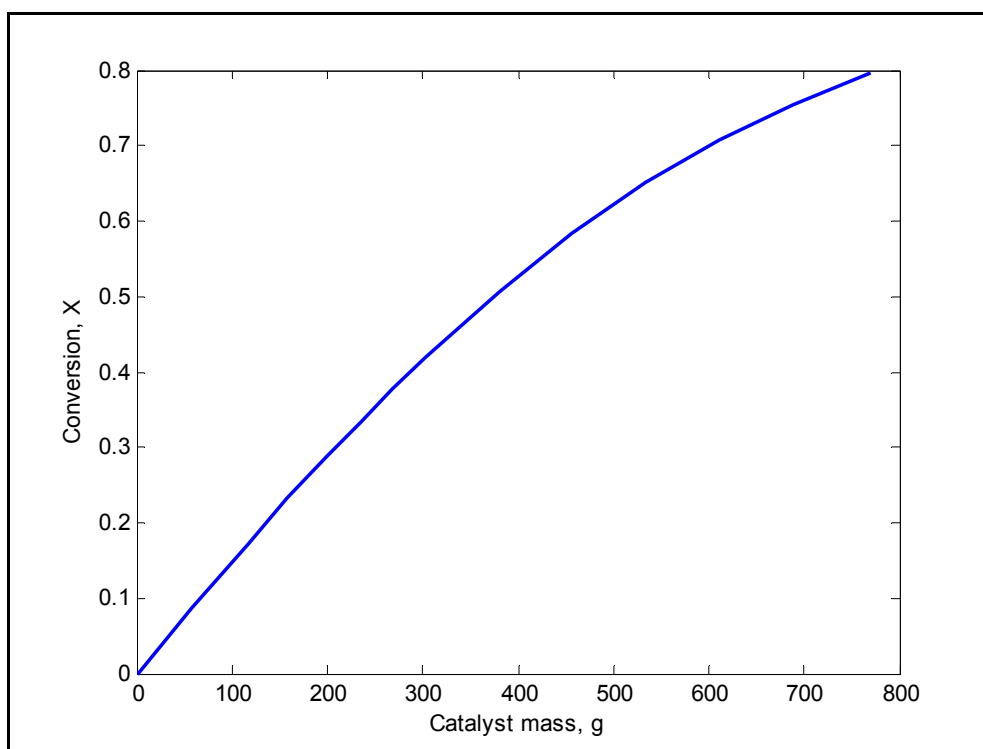


Figure 4.24. Conversion of CO versus catalyst mass (g)
(Data Set 3, power-function heterogeneous model)

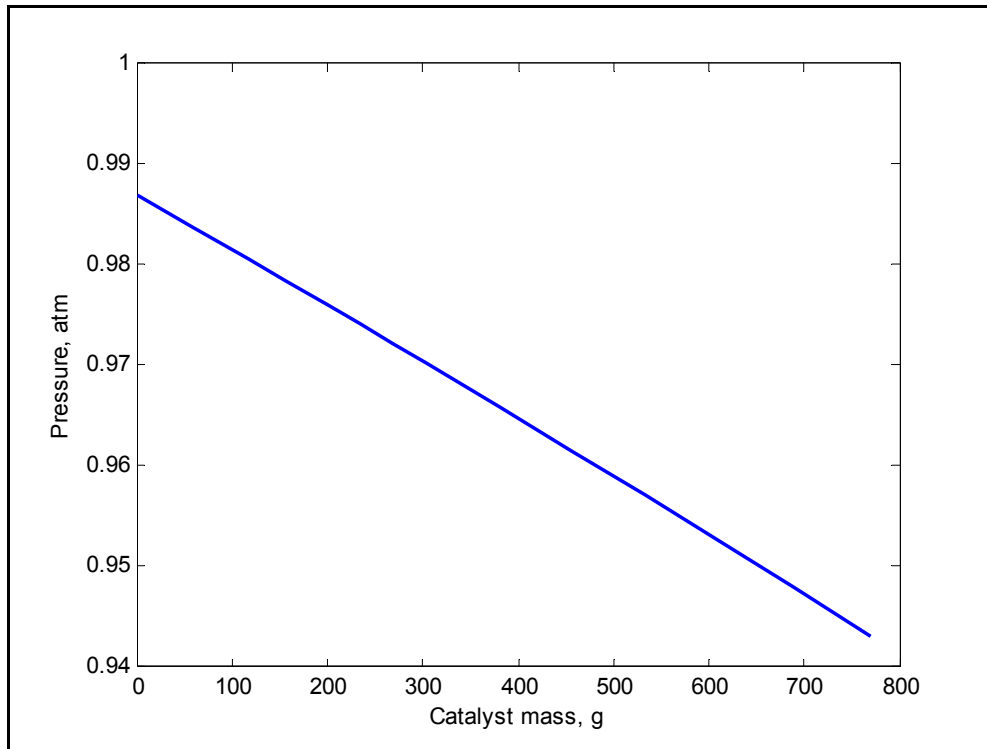


Figure 4.25. Pressure along the catalyst bed (atm) versus catalyst mass (g)
(Data Set 3, power-function heterogeneous model)

4.2. Monolith Reactor

4.2.1. Pseudo-Homogeneous Model

In this work, MATLAB codes are written for the simulations of the LTS reaction in an adiabatic monolith reactor by applying a pseudo-homogeneous model in which both external and internal mass and heat transport resistances are neglected. Only a single channel of the monolith is considered for the simulations since the flow is assumed to be laminar and distributed uniformly over the cross-section of the monolith reactor and knowledge of the number of channels is sufficient to estimate the behavior of the complete monolith [45, 53]. Two data sets, namely, Data Set 3 [51] above and Data Set 4 [53] are used in the simulations.

4.2.1.1. Data Set 4 and Power Function Kinetic Model for Pt-CeO₂-Al₂O₃: Quiney et al. [53] used a power law rate expression for a Pt-CeO₂-Al₂O₃ catalyst together with a one-dimensional heterogeneous model that accounts for interfacial and intraparticle gradients to describe the WGS behavior of monolithic structures. The following kinetic expression (Equation 4.21–4.23) was derived for WGS over Pt-CeO₂-Al₂O₃ [53] to be used in their simulations:

$$K_{eq} = \exp\left(\frac{-36}{R}\right) \times \exp\left(\frac{38060}{R \times T}\right) \quad (4.21)$$

$$\beta = \frac{P_{CO_2} \times P_{H_2}}{K_{eq} \times P_{CO} \times P_{H_2O}} \quad (4.22)$$

$$r_{CO} = 4.3 \times 10^5 \times \exp\left(-\frac{76800}{R \times T}\right) \times (P_{CO}^{0.13} \times P_{H_2O}^{0.49} \times P_{CO_2}^{-0.12} \times P_{H_2}^{-0.45} \times (1 - \beta)) / 1000 \quad (4.23)$$

$$r_{H_2O} = r_{CO} \quad (4.24)$$

$$r_{CO_2} = -r_{CO} \quad (4.25)$$

$$r_{H_2} = -r_{CO} \quad (4.26)$$

$$r_{N_2} = 0 \quad (4.27)$$

A schematic drawing of a washcoat over a square channel of a monolith is given in **Figure 4.26**. It was stated that the thicker layers of the washcoat were likely to adhere in the corners of the channels [53]. While the layer thickness of the sides of the square channel is only 20 μm, it is 170 μm thick in the corner sections. The properties of the monolith reactor used in the simulations are given in **Table 4.14**.

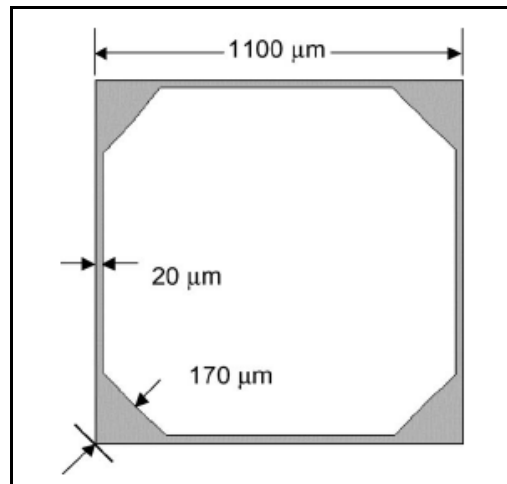


Figure 4.26. Schematic drawing of washcoat used in the simulations [53]

Table 4.14. Properties of the monolith reactor [53]

Number of channels per square inch (cell density) (cpsi)	400
Inner channel diameter before coating (cm)	0.110
Wall thickness (cm)	0.015
Washcoat porosity	0.4
Washcoat tortuosity	4.0
BET washcoat ($\text{m}^2 \text{g}^{-1}$)	69
Washcoat cross-sectional area (cm^2)	1.66×10^{-3}
Washcoat density (g cm^{-3})	1.50

The parameters related to monolith geometry which are used in the simulations of the present study are given below [46].

$$n = \frac{1}{L^2} \quad (4.28)$$

$$c = A \times n \quad (4.29)$$

$$GSA = 4 \times n \times \left[(L - t) - (4 - \pi) \times \frac{R_m}{2} \right] \quad (4.30)$$

$$OFA = n \times \left[(L - t)^2 - (4 - \pi) \times R_m^2 \right] \quad (4.31)$$

$$D_h = 4 \times \left(\frac{OFA}{GSA} \right) \quad (4.32)$$

The equation for calculating the bulk density of the catalyst bed should also be modified for the monolith reactor due to the presence of the channels [46].

$$\rho_b = \rho_s \times (1 - \varepsilon) \times (1 - OFA) \quad (4.33)$$

Since the composition of the gas mixture given by Quiney et al. [53] belongs to the outlet of an autothermal reformer, firstly the simulation of the HTS reaction in an adiabatic monolith reactor is carried out using a pseudo-homogeneous model and applying the inlet conditions given in **Table 4.15**.

Table 4.15. Inlet conditions for the monolith HTS reactor [53]

Temperature (K)	Pressure (atm)	Steam feed flow (gmol s ⁻¹)	Dry-gas feed flow (gmol s ⁻¹)	Dry-gas composition (vol. %)			
				CO	CO ₂	H ₂	N ₂
563.15	2.96	0.0310	0.1040	12.98	10.38	41.54	35.10

Diameter of the monolith used was given as 10 cm [53]; in the present work, the length of the monolith is optimized such that the amount of the catalyst per channel in the paper is almost equal to the value calculated by the simulation. As seen in **Table 4.16**, the length of the monolith is calculated to be 12.50 cm for the HTS reactor.

Only the outlet temperature of the HTS reactor and the amount of the catalyst used are reported by Quiney et al. [53]. The results of the MATLAB simulation are compared with these values in **Table 4.17**. The outlet temperatures of the product gas and the

required amount of catalyst are in good agreement. The pressure drop along the monolith calculated by the Equation 3.10 is found to be 3.5×10^{-8} atm, which is negligible.

Table 4.16. Determination of the monolith length for the monolith HTS reactor
(Pt-CeO₂-Al₂O₃)

Length of monolith (cm)	L_m	12.50
Diameter of monolith (cm)	D_m	10.00
L_m / D_m	—	1.25
Volume of monolith (cm³)	V	981.75
Calculated catalyst mass / channel (g/channel)	W_c	0.0454
Given catalyst mass / channel (g/channel) [53]	W_g	0.0458
Error per cent for catalyst mass / channel	%	0.87

Table 4.17. The properties of the product gas leaving the monolith HTS reactor
(Pt-CeO₂-Al₂O₃)

	Present Study	Quiney et al. [53]	Difference %
y CO %	2.578	-	-
y H₂O %	15.540	-	-
y CO₂ %	15.422	-	-
y H₂ %	39.422	-	-
y N₂ %	27.037	-	-
T (K)	645.71	648.15	0.38
Conversion	0.742	-	-
W (g)	228.18	230.00	0.79

The product stream of the monolith HTS reactor, the gas composition of which is given in **Table 4.17**, becomes the inlet stream of the monolith LTS reactor. The same procedure is applied to the LTS reactor by using the same kinetic expression for the Pt-

CeO₂-Al₂O₃ catalyst and the same properties of the monolith reactor. The length of the monolith is determined to be 39.4 cm for a diameter of 10 cm as shown in **Table 4.18**.

Table 4.18. Determination of the monolith length for the monolith LTS reactor
(Pt-CeO₂-Al₂O₃)

Length of monolith (cm)	L_m	39.40
Diameter of monolith (cm)	D_m	10.00
L_m / D_m	—	3.94
Volume of monolith (cm³)	V	3094.47
Calculated catalyst mass / channel (g/channel)	W_c	0.1432
Given catalyst mass / channel (g/channel) [53]	W_g	0.1432
Error per cent for catalyst mass / channel	%	0.00

Only the outlet temperature of the LTS reactor and the amount of catalyst used are reported in the paper. The results of the MATLAB simulation are compared with these values in **Table 4.19**. The reported and the calculated values of the LTS reactor outlet temperature and of the required catalyst mass are found to be very close to each other. The pressure drop along the monolith calculated by the Equation 3.10 is found to be 8.5×10^{-8} atm, which is negligible.

Both **Table 4.17** and **Table 4.19** compares results of Quiney et al. [53] from a heterogeneous channel model with those obtained in the simulations of the present work using a pseudo-homogeneous channel model. The agreement in reactor exit temperatures and catalyst requirements demonstrates the applicability of pseudo-homogeneous models for describing the behavior of monolith channels in cases, where heat effects are moderate.

The corresponding temperature, molar flow rates of the components, CO level in the downstream and CO conversion profiles are plotted in **Figure 4.27–Figure 4.30** respectively for the HTS reactor and in **Figure 4.31–Figure 4.34** respectively for the LTS reactor.

Table 4.19. The properties of the product gas leaving the monolith LTS reactor
(Pt-CeO₂-Al₂O₃)

	Present Study	Quiney et al. [53]	Difference %
y CO %	0.974	-	-
y H ₂ O %	13.937	-	-
y CO ₂ %	17.026	-	-
y H ₂ %	41.027	-	-
y N ₂ %	27.037	-	-
T (K)	551.37	555.15	0.68
Conversion	0.622	-	-
W (g)	719.72	720.0	0.04

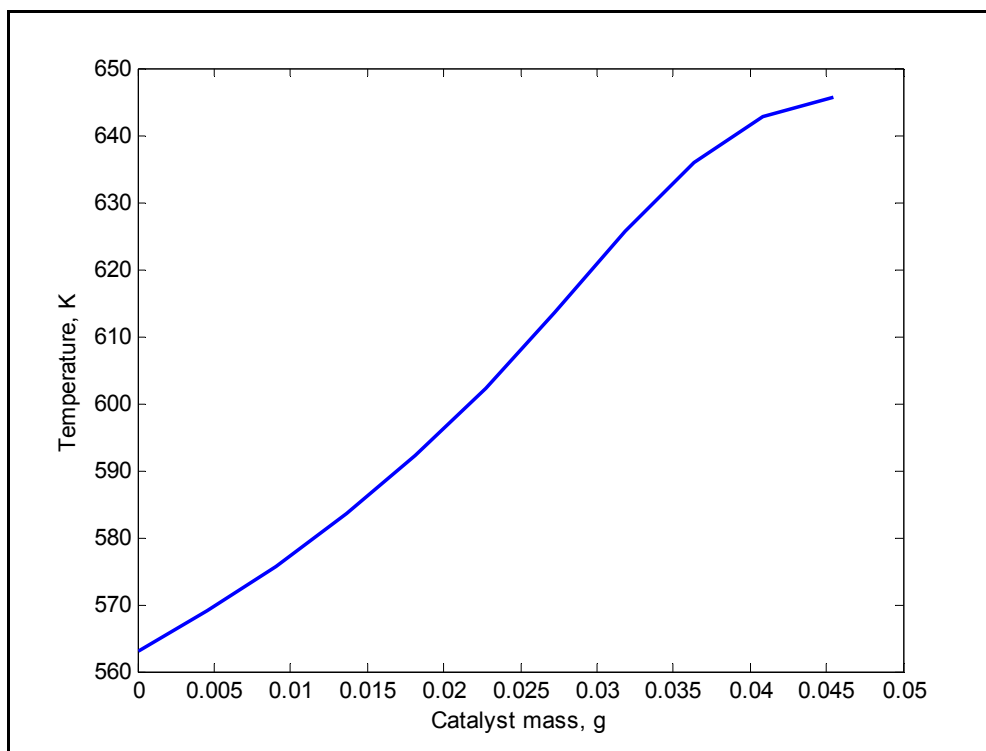


Figure 4.27. Temperature of bulk gas (K) versus catalyst mass (g) for HTS
(Pt-CeO₂-Al₂O₃)

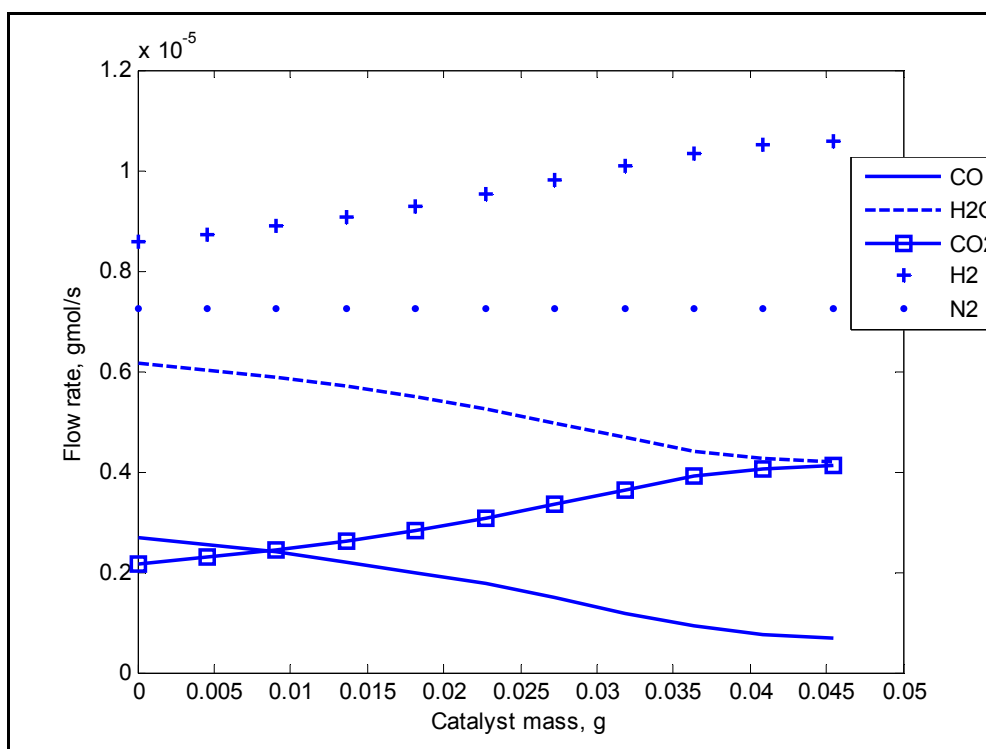


Figure 4.28. Flow rate of components in bulk gas (gmol s^{-1}) versus catalyst mass (g) for HTS (Pt-CeO₂-Al₂O₃)

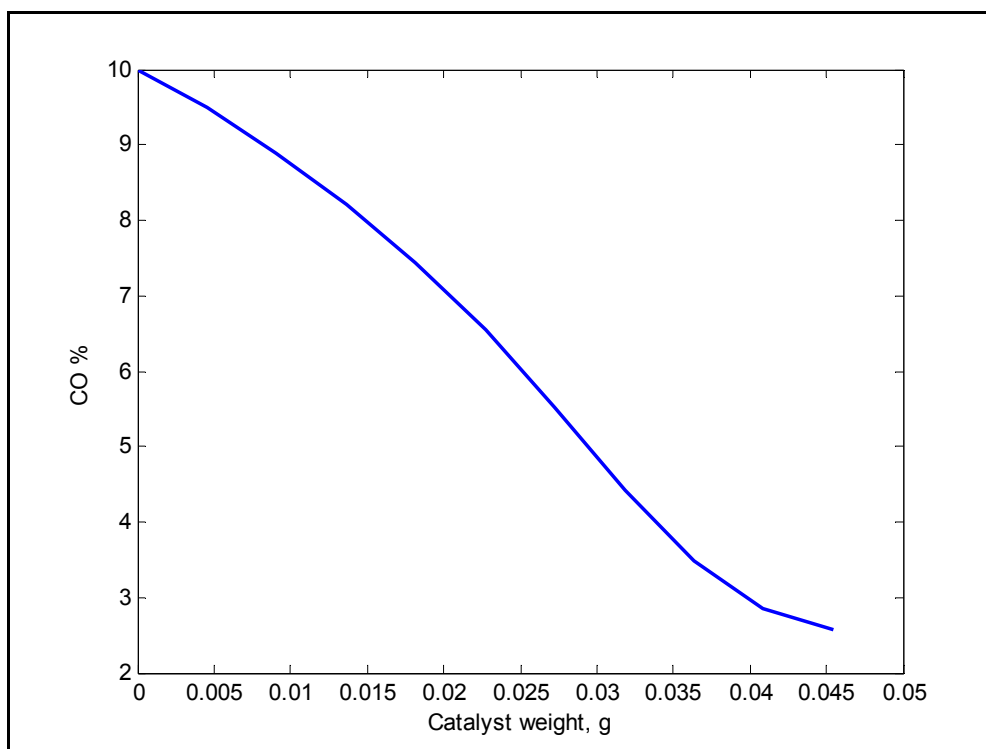


Figure 4.29. CO per cent of the bulk gas versus catalyst mass (g) for HTS (Pt-CeO₂-Al₂O₃)

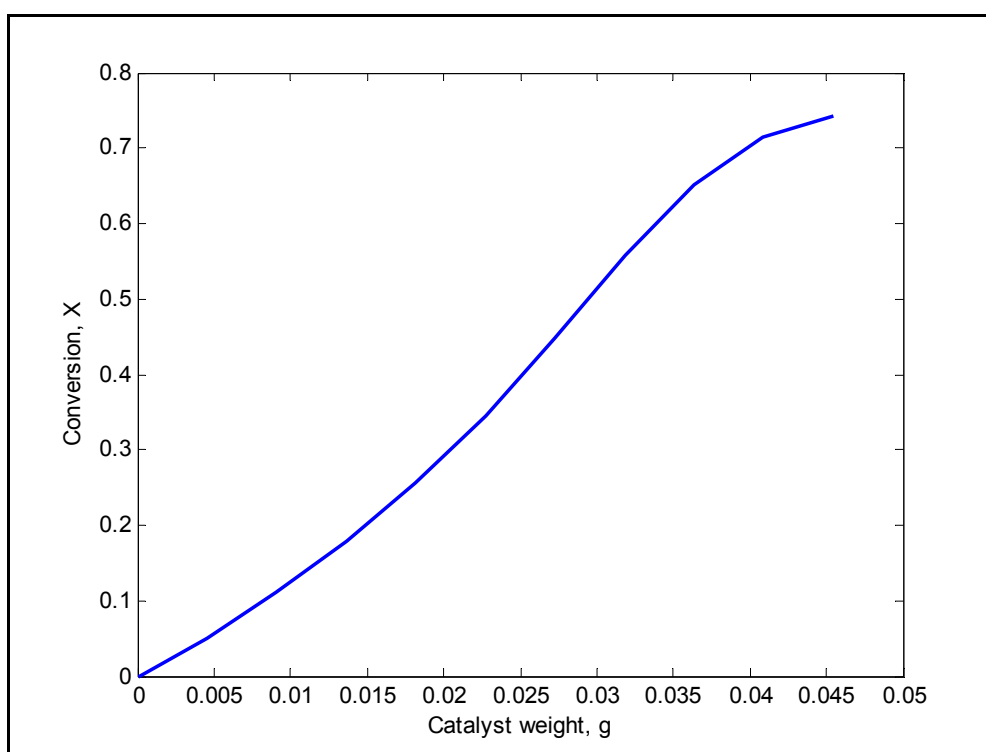


Figure 4.30. Conversion of CO versus catalyst mass (g) for HTS
(Pt-CeO₂-Al₂O₃)

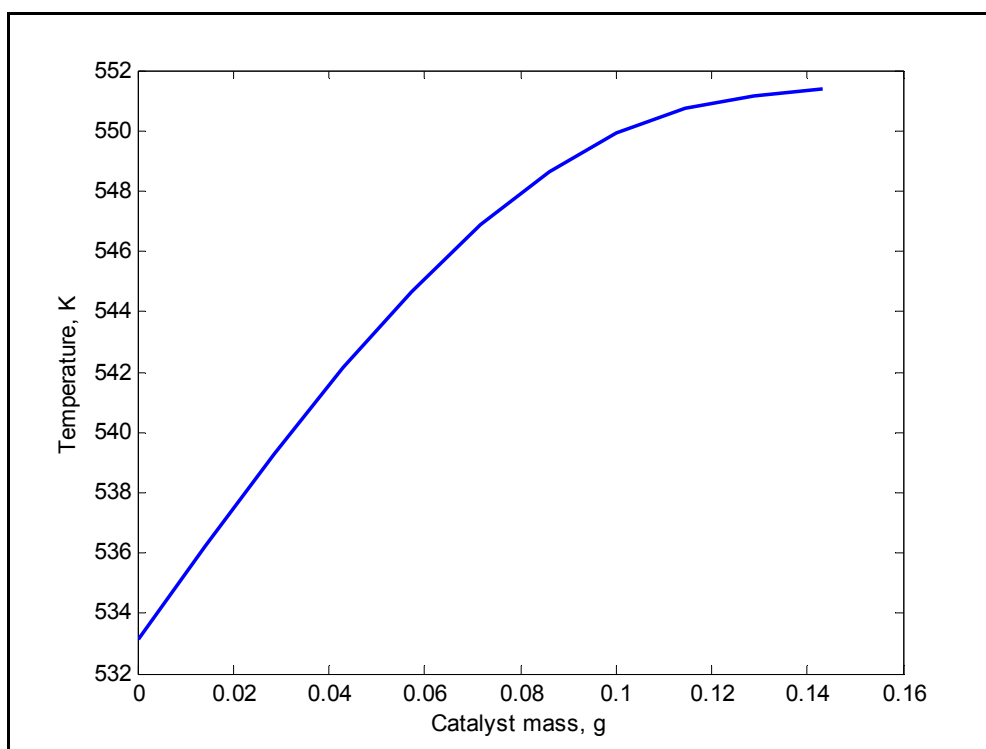


Figure 4.31. Temperature of bulk gas (K) versus catalyst mass (g) for LTS
(Pt-CeO₂-Al₂O₃)

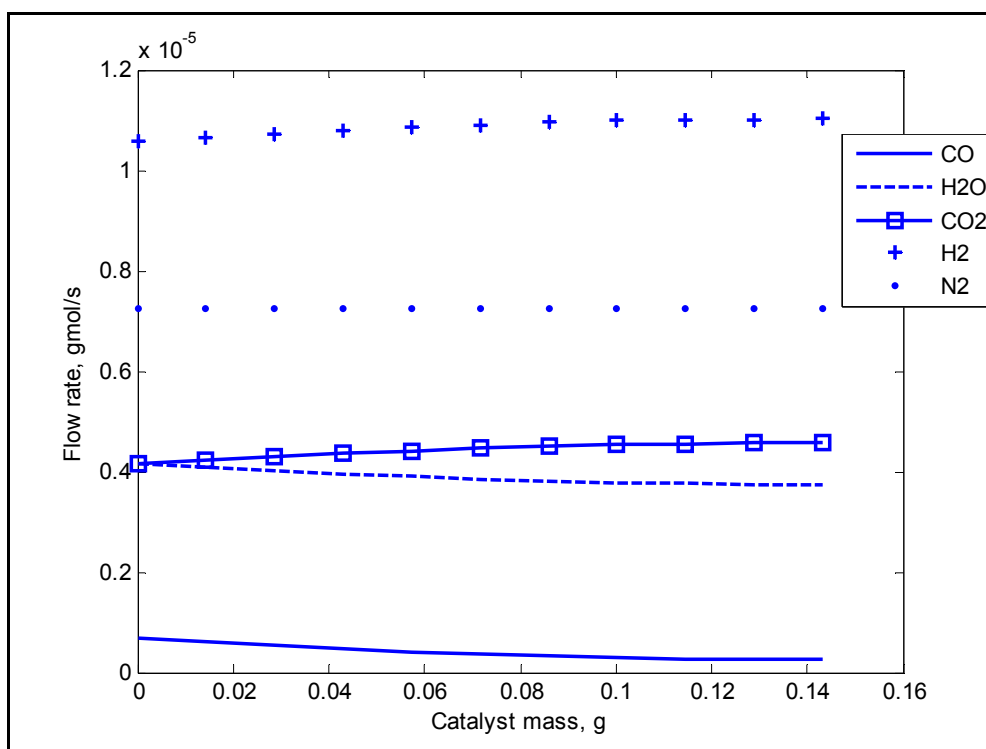


Figure 4.32. Flow rate of components in bulk gas (gmol s^{-1}) versus catalyst mass (g) for LTS (Pt-CeO₂-Al₂O₃)

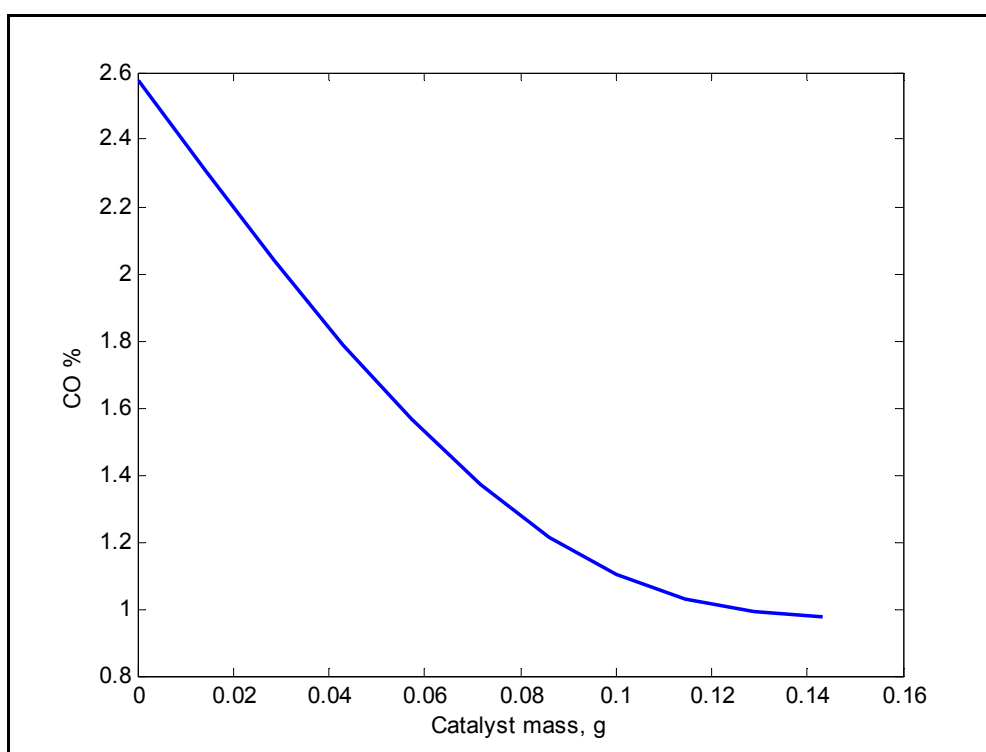


Figure 4.33. CO per cent of the bulk gas versus catalyst mass (g) for LTS (Pt-CeO₂-Al₂O₃)

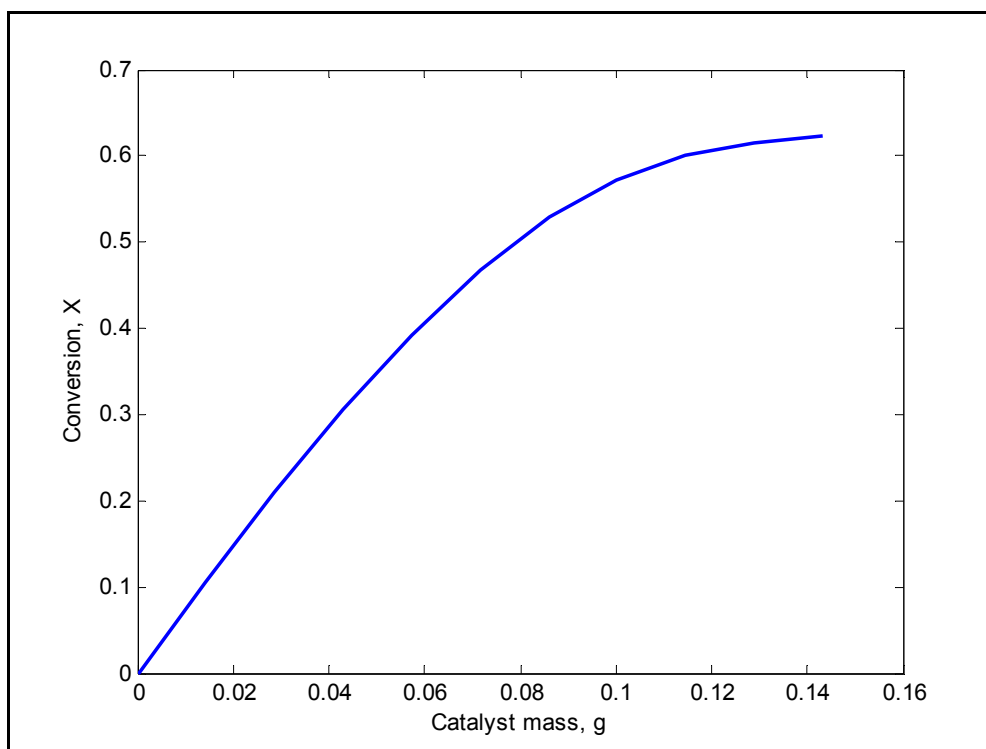


Figure 4.34. Conversion of CO versus catalyst mass (g) for LTS
(Pt-CeO₂-Al₂O₃)

The same conditions given above for the LTS reactor are applied to Cu-ZnO-Al₂O₃ catalyst instead of Pt-CeO₂-Al₂O₃ for the same conversion level of 0.622, and the monolith length is determined as 6.30 cm for a diameter of 10 cm using the power function rate expression used with Data Sets 2 and 3 (**Table 4.20**).

Table 4.20. Determination of the monolith length for the monolith LTS reactor
(Cu-ZnO-Al₂O₃)

Length of monolith (cm)	L_m	6.30
Diameter of monolith (cm)	D_m	10.00
L_m / D_m	—	0.63
Volume of monolith (cm³)	V	494.80
Calculated catalyst mass / channel (g/channel)	W_c	0.0284
Given catalyst mass / channel (g/channel)	W_g	0.1432
Error per cent for catalyst mass	%	80.17

In **Table 4.21**, the product gas composition and the outlet temperature of the LTS reactor, the CO conversion and the calculated catalyst mass obtained by the present simulation are given for Pt and Cu-based catalyst separately. For the same conversion, less amount of Cu-ZnO-Al₂O₃ catalyst is found out to be enough, when it is compared with Pt-CeO₂-Al₂O₃ catalyst. As a result, the monolith length decreases from 39.40 cm to 6.30 cm and the monolith volume decreases from 3094 cm³ to 495 cm³. Since the outlet temperature for the Pt-based catalyst is very close to that for the Cu-based catalyst, the difference in the amount of the catalyst mass is likely to be due to the higher activity of Cu-based catalyst. The pressure drop along the monolith calculated by the Equation 3.10 is found to be 1.4×10^{-8} atm, which is negligible. The temperature, component flow, CO level and CO conversion profiles for the Cu-based catalyst are presented in **Figure 4.35–Figure 4.38**.

Table 4.21. Comparison of product gas compositions for Pt and Cu-based catalysts

	Cu-based Catalyst	Pt-based Catalyst	Difference between Pt and Cu-based Catalysts (%)
y CO %	0.973	0.974	0.001
y H₂O %	13.936	13.937	0.000
y CO₂ %	17.027	17.026	0.000
y H₂ %	41.027	41.027	0.000
y N₂ %	27.037	27.037	0.000
T (K)	551.38	551.37	0.00
Conversion	0.622	0.622	0.000
W (g cat)	142.74	719.72	80.17

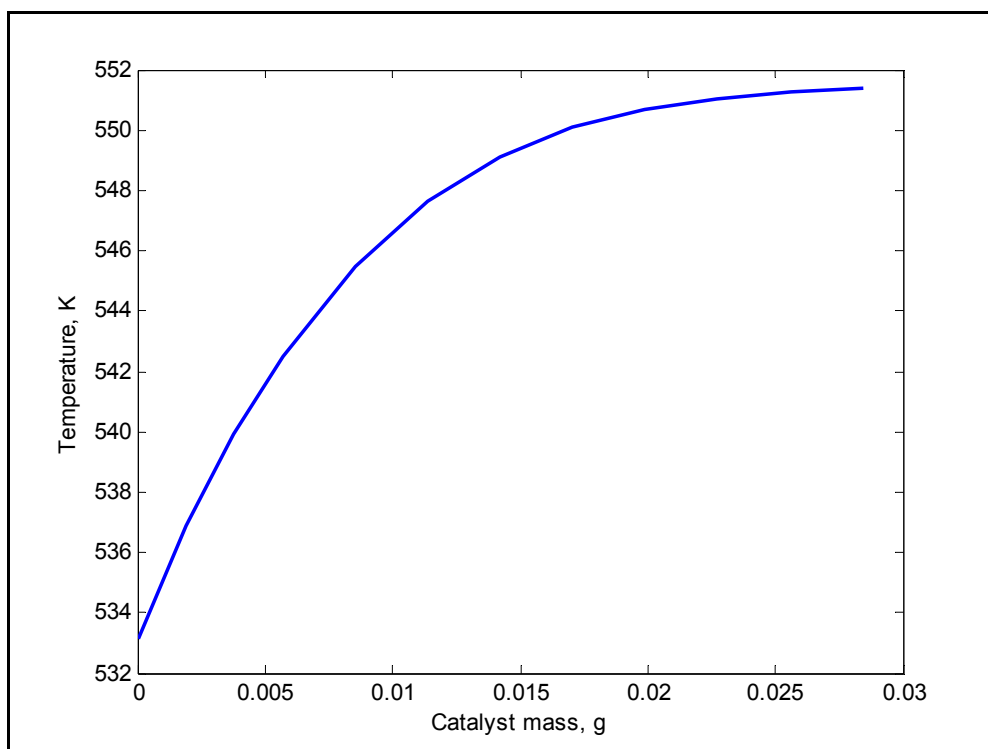


Figure 4.35. Temperature of bulk gas (K) versus catalyst mass (g)
(Cu-ZnO-Al₂O₃)

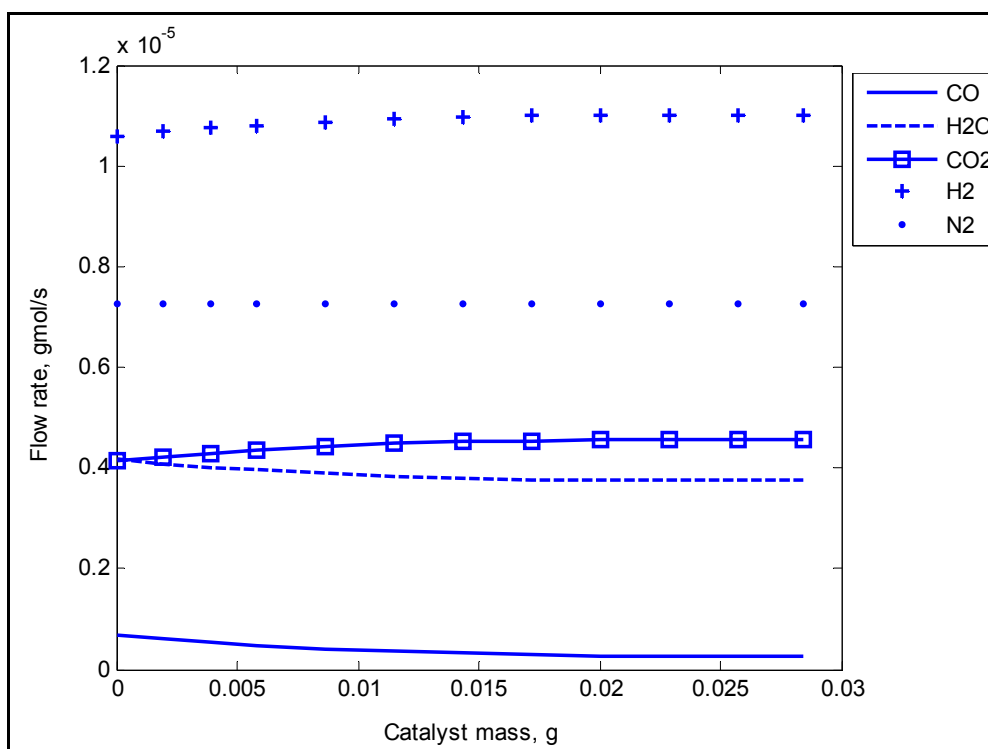


Figure 4.36. Flow rate of components in bulk gas (gmol s⁻¹) versus catalyst mass (g)
(Cu-ZnO-Al₂O₃)

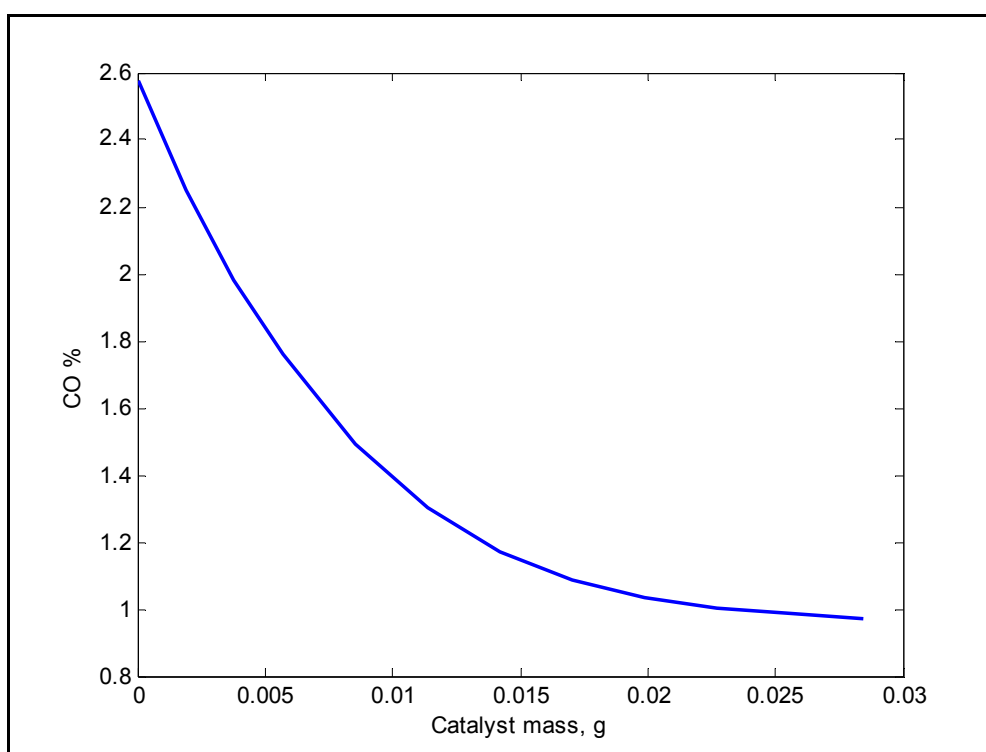


Figure 4.37. CO per cent of the bulk gas versus catalyst mass (g)
(Cu-ZnO-Al₂O₃)

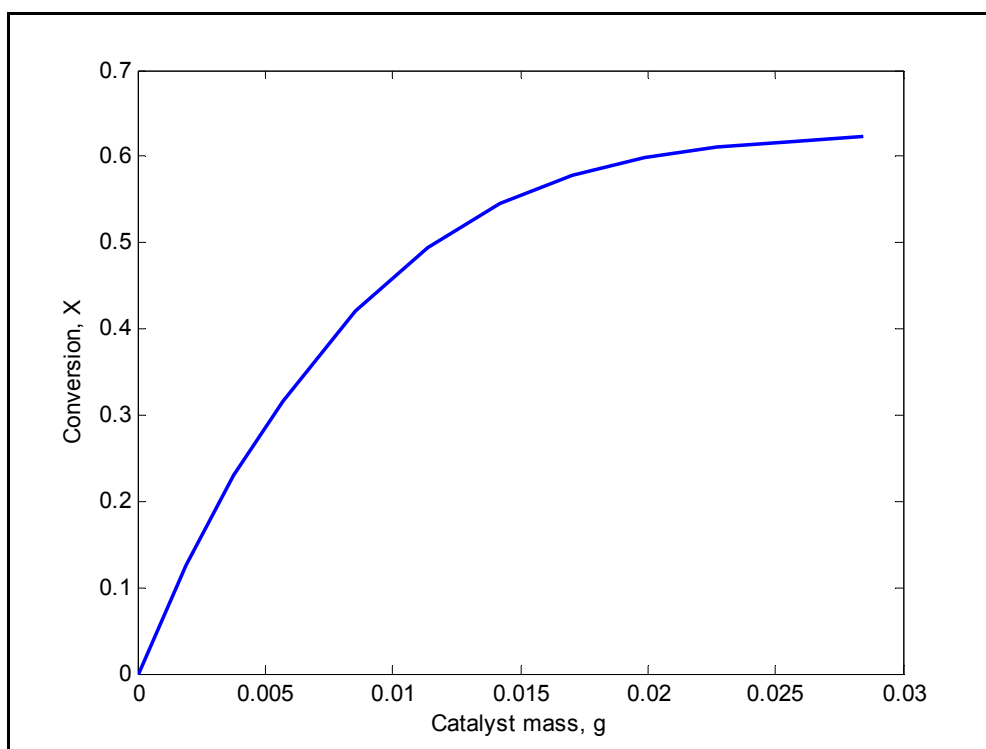


Figure 4.38. Conversion of CO versus catalyst mass (g)
(Cu-ZnO-Al₂O₃)

The mass and energy balance equations are based on the catalyst mass so far and they are converted to the catalyst length basis to compare the results. For Pt-CeO₂-Al₂O₃, the LTS reaction is simulated by applying the same monolith and reactor geometry given in **Table 4.14**. The diameter of the monolith is 10 cm and the length of the monolith is taken as 39.40 cm, as calculated in the previous simulations (**Table 4.18**). 0.04 per cent and 1.08 per cent error are calculated for the amount of catalyst required and for the outlet temperature of the LTS reactor, respectively.

When the results of the simulations based on the monolith length and the monolith mass are compared in **Table 4.22** for the same amount of the monolith and the reactor dimensions, less CO conversion is obtained for the length-based modeling. The mole fraction of CO in the product gas is 20.42 per cent higher due to the less conversion. The outlet temperature is also less than the value obtained for the mass-based modeling. The temperature, component flow, CO level and CO conversion profiles for the Cu-based catalyst are presented in **Figure 4.39–Figure 4.42**.

Table 4.22. Comparison of the results obtained for the model equations based on monolith mass and monolith length (Pt-CeO₂-Al₂O₃)

	Length-based Modeling	Mass-based Modeling	Difference %	Quiney et al. [53]	Error % Length-based Model	Error % Mass-based Model
y CO %	1.173	0.974	20.42	-	-	-
y H₂O %	14.135	13.937	1.43	-	-	-
y CO₂ %	16.828	17.026	1.17	-	-	-
y H₂ %	40.828	41.027	0.48	-	-	-
y N₂ %	27.037	27.037	0.00	-	-	-
T (K)	549.13	551.37	0.41	555.15	1.08	0.68
Conversion	0.545	0.622	12.40	-	-	-
W (g)	719.74	719.72	0.00	720.0	0.04	0.04

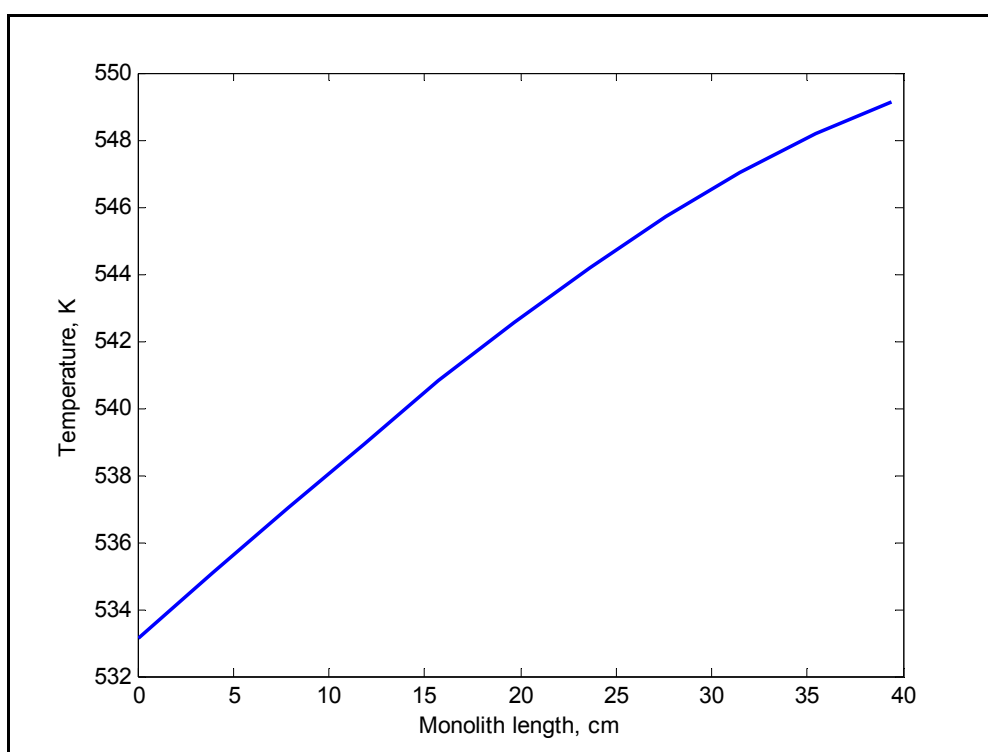


Figure 4.39. Temperature of bulk gas (K) versus catalyst mass (g)
(Pt-CeO₂-Al₂O₃)

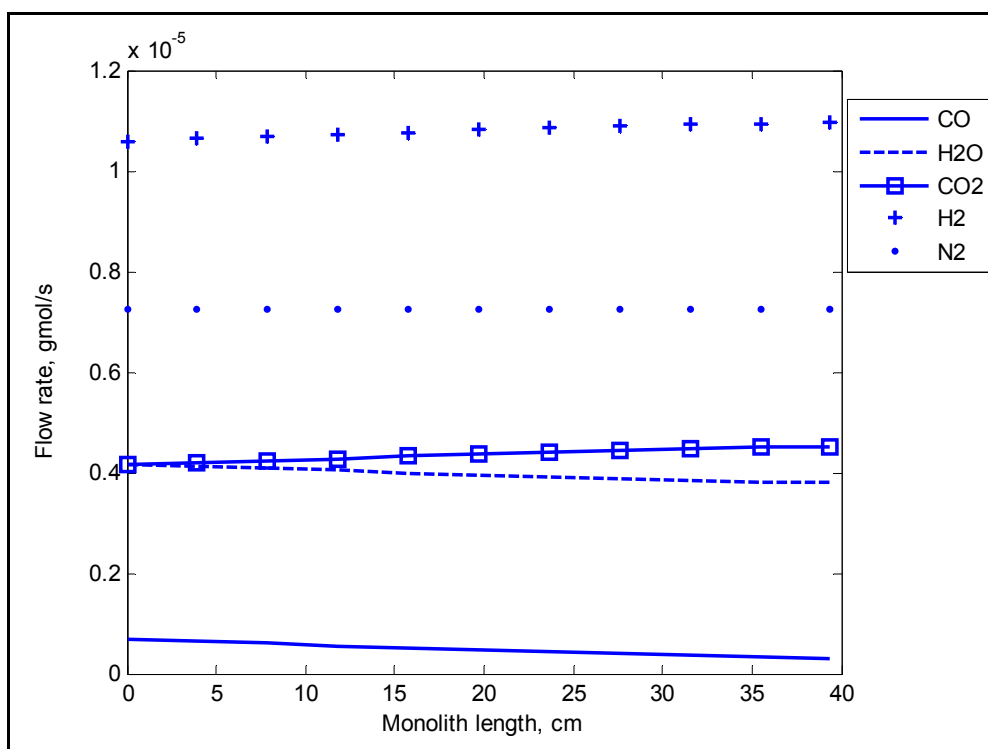


Figure 4.40. Flow rate of components in bulk gas (gmol s⁻¹) versus catalyst mass (g)
(Pt-CeO₂-Al₂O₃)

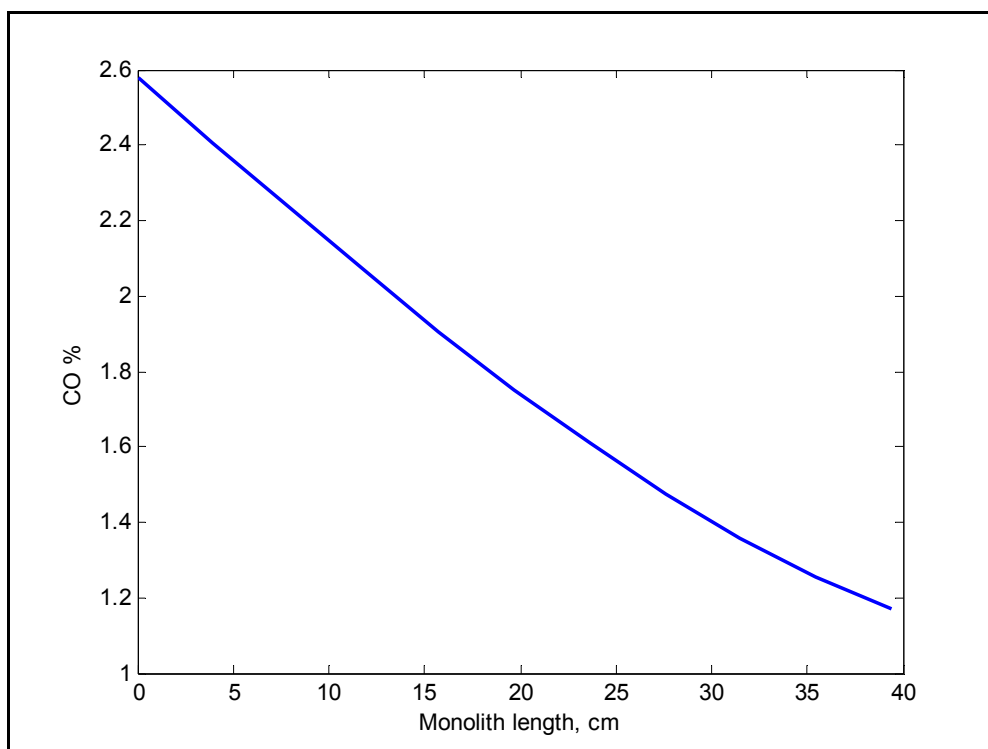


Figure 4.41. CO per cent of the bulk gas versus catalyst mass (g)
(Pt-CeO₂-Al₂O₃)

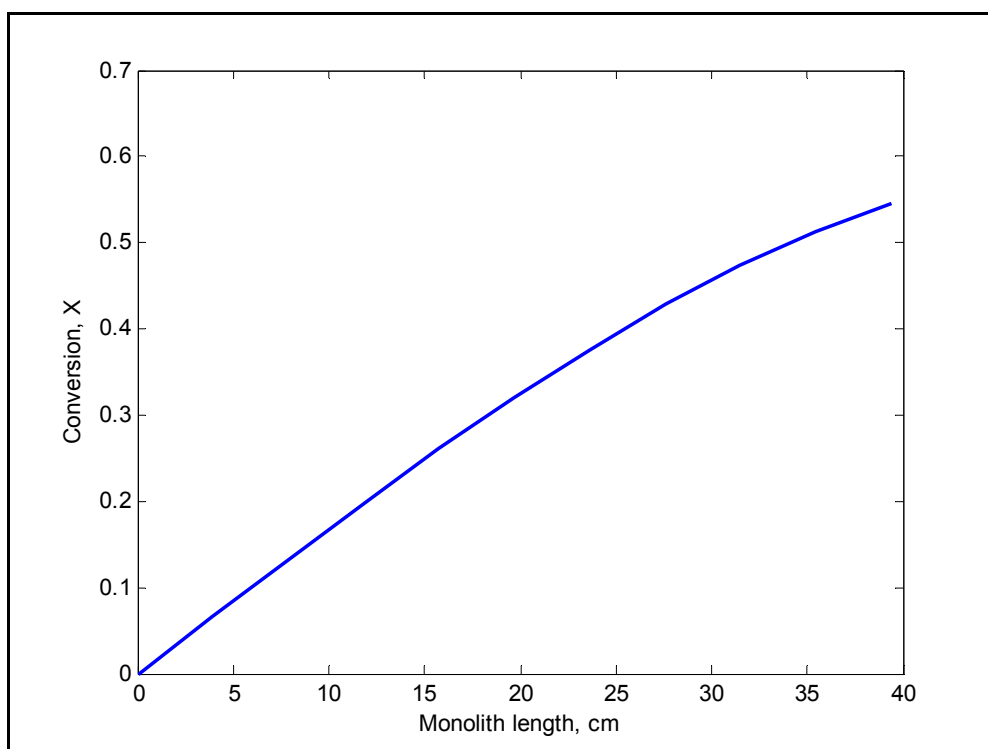


Figure 4.42. Conversion of CO versus catalyst mass (g)
(Pt-CeO₂-Al₂O₃)

4.2.1.2. Data Set 3 and Power Function Kinetic Model for Cu-ZnO-Al₂O₃: In this section, data taken from Tan [51] are applied to a monolith reactor instead of a packed-bed reactor by using the pseudo-homogeneous model. The aim of this is to find out the required monolith catalyst dimensions for 0.80 CO conversion and the results are given in **Table 4.23**. A monolith with a diameter of 12 cm and a length of 22.90 cm, which gives a total catalyst mass of 748.23 g, can be used in case of a monolith reactor to obtain the same conversion.

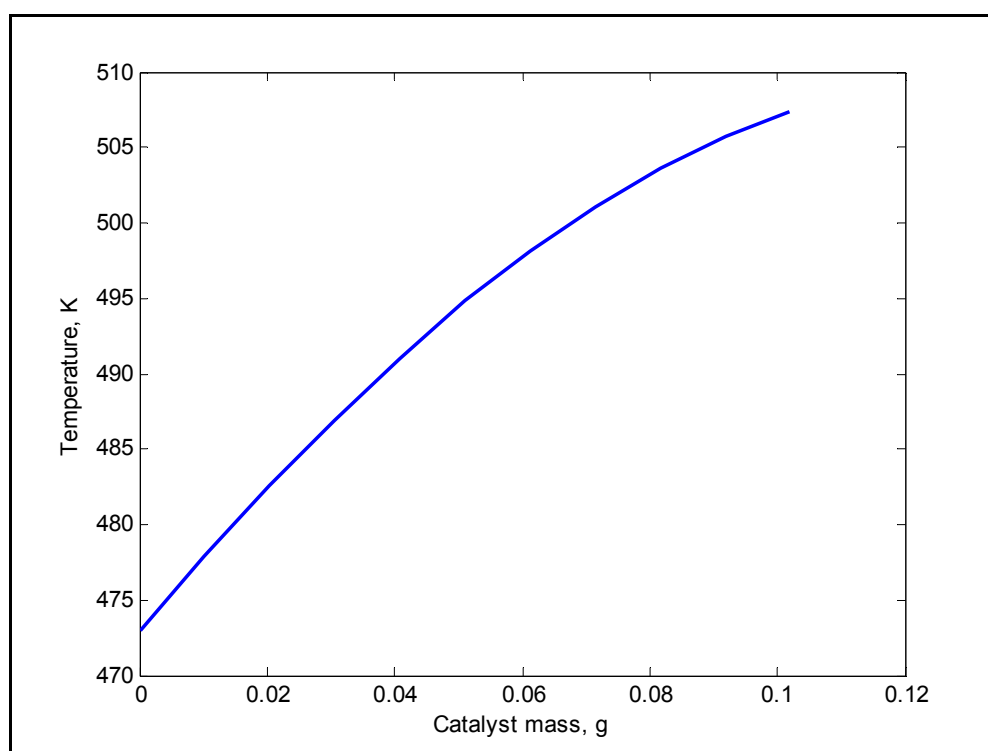
Table 4.23. Determination of the monolith geometry for LTS reactor (Data Set 3)

Length of monolith (cm)	L_m	12.00
Diameter of monolith (cm)	D_m	22.60
L_m / D_m	—	1.88
Volume of monolith (cm³)	V	2556
Catalyst mass calculated / channel for Cu (g/channel)	W_c	0.1020
Total number of channels	c	7238
Total catalyst mass	W	738.43

The results of the simulations for the LTS reaction in a monolith reactor are given in **Table 4.24**. The calculated values are very close to the given data except 2.62 per cent difference in the mole fraction of CO₂ in the product gas. The pressure drop along the monolith is found to be 3.1×10^{-8} atm, which is negligible. The temperature, component flow, CO level and CO conversion profiles for the Cu-based catalyst are presented in **Figure 4.43–Figure 4.46**.

Table 4.24. The properties of the product gas leaving the LTS reactor (Data Set 3)

	Present Study Monolith Simulation	Tan [51] Packed- bed Simulation	Difference %
y CO %	0.756	0.759	0.43
y H₂O %	17.453	17.498	0.26
y CO₂ %	9.639	9.393	2.62
y H₂ %	29.284	29.363	0.27
y CH₄ %	6.401	6.419	0.27
y N₂ %	36.468	36.568	0.27
T (K)	507.42	510.00	0.51
Conversion	0.796	0.796	0.04

**Figure 4.43.** Temperature of bulk gas (K) versus catalyst mass (g)
(Data Set 3)

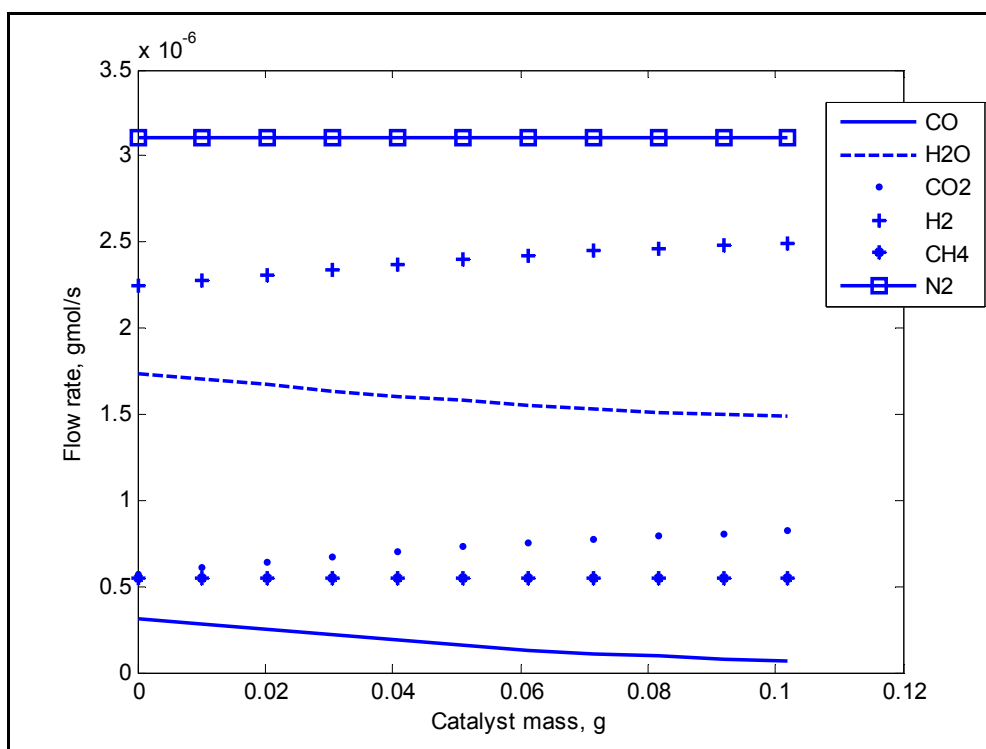


Figure 4.44. Flow rate of components in bulk gas (gmol s^{-1}) versus catalyst mass (g)
(Data Set 3)

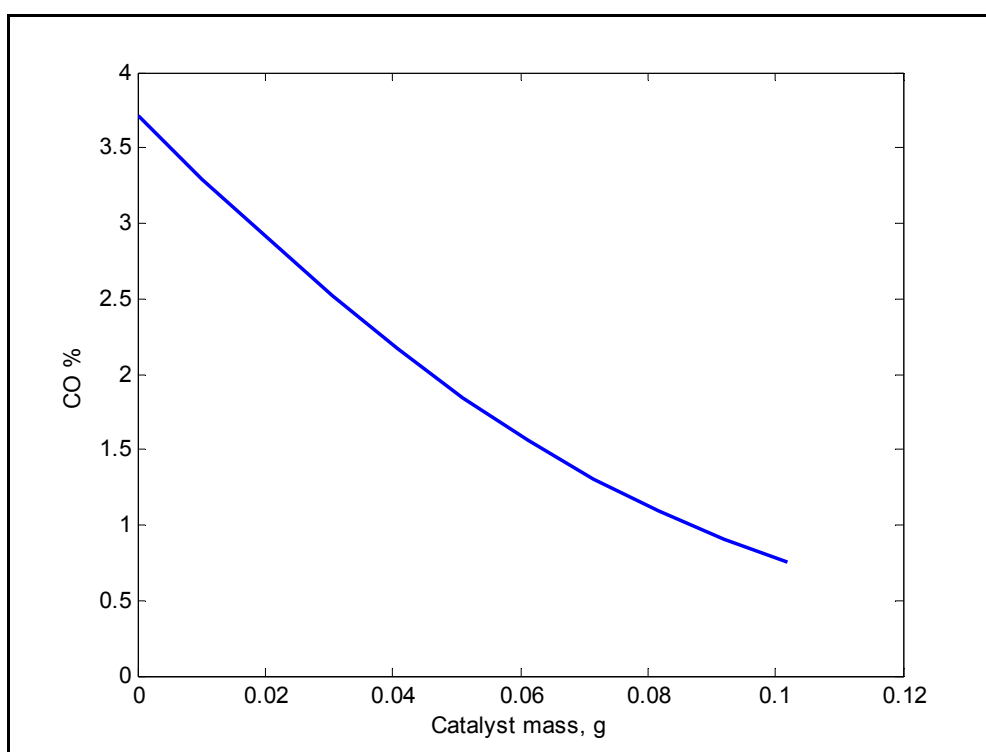


Figure 4.45. CO per cent of the bulk gas versus catalyst mass (g)
(Data Set 3)

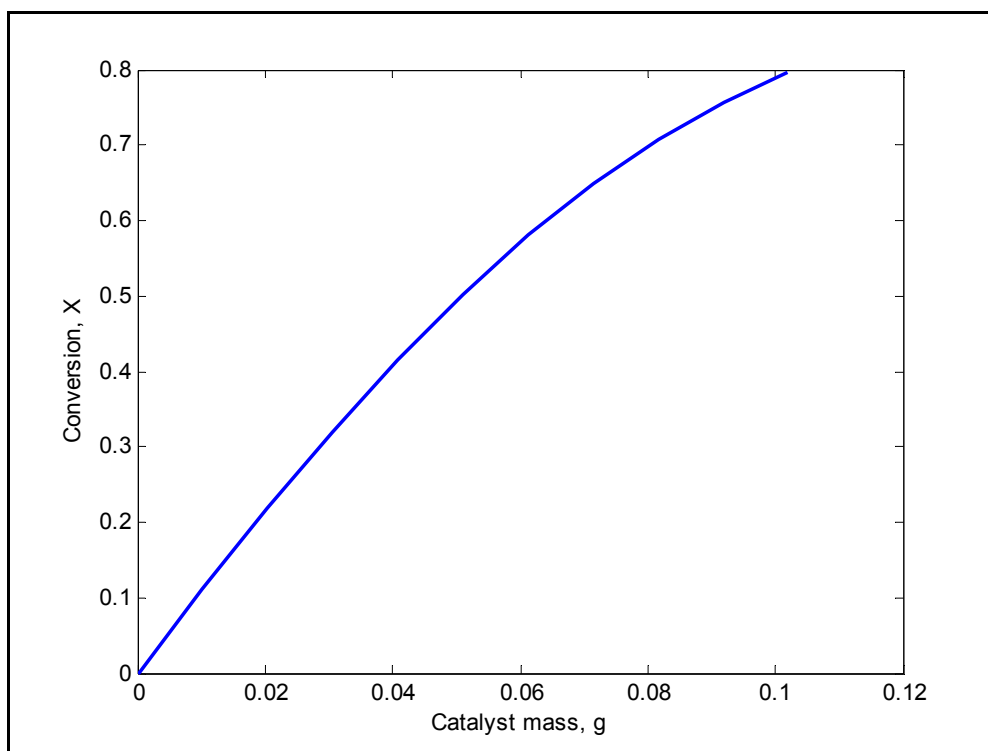


Figure 4.46. Conversion of CO versus catalyst mass (g)
(Data Set 3)

4.3. Comparison of Packed-Bed and Monolith Reactors

Data taken from the work of Tan [51] are used in the simulations for both packed-bed and monolith reactors by applying pseudo-homogeneous model together with a power function kinetic model, and the results obtained in the two cases are compared in **Table 4.25**. For both reactors, the CO conversion, the product gas composition and the outlet temperature are the same. The pressure drop is negligible for the monolith reactor, while the pressure of bulk gas at the reactor outlet drops from 0.9869 atm to 0.9431 atm in the packed-bed reactor. The amount of the catalyst used in the monolith reactor is 31.55 g less than that used in the packed-bed reactor, but the volume of the packed-bed reactor is 1884.18 cm³ less than that of the monolith reactor. Although the amount of the catalyst used in the monolith reactor is less, the reason for its higher volume is that the bulk catalyst density of the monolith is smaller due to the presence of the channels.

Table 4.25. Comparison of packed-bed and monolith reactors for pseudo-homogeneous model (Data Set 3)

LTS Outlet Properties	Pseudo-homogeneous model-Packed-bed reactor	Pseudo-homogeneous model-Monolith reactor
y CO %	0.756	0.756
y H₂O %	17.453	17.453
y CO₂ %	9.639	9.639
y H₂ %	29.284	29.284
y CH₄ %	6.401	6.401
y N₂ %	36.468	36.468
T (K)	507.42	507.42
P (atm)	0.9431	-
Conversion	0.7962	0.7962
W (g)	770.00	738.45
V (cm³)	671.82	2556.00

4.4. Comparison of Pseudo-Homogeneous and Heterogeneous Models

Data taken from the study by Francesconi et al. [43] are used in the simulations of the LTS reaction in the packed-bed reactor by applying pseudo-homogeneous and heterogeneous models separately. The results obtained for the same catalyst bed volume in both models are given in **Table 4.26**. The calculated amount of the catalyst is the same for both models, since the same catalyst is used and its solid density and porosity values do not change. The CO conversion, the product gas composition, the outlet temperature and the outlet pressure are almost the same for both models, which shows that the external heat transfer effects are negligible in the case of reactions with relatively mild heat effects.

Table 4.26. Comparison of pseudo-homogeneous and heterogeneous models for packed-bed reactor (Data Set 2)

LTS Outlet Properties	Pseudo-homogeneous model- Packed-bed reactor	Heterogeneous model- Packed-bed reactor
y CO %	0.259	0.259
y H₂O %	24.172	24.172
y CO₂ %	18.703	18.703
y H₂ %	51.191	51.191
y CH₄ %	5.676	5.676
T (K)	489.49	489.53
P (atm)	0.9636	0.9636
Conversion	0.9676	0.9675
W (g)	1680.91	1680.91
V (cm³)	1460	1460

Data taken from Tan [51] are also used in LTS simulations in the packed-bed reactor by applying both pseudo-homogeneous and heterogeneous models separately and these results are compared in **Table 4.27**. For the same amount of the catalyst used in the reactor, the CO conversion, the product gas composition, the outlet temperature and the outlet pressure are almost the same for both models, which again shows that the external heat transfer effects are negligible in LTS converters.

Table 4.27. Comparison of pseudo-homogeneous and heterogeneous models for packed-bed reactor (Data Set 3)

LTS Outlet Properties	Pseudo-homogeneous model- Packed-bed reactor	Heterogeneous model- Packed-bed reactor
y CO %	0.756	0.755
y H₂O %	17.453	17.452
y CO₂ %	9.639	9.640
y H₂ %	29.284	29.284
y CH₄ %	6.401	6.401
y N₂ %	36.468	36.468
T (K)	507.42	507.48
P (atm)	0.9431	0.9430
Conversion	0.7962	0.7964
W (g)	770.00	770.00
V (cm³)	671.82	671.82

5. CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

In this thesis, steady-state mathematical modeling of the water-gas shift reaction is studied in packed-bed and monolith reactors by applying the one-dimensional pseudo-homogeneous model to both reactor types and the one-dimensional heterogeneous model only to the packed-bed reactor at steady-state. Reactor dimensions, catalyst properties, kinetic rate equations and other relevant data used in the simulations are taken from the literature [43, 50, 51, 53]. Mathematical models are developed by writing the appropriate mass, energy and momentum balances and MATLABTM numerical computation software is used to solve these ODEs simultaneously by using the boundary conditions to calculate the required catalyst mass for the desired conversion to keep the CO amount in the WGS reactor downstream less than 1 per cent. The major conclusions that can be drawn from this study are given below:

- For Data Set 1, the results obtained by the MATLAB code written match very well with those given in the related paper, which means that the mathematical models developed by applying one-dimensional pseudo-homogeneous model for the packed-bed reactor are correct and the code runs properly.
- One-dimensional heterogeneous model including both external and internal mass and energy transport had been applied to the packed-bed reactor of Data Set 2. In this thesis, both the one-dimensional pseudo-homogeneous model and the heterogeneous model considering only external heat transfer are both applied to Data Set 2, and the comparison of the simulation results of these two models are found to be very close to each other as well as to the results reported in the original paper, which shows that the use of a pseudo-homogeneous reactor model gives results similar to a heterogeneous model, since the LTS reaction is only mildly exothermic and the external heat transfer resistances are not appreciable. The same conclusion is also

obtained from the results of the simulations based on Data Set 3, where the one-dimensional pseudo-homogeneous model was originally used.

- The one-dimensional heterogeneous model accounting for both interphase and intraparticle mass and heat transfer effect had been applied to the monolith reactor of Data Set 4. In this thesis, the one-dimensional pseudo-homogeneous model is applied to the monolith reactor by using the same Data Set 4 and approximately the same amount of catalyst; the outlet temperatures obtained are found to be very similar, indicating that the use of a pseudo-homogeneous reactor model to describe micro-channel behavior gives results similar to a heterogeneous model, since the LTS reaction is only mildly exothermic and the external heat transfer resistances are not appreciable.
- Data Set 3, which is used in the modeling of a packed-bed reactor, is also used for the one-dimensional pseudo-homogeneous modeling of a monolith reactor. The catalyst requirement of the monolith reactor is 31.55 g less than that calculated for the packed-bed reactor; but the volume of the packed-bed reactor is about 1884 cm³ or 1.88 L less than that of the monolith reactor. Although the amount of the catalyst used in the monolith reactor is less, the reason for its higher volume is that the bulk catalyst density of the monolith is much smaller due to the presence of the channels.
- For Data Set 4; when the mathematical equations derived for monolith reactors on a catalyst mass basis are converted to monolith length basis, the conversions calculated deviate by about 12 per cent, which directly causes approximately 20 per cent difference in the downstream CO level. This is likely to result from the uncertainty about the definitions of the monolith parameters, which are used in the conversion.
- The WGS performance of the monolith reactor is simulated for both Pt-based and Cu-based catalysts, and the simulation results indicate that the Cu-based catalyst is found to be more active than Pt-based catalyst.
- Pressure drop occurs along the catalyst bed in the packed-bed reactor due to the presence of packing while the pressure drop along the monolith reactor is negligible.

5.2. Recommendations

The following studies can be made to improve or modify the mathematical models used in the present work:

- The mathematical models developed for the packed-bed reactor can be modified to include terms describing the behavior of membrane reactors for further comparison.
- Considering that the flow regime in micro-channels of the monolith is laminar, heterogeneous models with relevant diffusional resistances can be developed for use with reactions involving more drastic heat effects.

APPENDIX A: PHYSICAL PROPERTIES OF THE SPECIES

Heat Capacity of Species [54]

Table A. 1. Constants for the heat capacity equation

	CO	H ₂ O	CO ₂	H ₂	CH ₄	N ₂
C1	3.376	3.470	5.457	3.249	1.702	3.280
C2	0.557×10^{-3}	1.450×10^{-3}	1.045×10^{-3}	0.422×10^{-3}	9.081×10^{-3}	0.593×10^{-3}
C3	0	0	0	0	-2.164×10^{-6}	0
C4	-0.031×10^5	0.121×10^5	-1.157×10^5	0.083×10^5	0	0.040×10^5

$$Cp_i = (C1_i + C2_i \times T + C3_i \times T^2 + C4_i \times T^{-2}) \times R \quad (\text{A } 1)$$

Heat Capacity of Bulk Fluid [56]

$$Cp_f = \sum_i Cp_i \times y_i \quad (\text{A } 2)$$

Enthalpy of Reaction [54]

Constants for the heat of reaction equation

$$dC1 = \frac{d}{a} C1_{H_2} + \frac{c}{a} C1_{CO_2} - \frac{b}{a} C1_{H_2O} - \frac{a}{a} C1_{CO} \quad (\text{A } 3)$$

$$dC2 = \frac{d}{a} C2_{H_2} + \frac{c}{a} C2_{CO_2} - \frac{b}{a} C2_{H_2O} - \frac{a}{a} C2_{CO} \quad (\text{A } 4)$$

$$dC3 = \frac{d}{a} C3_{H_2} + \frac{c}{a} C3_{CO_2} - \frac{b}{a} C3_{H_2O} - \frac{a}{a} C3_{CO} \quad (\text{A } 5)$$

$$dC4 = \frac{d}{a}C4_{H_2} + \frac{c}{a}C4_{CO_2} - \frac{b}{a}C4_{H_2O} - \frac{a}{a}C4_{CO} \quad (A\ 6)$$

For LTS; $a = b = c = d = 1$

$$\Delta H^0(T_{ref}) = -41100\text{ J gmol}^{-1} \quad (A\ 7)$$

$$T_{ref} = 298.15\text{ K} \quad (A\ 8)$$

$$\Delta H_{Rxn} = \Delta H^0(T_{ref}) + R \times \left[dC1 \times (T - T_{ref}) + \frac{dC2}{2} \times (T^2 - T_{ref}^2) + (-dC4) \times \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right] \quad (A\ 9)$$

Ideal Gas Gibbs Energy of Species [55]

Table A. 2. Constants for the Gibbs energy equation

	CO	H ₂ O	CO ₂	H ₂	CH ₄
G1	-110.73	-240.47	-393.47	0	-70.372
G2	-0.0866	0.0342	-0.0032	0	0.048
G3	-9×10^{-6}	2×10^{-5}	2×10^{-7}	0	7×10^{-5}
G4	8×10^{-9}	-1×10^{-8}	9×10^{-10}	0	-4×10^{-8}
G5	-2×10^{-12}	2×10^{-12}	-3×10^{-13}	0	8×10^{-12}

$$G_i^{ig} = G1_i + G2_i \times T + G3_i \times T^2 + G4_i \times T^3 + G5_i \times T^4 \quad (A\ 10)$$

Ideal Gas Gibbs Energy of Reaction [55]

$$G_{Rxn}^{ig} = \frac{d}{a}G_{H_2} + \frac{c}{a}G_{CO_2} - \frac{b}{a}G_{H_2O} - \frac{a}{a}G_{CO} \quad (A\ 11)$$

Viscosity of Species [56]

Table A. 3. Lennard-Jones parameters

	CO	CO₂	H₂	CH₄	N₂
Collision diameter, CD (Å)	3.590	3.996	2.915	3.780	3.667
Epsilon / Kappa, LJ (K)	110	190	38	154	99.8

$$LJ_a = LJ_{H_2} \quad (A\ 12)$$

$$LJ_b = (LJ_{CO} + LJ_{CO_2} + LJ_{CH_4} + LJ_{N_2}) / 4 \quad (A\ 13)$$

$$LJ_{ave} = (LJ_a \times LJ_b)^{0.5} \quad (A\ 14)$$

$$T^* = T / LJ_{ave} \quad (A\ 15)$$

$$\delta = \frac{1.16145}{T^{*0.14874}} + \frac{0.52487}{\exp(0.77320 \times T^*)} + \frac{2.16178}{\exp(2.43787 \times T^*)} \quad (A\ 16)$$

$$\mu_i = 2.6693 \times 10^{-5} \times \frac{\sqrt{M_i \times T}}{CD_i \times \delta} \quad (A\ 17)$$

$$\mu_{H_2O} = 1.73 \times 10^{-4} \quad [55] \quad (A\ 18)$$

Viscosity of Gas Mixture [56]

$$\Phi_{ab} = \frac{1}{\sqrt{8}} \times \left(1 + \frac{M_a}{M_b}\right)^{-1/2} \times \left[1 + \left(\frac{\mu a}{\mu b}\right)^{1/2} \times \left(\frac{M_a}{M_b}\right)^{1/4}\right]^2 \quad (A\ 19)$$

$$\mu_f = \sum_{i=1}^n \frac{y_i \times \mu_i}{\sum_j y_j \times \Phi_{ab}} \quad (\text{A } 20)$$

a = for H_2 , b = for mixture of CO , CO_2 , CH_4 and / or N_2

Diffusivity of Bulk Fluid [56]

$$CD_a = CD_{\text{H}_2} \quad (\text{A } 21)$$

$$CD_b = (CD_{\text{CO}} + CD_{\text{CO}_2} + CD_{\text{CH}_4} + CD_{\text{N}_2}) / 4 \quad (\text{A } 22)$$

$$CD_{ave} = \frac{CD_a + CD_b}{2} \quad (\text{A } 23)$$

$$CI_{ave} = \frac{1.06036}{T^{*0.15610}} + \frac{0.19300}{\exp(0.47635 \times T^*)} + \frac{1.03587}{\exp(1.52996 \times T^*)} + \frac{1.76474}{\exp(3.89411 \times T^*)} \quad (\text{A } 24)$$

$$D_{ab} = 0.0018583 \times \sqrt{T^3 \times \left(\frac{1}{M_a} + \frac{1}{M_b} \right)} \times \frac{1}{P \times CD_{ave}^2 \times CI_{ave}} \quad (\text{A } 25)$$

Effective Diffusivity of Bulk Fluid [42]

$$D_e = \frac{D_{ab} \times \varepsilon \times \sigma}{\tau} \quad (\text{A } 26)$$

Thermal Conductivity of Species [56]

$$\lambda_i = \left(Cp_i + \left(\left(\frac{5}{4} \right) \times R \right) \right) \times \left(\frac{\mu_i}{M_i} \right) \quad (\text{A } 27)$$

Thermal Conductivity of Bulk Fluid [43]

$$\lambda_f = \frac{\sum_i M_i \times y_i \times Cp_i}{\sum_i M_i \times y_i} \quad (\text{A } 28)$$

Dimensionless Numbers [44]

$$Sc = \frac{\mu_f}{\rho_b \times D_{ab}} \quad (\text{A } 29)$$

$$Pr = \frac{Cp_f \times \mu_f}{\lambda_f} \times \frac{1}{M_{ave}} \quad (\text{A } 30)$$

$$Re = \frac{D_p \times G}{\mu_f} \quad (\text{A } 31)$$

$$Nu = 2 + \left(1.1 \times Pr^{(1/3)} \times Re^{0.6} \right) \quad (\text{A } 32)$$

$$Sh = 2 + \left(1.1 \times Sc^{(1/3)} \times Re^{0.6} \right) \quad (\text{A } 33)$$

Heat and Mass Transfer Coefficients [44]

$$h_f = \frac{Nu \times \lambda_f}{D_p} \quad (\text{A } 34)$$

$$k_f = \frac{Sh \times D_{ab}}{D_p} \quad (\text{A } 35)$$

APPENDIX B: FIGURES

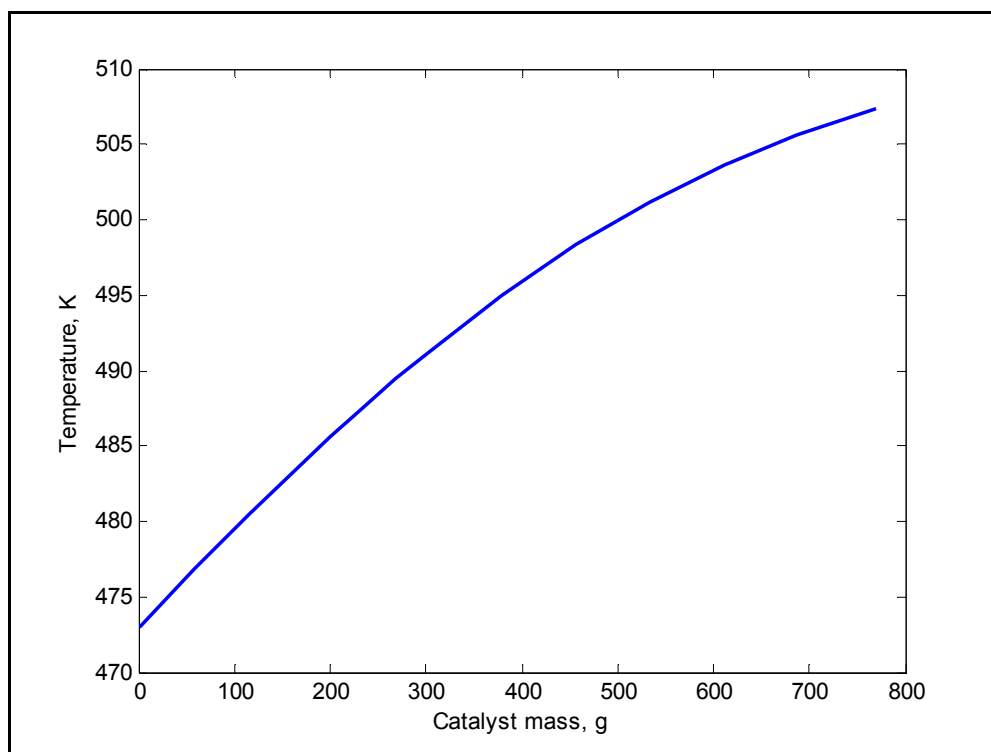


Figure B. 1. Temperature of bulk gas (K) versus catalyst mass (g)
(CO conversion = 0.80, Data Set 3, power-function pseudo-homogeneous model)

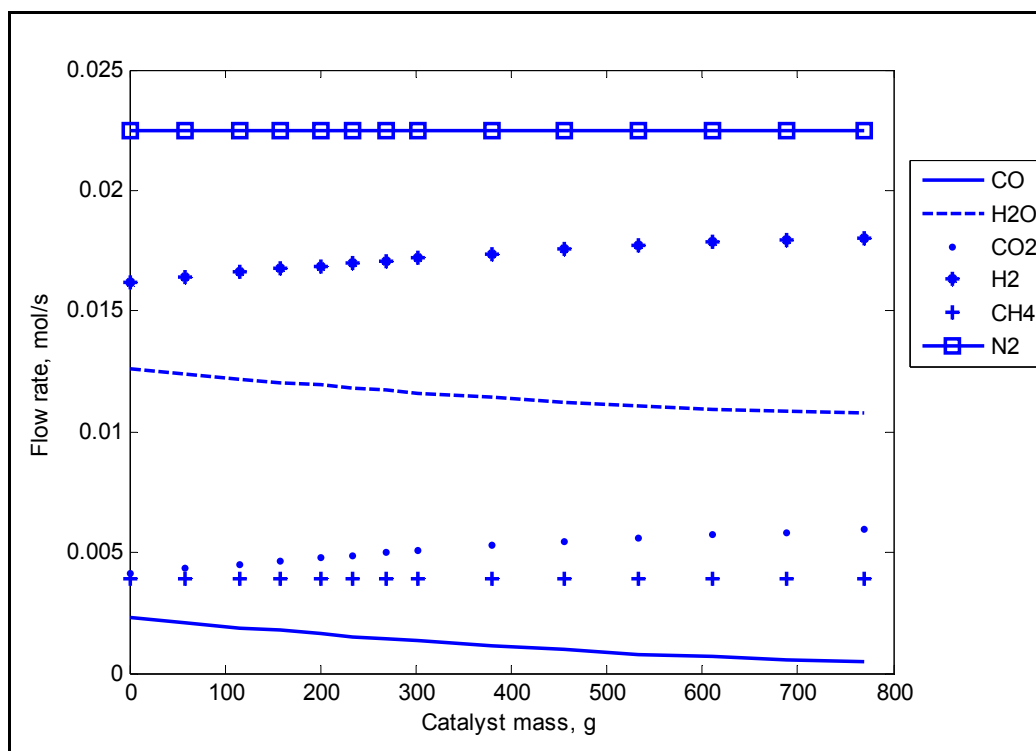


Figure B. 2. Flow rate of components in the bulk gas (gmol s^{-1}) versus catalyst mass (g) (CO conversion = 0.80, Data Set 3, power-function pseudo-homogeneous model)

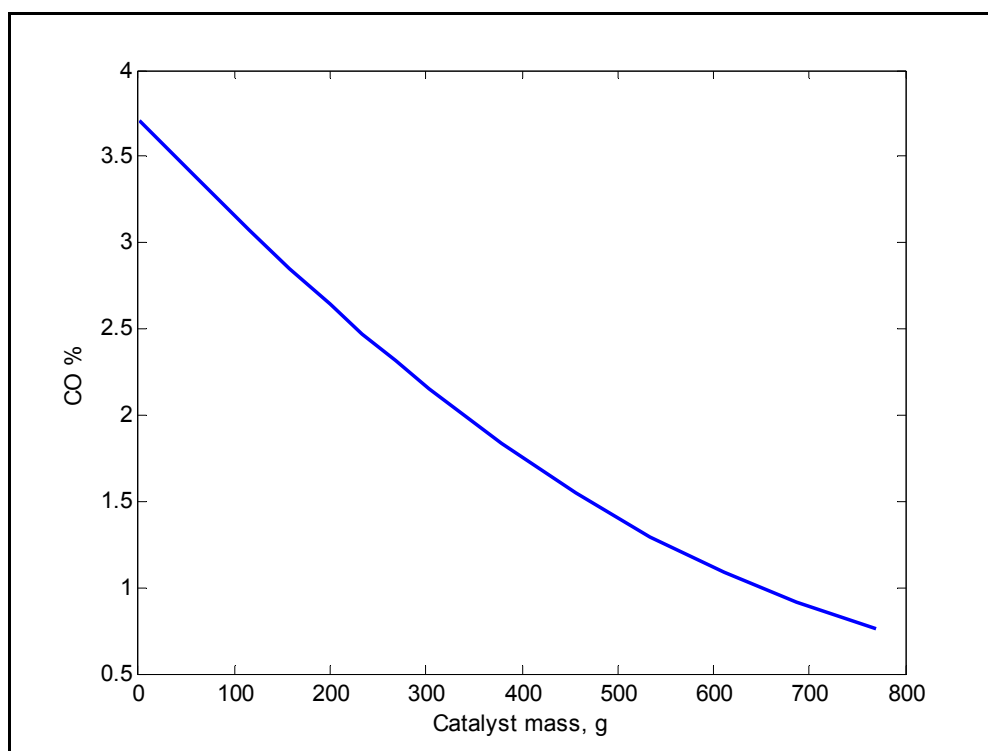


Figure B. 3. CO per cent of the bulk gas versus catalyst mass (g) (CO conversion = 0.80, Data Set 3, power-function pseudo-homogeneous model)

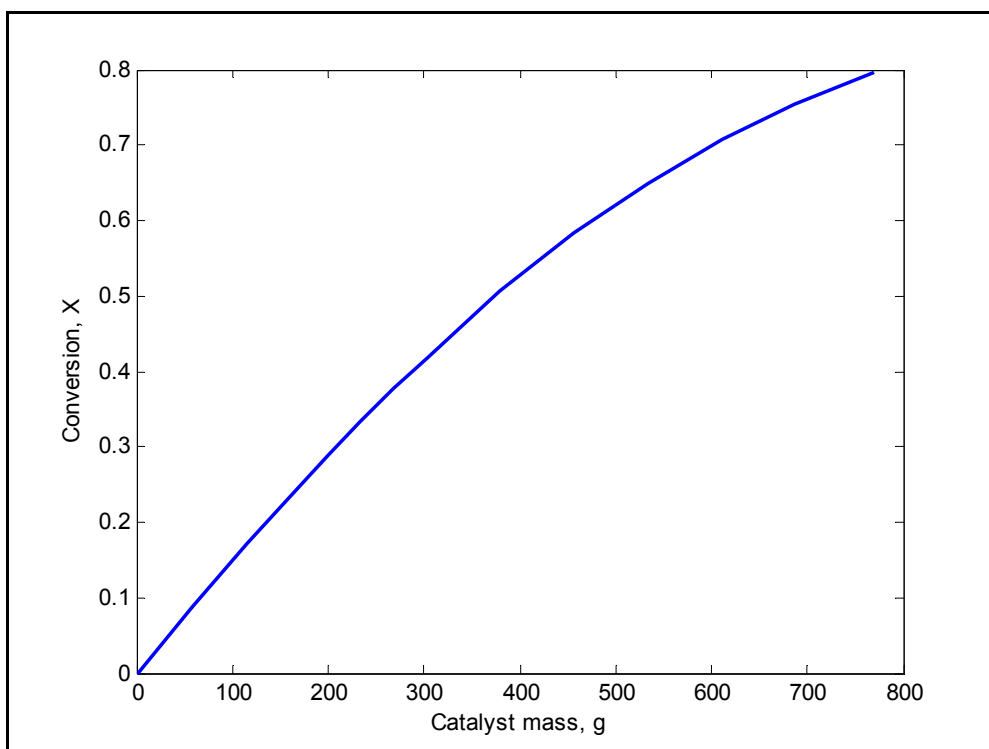


Figure B. 4. Conversion of CO versus catalyst mass (g)
(CO conversion = 0.80, Data Set 3, power-function pseudo-homogeneous model)

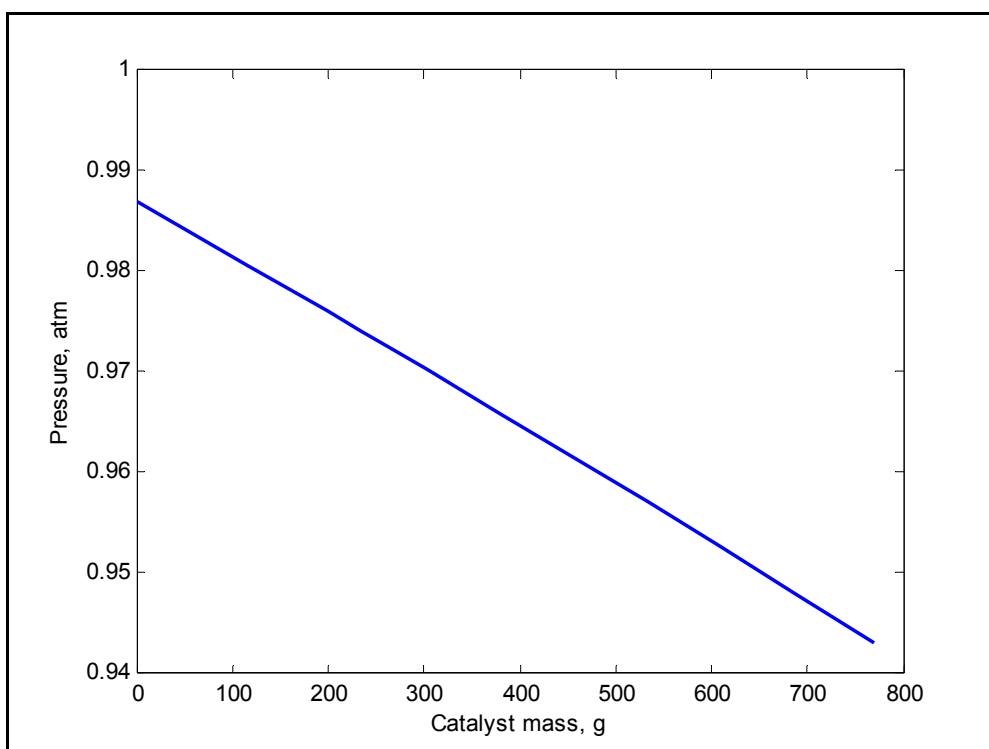


Figure B. 5. Pressure of the bulk gas (atm) versus catalyst mass (g)
(CO conversion = 0.80, Data Set 3, power-function pseudo-homogeneous model)

REFERENCES

1. Song, C., “Fuel processing for low-temperature and high-temperature fuel cells Challenges and opportunities for sustainable development in the 21st century”, *Catalysis Today*, Vol. 77, pp. 17–49, 2002.
2. Carrette, L., K. A. Friedrich and U. Stimming, “Fuel Cells–Fundamentals and Applications”. *Fuel Cells*, Vol. 1, No. 1, pp. 5–39, 2001.
3. Ahmed, S. and M. Krumpelt, “Hydrogen from Hydrocarbon Fuels for Fuel Cells”, *International Journal of Hydrogen Energy*, Vol. 26, pp. 291–301, 2001.
4. Sopian, K. and W. R. W. Daud, “Challenges and future developments in proton exchange membrane fuel cells”, *Renewable Energy*. Vol. 31, pp. 719–727, 2006.
5. Trimm, D. L. and Z. İ. Önsan, “Onboard Fuel Conversion for Hydrogen-Fuel Cell-driven Vehicles”, *Catalysis Reviews: Science and Engineering*, Vol. 43, pp. 31–84, 2001.
6. Ladebeck, J. R. and J. P. Wagner, “Catalyst Development for Water Gas Shift”, in W. Vielstich, A. Lamm and H. A. Gasteiger (editors), *Handbook of Fuel Cells – Fundamentals, Technology and Applications*, Vol. 3, Part 2, pp. 190–201, John Wiley, Chichester, 2003.
7. Perry, R. H., D. W. Green and J. O. Maloney, 1999, *Perry’s Chemical Engineers’ Handbook*, 7th ed., McGraw-Hill, USA.
8. Dodfuelcell, Overview of Fuel Cells, On-line publication (<http://www.dodfuelcell.com/fcdescriptions.html>), viewed in 2008.

9. Hart, D., “Sustainable energy conversion: fuel cells – the competitive option?”, *Journal of Power Sources*, Vol. 86, pp. 23–27, 2000.
10. Chalk, S. G., J. F. Miller and F. W. Wagner, “Challenges for fuel cells in transport applications”, *Journal of Power Sources*, Vol. 86, pp. 40–51, 2000.
11. Dufour, A. U., “Fuel cells – a new contributor to stationary power”, *Journal of Power Sources*, Vol. 71, pp. 19–25, 1998.
12. Trimm, D. L., “Minimization of carbon monoxide in a hydrogen stream for fuel cell application”, *Applied Catalysis A: General*, Vol. 296, pp. 1–11, 2005.
13. Joensen, F. and J. R. Rostrup-Nielsen, “Conversion of hydrocarbons and alcohols for fuel cells”, *Journal of Power Sources*, Vol. 105, pp. 195–201, 2002.
14. Rostrup-Nielsen, R., “Conversion of hydrocarbons and alcohols for fuel cells”, *Physical chemistry chemical physics*, Vol. 3, pp. 283–288, 2001.
15. Marino, F. J., E. G. Cerrella, S. Duhalde, M. Jobbagy and M. A. Laborde, “Hydrogen from steam reforming of ethanol. Characterization and performance of copper-nickel supported catalysts”, *International Journal of Hydrogen Energy*, Vol. 23, No. 12, pp. 1095–1101, 1998.
16. Haga, F., T. Nakajima, H. Miya and S. Mishima, “Catalytic properties of supported cobalt catalysts for steam reforming of ethanol”, *Catalysis Letters*, Vol. 48, pp. 223–227, 1997.
17. Haga, F., T. Nakajima, K. Yamashita and S. Mishima, “Effect of crystallite size on the catalysis of alumina-supported cobalt catalyst for steam reforming of ethanol”, *Reaction Kinetics & Catalysis Letters*, Vol. 63, No. 2, pp. 253–259, 1998.

18. Bodke, A. S., S. S. Bharadwaj and L. D. Schmidt, "The Effect of Ceramic Supports on Partial Oxidation of Hydrocarbons over Noble Metal Coated Monoliths", *Journal of Catalysis*, Vol. 179, pp. 138–149, 1998.
19. Docter, A. and A. Lamm, "Gasoline fuel cell systems", *Journal of Power Sources*, Vol. 184, pp. 194–200, 1999.
20. Choudhary, V. R., B. S. Uphade and A. S. Mamman, "Oxidative Conversion of Methane to Syngas over Nickel Supported on Commercial Low Surface Area Porous Catalyst Carriers Precoated with Alkaline and Rare Earth Oxides", *Journal of Catalysis*, Vol. 172, pp. 281–293, 1997.
21. Choudhary, V. R., A. M. Rajput and A. S. Mamman, "NiO-Alkaline Earth Oxide Catalysts for Oxidative Methane-to-Syngas Conversion: Influence of Alkaline Earth Oxide on the Surface Properties and Temperature-Programmed Reduction/Reaction by H₂ and Methane", *Journal of Catalysis*, Vol. 178, pp. 576–585, 1998.
22. Velu, S., K. Suzuki and T. Osaki, "Selective production of hydrogen by partial oxidation of methanol over catalysts derived from CuZnAl-layered double hydroxides", *Catalysis Letters*, Vol. 62, pp. 159–167, 1999.
23. Cubeiro, M. L. and J. L. G. Fierroy, "Selective Production of Hydrogen by Partial Oxidation of Methanol over ZnO-Supported Palladium Catalysts", *Journal of Catalysis*, Vol. 179, pp. 150–162, 1998.
24. Tsipouriari, V. A., Z. Zhang and X. E. Verykios, "Catalytic Partial Oxidation of Methane to Synthesis Gas over Ni-Based Catalysts I. Catalyst Performance Characteristics", *Journal of Catalysis*, Vol. 179, pp. 283–291, 1998.
25. Giroux, T., S. Hwang, Y. Liu, W. Ruettinger and L. Shore, "Monolithic structures as alternatives to particulate catalysts for the reforming of hydrocarbons for hydrogen generation", *Applied Catalysis B: Environmental*, Vol. 56, pp. 95–110, 2005.

26. Farrauto, R. J., "Introduction to solid polymer membrane fuel cells and reforming natural gas for production of hydrogen", *Applied Catalysis B: Environmental*, Vol. 56, pp. 3–7, 2005.
27. Goerke, O., P. Pfeifer and K. Schubert, "Water gas shift reaction and selective oxidation of CO in microreactors", *Applied Catalysis A: General*, Vol. 263, pp. 11–18, 2004.
28. Hilarie, S., X. Wang, T. Luo, R. J. Gorte and J. Wagner, "A comparative study of water-gas-shift reaction over ceria supported metallic catalysts", *Applied Catalysis A: General*, Vol. 215, pp. 271–278, 2001.
29. Pattrick, G., E. van der Lingena, C. W. Corti, R. J. Holliday and D. T. Thompson, "The potential for use of gold in automotive pollution control technologies: a short review", *Topics in Catalysis*, Vol. 30/31, pp. 273–279, 2004.
30. Shido, T. and Y. Iwasawa, "Reactant-Promoted Reaction Mechanism for Water-Gas Shift Reaction on Rh-Doped CeO_2 ", *Journal of Catalysis*, Vol. 141, pp. 71–81, 1993.
31. Shido, T. and Y. Iwasawa, "Reactant-promoted reaction mechanism for water-gas shift reaction on ZnO, as the genesis of surface catalysis", *Journal of Catalysis*, Vol. 129, pp. 343–355, 1991.
32. Bunluesin, T., R. J. Gorte and G. W. Grahamb, "Studies of the water-gas-shift reaction on ceria-supported Pt, Pd, and Rh: implications for oxygen-storage properties", *Applied Catalysis B: Environmental*, Vol. 15, pp. 107–114, 1998.
33. Li, Y., Q. Fu and M. Flytzani-Stephanopoulos, "Low-temperature water-gas shift reaction over Cu- and Ni-loaded cerium oxide catalysts", *Applied Catalysis B: Environmental*, Vol. 27, pp. 179–191, 2000.
34. Tinkle, M. and J. A. Dumesic, "Isotopic exchange measurements of the rates of adsorption/desorption and interconversion of CO and CO_2 over chromia-promoted

- magnetite: Implications for water-gas shift”, *Journal of Catalysis*, Vol. 103, pp. 65–78, 1987.
35. Campbell, C. T. and K. A. Daube, “A surface science investigation of the water-gas shift reaction on Cu(111)”, *Journal of Catalysis*, Vol. 104, pp. 109–119, 1987.
36. Colbourn, E., R. A. Hadden, H. D. Vandervell, K. C. Waugh and G. Webb, “Adsorption of water on polycrystalline copper: relevance to the water gas shift reaction”, *Journal of Catalysis*, Vol. 130, pp. 514–527, 1991.
37. Rhodes, C., G. J. Hutchings and A. M. Ward, “Water-gas shift reaction: finding the mechanistic boundary”, *Catalysis Today*, Vol. 23, pp. 43–58, 1995.
38. Amenomiya, Y. and G. Pleizier, “Alkali-promoted alumina catalysts: II. Water-gas shift reaction”, *Journal of Catalysis*, Vol. 76, pp. 345–353, 1982.
39. Shido, T., K. Asakura and Y. Iwasawa, “Reactant-promoted reaction mechanism for catalytic water-gas shift reaction on MgO”, *Journal of Catalysis*, Vol. 122, pp. 55–67, 1990.
40. Jacobs, G., P. M. Patterson, L. Williams, E. Chenu, D. Sparks, G. Thomas and B. H. Davis, “Water-gas shift: in situ spectroscopic studies of noble metal promoted ceria catalysts for CO removal in fuel cell reformers and mechanistic implications”, *Applied Catalysis A: General*, Vol. 262, pp. 177–187, 2004.
41. Froment, G. F. and K. B. Bischoff, *Chemical Reactor Analysis and Design*, Second Edition, John Wiley & Sons, 1990.
42. Fogler, H. S., *Elements of Chemical Reaction Engineering*, Third Edition, Prentice–Hall, New Jersey, 1999.

43. Francesconi, J. A., M. C. Mussati and P. A. Aguirre, “Analysis of design variables for water-gas-shift reactors by model-based optimization”, *Journal of Power Sources*, Vol. 173, pp. 467–477, 2007.
44. Salomons, S., R. E. Hayes, M. Poirier and H. Sapoundjiev, “Modelling a reverse flow reactor for the catalytic combustion of fugitive methane emissions”, *Computers and Chemical Engineering*, Vol. 28, pp. 1599–1610, 2004.
45. Holder, R., M. Bollig, D. R. Anderson and J. K. Hochmuth, “A discussion on transport phenomena and three-way kinetics of monolithic converters”, *Chemical Engineering Science*, Vol. 61, pp. 8010–8027, 2006.
46. Cybulski, A. and J. A. Mouljin (editors), *Structured Catalysts and Reactors*, Second Edition, Taylor & Francis, Florida, 2006.
47. Geankoplis, C. J., *Transport Processes and Unit Operations*, Third Edition, Prentice–Hall, New Jersey.
48. Shampine, L. F. and M. W. Reichelt, “THE MATLAB ODE SUITE”, *Society for Industrial and Applied Mathematics*, Vol. 18, No. 1, pp. 1–22, 1997.
49. Shampine, L. F., M. W. Reichelt and J. A. Kierzenka, “Solving Index-I DAEs in MATLAB and Simulink”, *Society for Industrial and Applied Mathematics*, Vol. 41, No. 3, pp. 538–552, 1999.
50. Amadeo, N. E. and M. A. Laborde, “Hydrogen production from the low-temperature water-gas shift reaction: Kinetics and simulation of the industrial reactor”, *International Journal of Hydrogen Energy*, Vol. 20, pp. 949–956, 1995.
51. Tan, Ö., “Numerical Investigation of H₂ Production from Methane for Small-Scale Stationary PEM Fuel Cell Applications”, M. S. Thesis, Boğaziçi University, 2007.

52. Choi, Y. and H. G. Stenger, “Water gas shift reaction kinetics and reactor modeling for fuel cell grade hydrogen”, *Journal of Power Sources*, Vol. 124, pp. 432–439, 2003.
53. Quiney, A. S., G. Germani and Y. Schuurman, “Optimization of a water-gas shift reactor over a Pt/ceria/alumina monolith”, *Journal of Power Sources*, Vol. 160, pp. 1163–1169, 2006.
54. Smith, J. M., H. C. van Ness and M. M. Abbott, *Introduction to Chemical Engineering Thermodynamics*, Seventh Edition, McGraw–Hill, 2005.
55. Lide, D. R., ed., *CRC Handbook of Chemistry and Physics, Internet Version 2005*, <http://www.hbcpnetbase.com>, CRC Press, Boca Raton, FL, 2005.
56. Bird, R. B., W. E. Stewart and E. N. Lightfoot, *Transport Phenomena*, Second Edition, John Wiley & Sons, 2002.