

DESIGN, CONSTRUCTION AND TESTING OF A LAB SCALE FUEL PROCESSOR
PROTOTYPE FOR DYNAMIC PERFORMANCE STUDIES

by

Melek Selcen Başar

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to my brother

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ABSTRACT

DESIGN, CONSTRUCTION AND TESTING OF A LAB SCALE FUEL PROCESSOR PROTOTYPE FOR DYNAMIC PERFORMANCE STUDIES

The aim of this study is to design, construct and test a fuel processor prototype for catalyst performance studies under steady-state and dynamic operation conditions. The propane fuel processor consisted of a main oven with three vertical ovens inside. In those units, three reactions, oxidative steam reforming (OSR), water gas shift (WGS) and preferential oxidation (PROX) were conducted. The system can be used to perform up to three serial reactions, like OSR, WGS and PROX or HTWGS, LTWGS and PROX. Additionally, the design of the system allowed keeping water vaporized in the system with the help of the main oven, the possibility of addition of new streams enabling either parallel operation of the reactions and/or simultaneous catalyst reduction steps. In this work, OSR and WGS reactions were performed in a serial fashion over 0.2%Pt-10%Ni/ γ -Al₂O₃ and 2%Au-1%Re/ZrO₂ catalysts, respectively. Oxygen/propane/steam flow rates and reaction temperatures were the experimental parameters used during the steady state and dynamic tests. Six sets of experiments, each including two ramp type perturbations, were performed during this study. Propane and oxygen conversions of nearly 100% were achieved in all experiments. Highest achieved selectivity (H₂/CO) was 37 for OSR temperature of 673 K and WGS temperature of 573 K, S/C ratio of 3 and C/O₂ ratio of 2.7 and for a total inflow of 100 ml/min, where the perturbation variable was steam flow rate. The test also showed the lowest CO concentration obtained at the WGS outlet as 0.57%. On line and real time analysis by a mass spectrometer allowed performing dynamic response tests. In inertia tests, steady state profiles were achieved at 36 minutes. In dynamic response tests, S-type steady state profiles were achieved for the given perturbations. Oxygen and propane ramp type perturbation tests showed better steady state profiles than that of the water tests with the required 1 hour 20 minutes for reaching steady state.

ÖZET

LABORATUAR ÖLÇEKLİ BİR YAKIT İŞLEMCİSİNİN DİNAMİK PERFORMANS TESTLERİ İÇİN DİZAYNI, YAPIMI VE TEST EDİLMESİ

Bu çalışmanın amacı; durağan ve dinamik çalışma koşullarındaki katalizör performans çalışmaları için bir yakıt işlemcisi prototipinin dizaynı, yapımı ve test edilmesidir. Propan yakıt işlemcisi içindeki üç fırınla birlikte bir adet ana fırından oluşmaktadır. Bu ünitelerde, ototermal reformlama (OR), su-gaz değişim (SGD) ve seçimli oksidasyon (SO) reaksiyonları yapılabilmektedir. Bu sistem OR, SG ve SO ya da yüksek sıcaklık SGD, düşük sıcaklık SGD ve seçimli oksidasyon şeklinde üç seri reaksiyona kadar performans ölçme amaçlı kullanılabilir. Ayrıca, sistemin dizaynı ana fırın yardımıyla suyun bütün sistem içinde buhar halde tutulmasına olanak sağlamasının yanında, yeni akışların eklenebilme ihtimali reaksiyonların paralel çalışmasına ve/veya katalizör indirgenme basamaklarının aynı anda yapılabilirliğine de olanak sağlamaktadır. Bu tez çalışmasında ototermal reformlama ve su-gaz değişim reaksiyonları sırasıyla $0.2\%Pt-10\%Ni/\gamma-Al_2O_3$ ve $2\%Au-1\%Re/ZrO_2$ katalizörleri ile gerçekleştirilmiştir. Oksijen/propan/su akış hızları ve reaksiyon sıcaklıkları durağan ve dinamik test çalışmalarında kullanılan deneysel parametrelerdir. Her biri iki adet rampa şeklinde değişiklik içeren altı set deney yapılmıştır. Propan ve oksijen çevirimleri tüm deneylerde 100% 'e yaklaşmıştır. Su akış hızının değiştirildiği deneyde, ototermal reformlama reaksiyonu deney sıcaklığı 673 K , su-gaz değişim reaksiyonu sıcaklığı 573 K , buhar karbon oranı 3, karbon oksijen oranı 2.7 ve dakikada 100 mililitrelik bir toplam akış için en yüksek seleksiyon (H_2/CO) değeri 37 olarak elde edilmiştir. Bu test aynı zamanda su-gaz değişim reaktör çıkışındaki en düşük karbon monoksit yüzdesini 0.57 olarak vermiştir. Kütle spektrometresi ile yapılan çevrimiçi ve gerçek zamanlı analiz dinamik testlere olanak sağlamıştır. Eylemsizlik testlerinde durağan profillere 36 dakikada ulaşılmıştır. Dinamik testlerde verilen değişikliklere göre S şeklinde durağan profiller elde edilmiştir. Oksijen ve propan testlerinde yapılan rampa şeklinde değişikliklere karşılık sistem 1 saat 20 dakikada durağan profile ulaşarak su testlerine göre daha iyi sonuçlar göstermiştir.

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LIST OF SYMBOLS/ABBREVIATIONS

F	Total flow rate
MW	Molecular weight
P	Pressure
R	Universal gas constant
T	Temperature
$\dot{V}$	Volumetric flow rate
W	Weight of the catalyst
X	Conversion
ρ	Density
BOS	Birleşik Oksijen Sanayi
C/O	Carbon to oxygen
CATREL	Catalysis and Reaction Engineering Laboratory
FPS	Fuel processor system
FPP	Fuel processor prototype
HDP	Homogeneous deposition precipitation
HPLC	High Performance Liquid Chromatography
HTWGS	High temperature water gas shift
IPOX	Indirect partial oxidation
LPG	Liquified petroleum gas
LTWGS	Low temperature water gas shift

MCFC	Molten carbonate fuel cell
MS	Mass spectrometer
OSR	Oxidative steam reforming
PEFC	Proton exchange/polymer electrolyte membrane fuel cell
POX	Partial oxidation
PROX	Preferential oxidation
S/C	Steam to carbon
SOFC	Solid oxide fuel cell
SR	Steam reforming
TOX	Total oxidation
WGS	Water gas shift

1. INTRODUCTION

Fuel cell technology is one of the most promising technologies for mobile and small scale stationary power generation applications due to a number of distinct advantages including: high energy efficiency, virtually zero emissions, and quiet and continuous operation (Vanston and Elliott, 2003). Challenges in hydrogen refueling, distribution and storage makes the on-board fuel processor technology as an important part of the fuel cell systems (Pukrushpan *et al.*, 2005). Fuel processors catalytically convert hydrocarbon fuels to hydrogen rich carbon monoxide free feed streams that are suitable to be used as the feed in fuel cell applications.

In a fuel processor, the conversion of hydrocarbon fuels to hydrogen is carried out usually by three reaction processes, which are reforming, water-gas shift (WGS) and preferential oxidation reactions (PROX). Commonly used process technologies for reforming of hydrocarbons involve steam reforming (SR), partial oxidation (POX) and oxidative steam reforming (OSR). Among these, OSR, which is the combined endothermic SR and exothermic POX, is favored due to the fact that in OSR, heat generation can be controlled by adjusting the feed proportions of fuel, air and steam. With these adjustments, not only the reaction temperature is determined, but also the reformat composition can be predicted (Chan and Wang, 2001; Sopena *et al.*, 2007). Since POX and OSR reactions are exothermic, the POX and OSR units do not require external heating; they can be heated up internally and quickly by the exothermic reactions of the fuels. Therefore, OSR is more dynamic than SR (Lin *et al.*, 2006; Moon *et al.*, 2008).

Typical OSR reformates contain 8-10% CO, around 20% CO₂, about 15-20% H₂O, and the balance mainly is H₂ and inert. Water gas shift reactors, which are used to reduce the carbon monoxide content further down to 0.5-1% in the reformer product, produces additional hydrogen as well. For polymer electrolyte membrane fuel cells (PEMFCs) the CO content must be reduced to below 50-100 ppm to avoid poisoning of the anode catalyst, which is accomplished in PROX reactors, where carbon monoxide is oxidized to carbon dioxide with air (Denkwitz *et al.*, 2007).

Dynamic response, i.e. the ability to change the processing rate, is a key parameter in fuel processor-fuel cell systems (Ahmed *et al.*, 2006). There are many publications focusing on dynamic behavior of fuel cells under various operating conditions. However, dynamic behavior of a fuel processor itself is as important as the fuel cell's dynamic behavior. Research on dynamic response of the fuel processor has received some attention; especially the relationship between feed conditions and dynamic response is studied (Lin *et al.*, 2006).

It is important to analyze the fuel processing unit in terms of its dynamic characteristics to obtain stable performance within its operating range. Knowledge of the dynamic behavior is crucial for the engineering of the fuel processor and can serve as a starting point for the design, suitable control strategies and optimum operation of fuel processor, when there are changes in feed and operating conditions (Lin *et al.*, 2006; Boehme *et al.*, 2008).

Liquefied petroleum gas (LPG), with propane as the main component (76%-99%), is a widely used hydrocarbon fuel for domestic and mobile use. Being in gaseous state under normal conditions, the possibility of storage and transport in liquid state under medium pressure, having highest hydrogen-to-carbon ratio and not containing aromatic compounds makes LPG an ideal fuel for hydrogen producing systems (Zhixiang *et al.*, 2006).

Vast amount of research papers have examined various aspects of the fuel processors. Some include overviews of the fuel processing technology, especially reforming technology; some include steady state performances and simulations of fuel processors, etc. Unfortunately, there are very few studies focusing on the dynamics and control of the fuel processors, and there are only some conference proceedings with a handful of journal papers (Lin *et al.*, 2006).

The published papers on dynamics of fuel processors usually include simulation models of developed fuel processors. The experimental set up and data are usually hindered. The lack of dynamic experimental data and use of commercial catalysts in the existing studies makes this thesis work valuable, which includes the design and construction of the fuel processor prototype, the investigation of the combined

performance of serial OSR and WGS units in terms of outlet CO and H₂ concentrations and analysis of the dynamic response/behavior of the FPP to the changes in various operating conditions in detail.

Chapter 2 of this study contains general information about fuel cells, fuel processing steps, catalysts and system dynamics as well as the information on relevant previous studies. In Chapter 3, experimental setups and procedures will be given in detail. In Chapter 4, details of the system design and the results of the conducted experiments on dynamic response will presented and discussed. The conclusions drawn from this work and some recommendations for future work are summarized in Section 5.

2. LITERATURE SURVEY

Worldwide demand for energy is growing at an alarming rate led by the rapidly increasing world population and higher standards of living. The increased demand is being met largely by oil and other non-renewable fossil fuels; however meeting this demand poses great challenges. Unfortunately, the combustion of hydrocarbon fuels for transportation and heating contributes over half of all greenhouse gas emissions and a large fraction of air and water pollutant emissions. The potential effects of climate change are very serious and most important of all, they are irreversible. Quick consumption and depletion of oil reserves, very high prices of oil, air and water pollution as well as global climate change and carbon dioxide emissions force the world to face urgency in developing alternative fuels. (European Commission, 2003; Gupta, 2009)

2.1. Hydrogen

Hydrogen is the simplest and most abundant element in the universe. Its high reactivity, zero emission characteristics, inexhaustibility and having an energy content three to four times higher than oil makes it an ideal alternative fuel. Unfortunately, it never occurs by itself and always combines with other elements such as oxygen and carbon. Therefore, it can be produced from all known energy systems based on different conventional primary energy carriers and sources besides being a by-product of many industrial processes. Hydrogen is not a primary energy source, but it can be used like electricity as a method of exchange for getting energy to where it is needed. Hydrogen and electricity are complementary and one can be converted into the other. Similar to electricity, hydrogen is a high-quality energy carrier, which can be used with a high efficiency and zero or near-zero emissions at the point of use. However, difficulties in the hydrogen transport and storage, the lack of a hydrogen infrastructure in the short term, along with the highly attractive energy density of hydrocarbon fuels, has created widespread research efforts in the field of distribution and on-board hydrogen generation from various fuels for fuel cell applications (Gupta, 2009; Kolb, 2008; Hordeski, 2009).

2.2. Fuel Cells

Fuel cells are electrochemical devices converting the energy of a fuel (usually hydrogen) directly into efficient, clean and on site electricity without combustion or thermal cycles. All fuel cells consist of an electrolyte layer in contact with an anode and a cathode on either side. Oxygen enters through the catalytic cathode and hydrogen diffuses to the anode catalyst where it later dissociates into protons and electrons. The oxidation reaction occurs on the anode side of the fuel cell, while reduction takes place on the cathode side (Sammes, 2006; Lee *et al.*, 2007). The oxygen for the fuel cell is normally supplied using air, which is readily available. However, there is not any available hydrogen distribution infrastructure and therefore many fuel cell systems include an incorporated Fuel Processing System (Avcı, 2003).

Fuel cells are classified according to the type of electrolyte used and also to the operating temperature. The most known types are proton exchange/polymer electrolyte membrane fuel cells (PEMFCs), molten carbonate fuel cells (MCFCs) and solid oxide fuel cells (SOFCs) (Gou *et al.*, 2010). Each type has its own advantage. SOFCs do not need pure hydrogen to generate electricity, because they can internally reform carbon monoxide and light hydrocarbons in the anode material (Yoon and Bae, 2010). High temperature PEMFCs require CO concentrations of around 1 vol. %. On the other hand low temperature PEMFCs, which are the most widely accepted technology for portable and small scale immobile applications, are more sensitive to CO and they cannot tolerate a CO concentration exceeding 10 ppm during fuel processing in the long term operation (Hessel *et al.*, 2005; Kolb *et al.*, 2008b). Fuel cell temperatures should be kept higher than 333 K and less than 373 K, in order to sustain reaction kinetics and to humidify the electrolyte to conduct protons (Avcı, 2003).

2.3. Fuel Processors

Fuel processors can be considered as little chemical factories in which conventional/raw/primary or renewable fuels are converted into carbon monoxide-free hydrogen rich fuel. During this conversion process, which is also called as reforming process; various by-products are formed such as carbon dioxide, carbon monoxide or

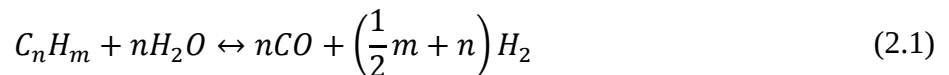
methane, depending on the hydrocarbon fuel type and operating conditions of the reforming process. Among the by-products, carbon monoxide is the most important one, since it poisons the catalysts and the electrodes of PEMFC, when its concentration is greater than 10 ppm. Thus, besides increasing hydrogen yield, minimizing carbon monoxide yield is a crucial target in developing fuel processing technologies (Hessel *et al.*, 2005; Chan and Wang; 2001).

A generic fuel processor consists of three units. In those serially connected units, different reactions, namely reforming, water gas shift, and preferential oxidation, is conducted sequentially. These units can be either separate units operating in series or they may be integrated.

2.3.1. Reforming Reactions

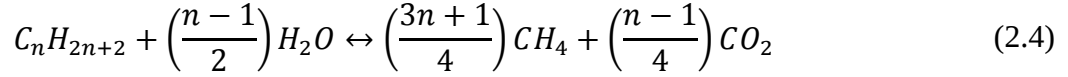
The most important parameters in reforming are steam to carbon and oxygen to carbon ratios in the feed mixture (Kolb, 2008). The reformer breaks down the fuel, producing a gas rich in hydrogen but containing other reaction products.

2.3.1.1. Steam Reforming. Steam reforming (Reaction (2.1)) of hydrocarbons on Ni promoted catalysts is the conventional, well known, cheapest and highly efficient process for providing synthesis gas (H_2 and CO), and for large scale hydrogen production (Schadel *et al.*, 2009; Çağlayan *et al.*, 2005). However, requirement of large amounts of energy input because of the high endothermicity of the reaction and the presence of catalyst deactivation due to coke deposition turn out to be major disadvantages of steam reforming reaction (Avcı *et al.*, 2001).

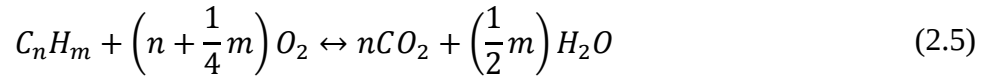


Methanation may also occur at low temperatures, producing considerable amounts of methane (Reactions (2.2), (2.3) and (2.4)).

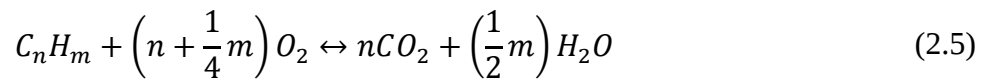
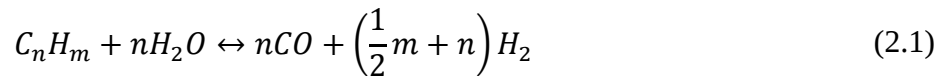




2.3.1.2. Total Oxidation. Since steam reforming is an endothermic reaction, sufficient heat should be introduced into the reactor in order to initiate the reaction. In order to supply this kind of energy, an exothermic reaction is required. Exothermic combustion of the unconverted hydrocarbon will be most suitable reaction to be coupled with the endothermic SR reaction. The catalyst of total oxidation reaction (TOX) (Reaction (2.5)) should be very active also in steam reforming reaction to ensure complete conversion of the hydrocarbon fuel (Reuse *et al.*, 2004)



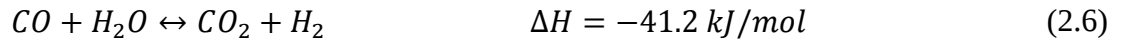
2.3.1.3. Oxidative Steam Reforming. Combining endothermic steam reforming and exothermic total oxidation reaction of hydrocarbon fuels result in oxidative steam reforming (OSR). Coupling of these two reactions results in an ideally thermally balanced system (Kolb *et al.*, 2008a). Beside hydrocarbon fuel, steam and air are the reactants. The amount of air or oxygen addition should be very well calculated in order to prevent carbon deposition (Kolb, 2008).



2.3.2. Water Gas Shift Reaction

CO concentration at the outlet stream of reforming reactor is usually in the range of 6-10% (Siddle *et al.*, 2003). The role of water gas shift reaction in a fuel processor is to provide a main CO cleanup step, and at the same time, to act as a second reactor to produce

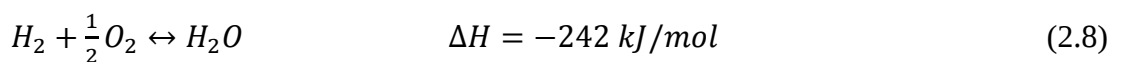
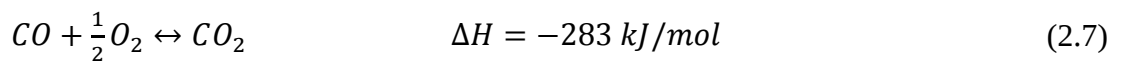
hydrogen after reforming step (Gonzales *et al.*, 2010). Conversion of CO (Reaction (2.6)) by WGS increases hydrogen yield, and simultaneously reduces the CO concentration from 10% to 0.5-1% (Luengnaruemitchai *et al.*, 2003; Siddle *et al.*, 2003)



The reaction is slightly exothermic, which is not favorable for the carbon monoxide equilibrium conversion when running shift reactors in the adiabatic mode (Hessel *et al.*, 2005). Conventionally, the reaction is carried out in two steps, namely, high temperature water gas shift reaction and low temperature water gas shift reaction. The one at high temperature is conducted over Fe_2O_3/Cr_2O_3 catalysts in the temperature range of 400-500 °C to reduce the carbon monoxide content to around 2-5%, whereas the latter one is carried out over Cu/ZnO catalysts between 200 and 400 °C to reduce the CO concentration further down to 1% (Luengnaruemitchai *et al.*, 2003; Hessel *et al.*, 2005).

2.3.3. Preferential Oxidation of Carbon monoxide

The removal of low concentrations of carbon monoxide from 0.5-1% to ppm levels is achieved by oxidation of carbon monoxide with air. This step is necessary, since even 0.5-1% CO levels are too high for the low temperature PEM fuel cells. Therefore, preferential oxidation (PROX) is performed to reduce the CO in the feed to 10 ppm or less. Unfortunately, the reaction (Reaction (2.7)) is accompanied by the undesired hydrogen oxidation side reaction (Reaction (2.8)) (Hessel *et al.*, 2005; Lee and Chu, 2003):



Şimşek suggested the commercial use of 1% Pt-0.25% SnO_x supported on HNO_3 -oxidized AC catalysts for PROX applications because of its 100% CO conversion under realistic conditions (Şimşek *et al.*, 2007).

2.4. Propane as Hydrocarbon Fuel

Liquefied petroleum gas or propane is a liquid byproduct of oil refining or natural-gas processing and has a cleaner burning properties than that of gasoline; LPG or propane produces fewer emissions, but not as clean as natural gas combustion (Hordeski, 2008). It also leaves fewer carbon deposits inside engines. Unlike natural gas, propane is heavier than air. Liquid propane has good energy density at low storage pressure and, therefore, it can be stored and transported economically. In addition, propane is available worldwide and, amongst all the fossil fuels, it contains the highest amount of hydrogen on a gravimetric basis (Kolb, 2008). Propane is not a potential contributor to groundwater pollution like most of the liquid fuels and has relatively lower human toxicity characteristics compared to methanol or gasoline (Sammes, 2006).

2.5. The Combined Fuel Processor/Fuel Cell Systems and the Importance of Dynamic Performance of Fuel Processor

On-board hydrogen generation as an alternative to hydrogen transport and storage, which are still challenging problems, led researchers to develop prototypes of complete fuel processor/fuel cell systems for portable, automobile, or residential applications (Lee and Chu, 2003). Consequently, a competition has started to develop and supply fuel processing technology to fuel cell industry. Many studies have been conducted about the steady state performances of combined fuel processor/fuel cell systems with different hydrocarbon fuels such as methane (Lin *et al.*, 2005), ethanol (Aicher *et al.*, 2009), isooctane (Kolb *et al.*, 2008a&b) and gasoline (Papadias *et al.*, 2006).

Dynamic response, the ability to quickly change the processing rate, is an important feature of the on-board fuel processor. A fuel processor is expected to go through often and rapid changes in processing rates. The dependence of the temperature profiles in a catalytic reactor to the processing rates became important, considering that the changes in temperature profiles affects the product quality in the intermediate steps and at the fuel processor exit as well. By solving temperature problem, a fuel processor's processing rates and response times depend only on the feed rates, type of fuel, air/oxygen feed ratio and water flow rate (Ahmed *et al.*, 2006).

Start-up time and transient behavior are the key requirements for the success of fuel cell vehicles, because the Fuel Processor System (FPS) response time is important for the overall Power Plant response. Testing of dynamic performance of a fuel processor is necessary in order to determine the best possible fuel processor design, control scheme and overall operating strategy. By investigating the effect of various operating parameters, associated with the fuel processor, it is possible to get information on possible operating strategy and to optimize steady state operation performance (Ramaswamy *et al.*, 2000).

A compact propane fuel processor was designed and developed by Dokupil and his team. The compact fuel processor consisted of a reformer/burner module and a CO-purification module, employing water-gas shift and single-stage preferential oxidation reactors. The study investigated the dynamic and steady state performance of the fuel processor in terms of the variation of propane flow rate to the reformer and burner, and steam to carbon ratio and oxygen to carbon monoxide ratio at the inlet of PROX reactor. The performance was tested by measuring the concentration of hydrogen and carbon monoxide at the outlet of the PROX reactor. Fast transient responses of the fuel processor with negligible fluctuation of reformat gas composition within the load variations were measured (Dokupil *et al.*, 2006).

In another study conducted by Chen and his colleagues, an experimental methane fuel processor consisting of series combined reformer, three water-gas-shift-reactors and a preferential reactor was constructed. According to Chen, CO concentration level should be taken into consideration in order to explore start-up strategy. Without changing process configuration, sensitivity analysis was carried out in order to see the effects of three manipulated variables, namely, methane feed flow, steam feed flow, and air feed rate, on rapid start-up of the Fuel Processor and on its dynamic modeling (Chen *et al.*, 2006). The studies conducted by Sommer (2004) and Beckhaus (2004) investigated the relationship between feed conditions and dynamic responses (Sommer *et al.*, 2004; Beckhaus *et al.*, 2004)

Many aspects of fuel processors should be considered for using it in on-site hydrogen production to be used as PEMFC feed. Those aspects include time and energy consumption for start-up, thermal efficiency, transient response during changes of hydrogen throughput,

concentration of carbon monoxide in the process gas stream, size and life time. These aspects depend significantly on the thermodynamics and kinetics of the catalytic reactions involved, as well as on construction and integration of the reactor units (Lee *et al.*, 2007).

2.6. Oxidative Steam Reforming Catalysts

Carbon deposition on the catalyst surface and the catalyst stability are considered as serious problems in the production of hydrogen through oxidative steam reforming. It is generally agreed that coke deposition is the major cause for activity loss and active metal degradation. Current research efforts on OSR have focused on the development of Al_2O_3 supported Ni-based catalysts having improved activity, yield, and stability characteristics by the addition of precious metals such as Pd, Pt, and Rh. Since oxidative steam reforming is a combination of steam reforming and total oxidation reactions, OSR catalysts should be active in both reactions. Transition metals like Ni, Co, Fe and noble metals Pt, Rh, Ru, Pd have been the most preferred promoters for hydrocarbon reforming. The studies on precious metal supported catalysts proved their superiority in the catalyst activity and stability, however, because of their high costs; optimization efforts are made in order to develop Ni-based catalysts with improved resistance to coke formation through very small additions of noble metals (Zhang *et al.*, 2009; Lim *et al.*, 2009; Vita *et al.*, 2010).

Wagner and his coworkers studied the propane oxidative steam reforming in Pd promoted $\text{CeO}_2/\text{Al}_2\text{O}_3$ supported catalysts. At temperatures ranging from 450 to 550 °C and for an oxygen to propane ratio of 2.5, a relatively high hydrogen to carbon monoxide ratio (2-2.5) in the product was obtained (Wagner *et al.*, 2008).

Perovskite-type catalysts shown by the general formula ABO_3 , where A is usually a rare earth cation (La, Gd, Pr, Nd, or Er) and B is a transition metal cation (Cr, Mn, Fe, Ni, Al, or Co) were preferred by some researchers instead of supported noble metal catalysts because of their lower cost, thermal stability and activity. In a study conducted by Lim and his colleagues the activities of Ni/LaAlO_3 and Ni-Ce/LaAlO_3 catalysts were tested with a reactant ratio of $\text{H}_2\text{O}/\text{C}_3\text{H}_8/\text{O}_2 = 8.96/1.0/1.1$ at a velocity of 9600 ml/g-cat h. Firstly, effect of La addition and amount of Ni were investigated. Higher propane conversions were observed on the Ni/LaAlO_3 catalyst containing 15% Ni than $\text{Ni}/\alpha\text{-Al}_2\text{O}_3$ between 300 and

700 °C. Secondly, the effect of Ce addition was investigated and concluded that Ce concentration affected the level of propane conversion rather than the H₂ yield (Lim *et al.*, 2009).

Higher catalytic stability is obtained with the use of mixed oxides derived from hydrotalcite-type catalysts because of the highly dispersed and homogeneously distributed metal particles. The performance of tertiary metal hydrotalcite-type catalysts (5% noble metal (Pt, Pd, and Ru)-doped Ni (15%)/MgAl) was examined in a continuous fixed-bed flow reactor between 300 to 700 °C in a study conducted by Lee and his team. 100% propane conversion was achieved on all the catalysts investigated at temperatures higher than 450 °C. The order of the propane conversion from highest to lowest was Pt-Ni/MgAl > Ru-Ni/MgAl > Pd-Ni/MgAl. The noble metal doping increased the degree of Ni dispersion, thus decreasing level of carbon on the catalyst surface (Lee *et al.*, 2009).

Ayabe carried out autothermal reforming of propane over monometallic Ni/Al₂O₃ catalyst. Although propane conversion 100% was achieved, use of propane as hydrocarbon fuel caused a large amount of carbon deposition, which resulted in the lower values of hydrogen concentration than the equilibrium values for low steam contents (Ayabe *et al.*, 2003).

Çağlayan studied the indirect partial oxidation of propane on bimetallic Pt-Ni/ δ -Al₂O₃ catalyst in the temperature range of 623-743 K. Pt-Ni/ δ -Al₂O₃ catalyst prepared by sequential impregnation was studied for the first time in the literature in this work. The results showed the superior performance characteristics of bimetallic catalysts compared to monometallic catalysts. Çağlayan explained these characteristics by the high energy efficiency of the bimetallic catalyst led by the transfer of energy from Pt sites which catalyzes exothermic TOX, to the Ni sites which catalyzes endothermic SR. She came to a conclusion that catalyst particles were acting like micro heat exchangers during OSR (Çağlayan *et al.*, 2005).

In another study conducted by Gökaliler and his coworkers, oxidative steam reforming of propane was carried out and the effect of Ni:Pt ratio on the performance of Pt-Ni/ δ -Al₂O₃ catalyst was investigated. Also, a trimetallic Pt-Ni-Au/ δ -Al₂O₃ catalyst was

additionally tested to observe Au addition in reforming catalysts. The results showed that catalysts prepared with 0.2% Pt-10% Ni and 0.3% Pt-15% Ni metal loadings have suppressed methanation reactions, enhanced H_2 production and increased WGS performance. It was also concluded that Au promotion as a third metal caused poor activity and selectivity with respect to bimetallic catalysts (Gökaliler *et al.*, 2008)

2.7. Water Gas Shift Catalysts

The interest for new water gas shift catalysts has been growing significantly in the last few years as a result of latest advances in fuel cell technology and the need for developing small scale fuel processors capable of converting hydrocarbon fuels into carbon monoxide free hydrogen on-board (Gonzales *et al.*, 2010). Conventional high temperature (Fe-Cr oxide) and low temperature (Cu-Zn- Al_2O_3) WGS catalysts are not applicable for portable and vehicular applications because of their insufficient durabilities and activities. Because of the slow kinetics observed at low temperature, the WGS unit is expected to be the largest component of a fuel processor and there is a strong necessity to reduce the volume and the weight of the whole processor has driven the research to develop more active WGS catalysts with properties fundamentally different from those in the industrial use (Boaro *et al.*, 2009). WGS catalysts for fuel cell applications should be sufficiently active in the temperature range of 200-280°C, thermally stable, and resistant to coke deposition. They also should be highly selective for high H_2O/CO ratios with no side reactions, especially methanation, consuming valuable hydrogen (Panagiotopoulou and Kondarides, 2007).

In water gas shift reaction, both the support and the metal play essential roles in the activity and stability of the catalyst. The most active formulations are based on noble and transition metals supported on reducible oxides. Noble metal catalysts supported on CeO_2 , ZrO_2 and TiO_2 are the most promising catalysts for WGS reaction.

Ceria is known as an oxygen-storage material, having high redox properties, while maintaining high dispersion for metal nanoparticles, hence giving high activity for CO oxidation at low temperature and high WGS activity. Additionally, the oxidation of ceria

by water to give hydrogen is thermodynamically favorable (El-Moemen *et al.*, 2009; Hurtado-Juan *et al.*, 2008; Luengnaruemitchai *et al.*, 2003).

A comparative study of water-gas-shift reaction over ceria-supported metallic catalysts was conducted by Hilaire and his co-workers. Pd, Ni, Fe and Co metals were used as transition metals. This study showed that ceria-supported transition metals were active catalysts for the water-gas-shift reaction. Pd/ceria and Ni/ceria showed essentially the same activities and were much more active than either Co/ceria or Fe/ceria (Hilaire *et al.*, 2004)

Gold-based catalysts received great attention, since Haruta and Date (2001) discovered that gold exhibited surprisingly high catalytic activity for CO oxidation at temperature as low as 200 K, when it was deposited as nanoparticles on metal oxides (Tabakova *et al.*, 2004). Recently, Au/CeO₂ catalysts turned out to be very active catalysts for the low-temperature WGS reaction, as gold promoter particularly showed to possess higher activity than other noble metals for the low temperature WGS reaction (Fu *et al.*, 2005).

Extraordinary activities of Au/CeO₂ catalysts led scientists to make extensive researches on the addition of a second active metal to gold catalysts. In a study conducted by Yu and his colleagues, the activities of bimetallic Au-M (M=Ni, Cu, Ag, Pt, and Pd) catalysts supported on CeO₂ were investigated. The WGS reaction activities over these catalysts decreased as the following order: Au-Pt/CeO₂ > Au-Ni/CeO₂ > Au/CeO₂ > Au-Cu/CeO₂ > Au-Ag/CeO₂ > Au-Pd/CeO₂. A carbon monoxide conversion of 78% was achieved with Au-Pt/CeO₂ catalyst at 250 °C. (Yu *et al.*, 2010)

The results obtained for the catalytic activity of different gold catalysts give rise to questions about the effect of the nature of the support, the choice of the preparation method, and the gold particle size on the reducibility of the metal oxide support and certainly on the WGS reaction mechanism.

Beside ceria supported Au catalysts, Au/ZrO₂ catalysts also showed exceptionally high activities for WGS reaction. In addition to the gold nanoparticles, the nature of zirconia was also found to play an essential role in the catalytic performance. The study

investigating the effect of crystal phase of zirconia on the performance of ZrO_2 supported gold catalysts concluded that monoclinic phases of ZrO_2 support led to much higher activity than that of the tetragonal phase (Li *et al.*, 2008).

Another study concerning Au/ZrO_2 catalysts investigated the relationship between textural and structural characteristics of mesoporous zirconia support, the state of gold particles and the WGS activity of catalyst prepared. In that study, the mesoporous zirconia supported nanosized gold catalyst was used in WGS reaction for the first time in literature. They came to conclusion that the structure of mesoporous zirconia support facilitated the formation of well-dispersed and stable gold particles on the surface upon calcination and reduction and thus strongly improved the catalytic performances (Idakiev *et al.*, 2006).

In recent years noble metal catalysts supported on CeO_2 and Ce-Zr mixed oxides have been intensely investigated as promising next-generation WGS catalysts, which exhibited much faster high-temperature kinetics than conventional ferrochrome catalysts and were not inhibited by CO_2 (Bi *et al.*, 2009). Ceria-Zirconia mixed oxides supported WGS catalysts were also studied by Radhakrishnan. In there, the effect of addition of rhenium metal to platinum/ceria-zirconia catalysts was investigated. It was found that rhenium nearly doubled the reaction rate of the supported platinum catalyst and that rhenium carbonyl was the optimal precursor for the deposition of the promoter on the catalyst surface (Radhakrishnan *et al.*, 2006).

The studies concerning the comparison of the reaction behavior between Pt-Re/TiO_2 and Pt-Re/ZrO_2 catalysts (Iida and Igarashi, 2006), the reaction over Pt-Re/TiO_2 and Pd-Re/TiO_2 catalysts (Sato *et al.*, 2005) and the reaction over Ir/TiO_2 and Ir-Re/TiO_2 catalysts (Sato *et al.*, 2006) concluded that the addition of Re metal accelerated the WGS reaction and increased the reactivity of the adsorbed CO species with steam.

Güven designed and developed an Au-based, bimetallic WGS catalyst to be used in a fuel processor. The catalyst composition and preparation method were the experimental parameters studied in the catalyst design and testing. The effect of Re addition to Au-based zirconia supported catalysts was also investigated. It was concluded that Re addition improved the catalytic activity significantly, suggesting that rhenium is a good promoter

for bimetallic gold based WGS catalysts. The optimum catalyst composition for WGS reaction was found to be 1% Re-2% Au/ZrO₂, prepared by impregnation of Re on ZrO₂ followed by deposition precipitation of Au (Güven, 2009).

3. EXPERIMENTAL WORK

3.1. Materials

3.1.1. Chemicals

All the chemicals used for catalyst preparation are presented in Table 3.1.

Table 3.1. Chemicals used for catalyst preparation

Chemicals	Formula	Specification	Source	MW (g/mol)
Zirconium oxide	ZrO_2	S.A.= 90 m ² /g	Alfa Aesar	123.22
Sodium carbonate	Na_2CO_3	99.9+%	Merck	105.99
Ammonium carbonate	$\text{CH}_6\text{N}_2\text{O}_2^*$ $\text{CH}_5\text{NO}_3(1:1)$	NH_3 : 30+%	Merck	157.13
Ammonium perrhenate	NH_4ReO_4	99.999%	Aldrich	268.24
Tetraammineplatinum (II) nitrate	$\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$	99.995+%	Aldrich	387.22
Gold (III) chloride trihydrate	$\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$	99.9+%	Aldrich	393.83
Cerium (III) nitrate hexahydrate	$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	98.5+%	Aldrich	434.23
Nickel(II) nitrate hexahydrate	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	99%	Merck	290.81
Aluminum Oxide	$\gamma\text{-Al}_2\text{O}_3$	99.98%	Alfa Aesar	101.96

3.1.2. Gases and Liquids

All of the gases used in this research were supplied by Birleşik Oksijen Sanayi (BOS) Gebze, KOCAELI. The specifications and uses of the gases and liquids in this study are listed in Table 3.2 and Table 3.3.

Table 3.2. Specifications and applications of the gases used

Gas/Standard	Specification	Application
Helium	99.99% BOS	Inert
Hydrogen	99.99% BOS	MS calibration, Reactant, Reducing agent
Oxygen	99.99% BOS	MS calibration, Reactant
Propane	99.99% BOS	MS calibration, Reactant

Table 3.3. Specifications and applications of the liquids used

Liquid	Specification	Application
Water	De-ionized	Aqueous solutions, Reactant

3.2. Experimental Systems

The experimental systems used in this study can be divided mainly into three groups:

- (i) **Catalyst Preparation Systems:** Systems used to prepare the support and to carry out impregnation and deposition precipitation steps of catalyst preparation.
- (ii) **Catalytic Reaction System:** The system consisted of a feed section including mass flow controllers for inlet gases, HPLC pump for water feed and a mixing zone; a reaction section (Fuel Processor Prototype, FPP, for catalyst testing) composed of a main oven including three fixed-bed flow reactors (only two of them were used in the current study) in separate vertical furnaces, where the temperature of all ovens were controlled by independent programmable temperature controllers.

- (iii) Product Analysis System: The analysis of compositions of the reactant and product gases using Hiden Analytical HPR-20 QIC mass spectrometer equipped with a Faraday/SEM detector.

3.2.1. Catalyst Preparation Systems

The system used for catalyst preparation by impregnation method included a Retsch UR1 ultrasonic mixer providing uniform mixing and contacting of the solution with the support, a vacuum pump, a Masterflex computerized-drive peristaltic pump used for addition of the solution to be impregnated, a büchner flask, a beaker and silicone tubing. The specific details are given in catalyst preparation procedure section, while the schematic representation of the impregnation method is given in Figure 3.2.

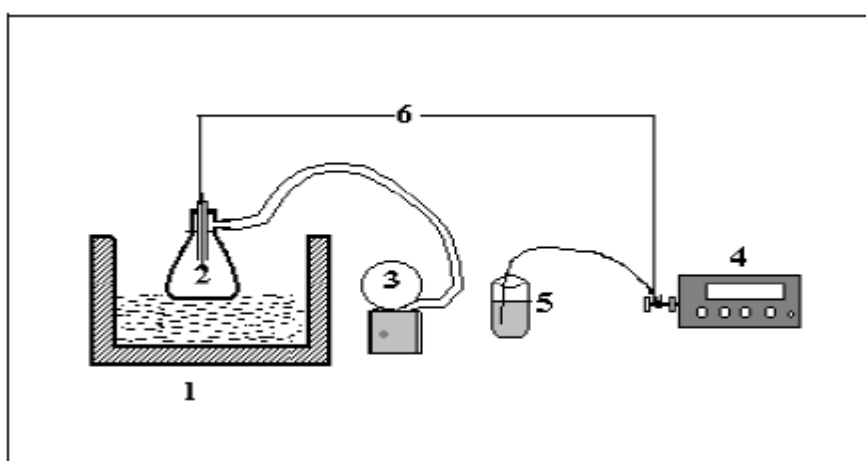


Figure 3.1. The impregnation system: 1.Ultrasonic mixer 2.Büchner flask
3.Vacuum pump 4.Peristaltic pump 5.Beaker 6.Silicone tubing (Öztürk, 2009)

Au nanoparticles deposited on the Re/ZrO₂ support by homogeneous deposition precipitation method required a stirrer, a heater circulation bath, a pH meter and a beaker. The specific details are given in catalyst preparation procedure section, while the schematic representation of the HDP process is given in Figure 3.2.

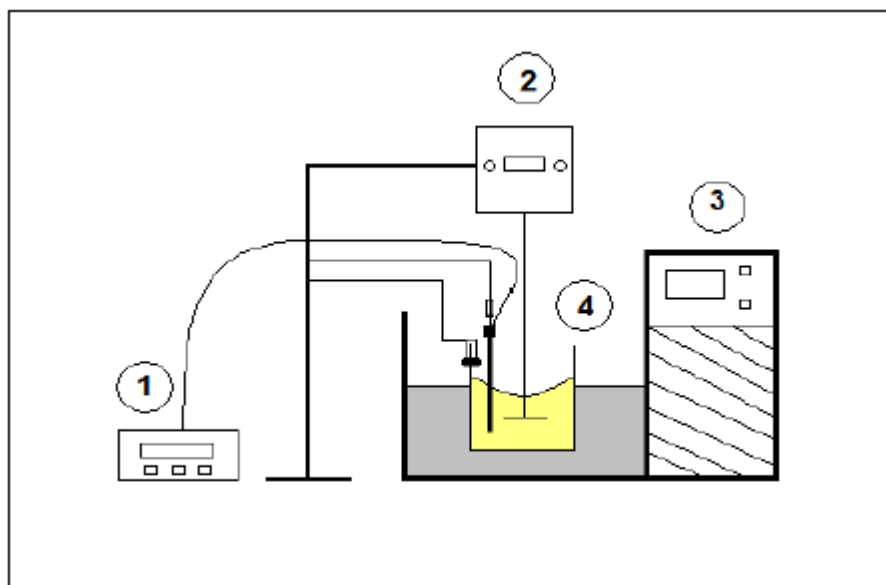


Figure 3.2. The HDP system: 1. pH meter, 2. Stirrer, 3. Heater circulation bath 4. Beaker (Güneş, 2009)

3.2.2. Catalytic Reaction System

The catalytic reaction system was designed and constructed in Catalyst Technology and Reaction Engineering Laboratory (CATREL). This system includes three main sections.

- Feed section
- Fuel processor prototype (FPP)
- Product analysis section

Feed preparation section, which was stationed before the FPP, consisted of mass flow control systems, 1/4", 1/8" and 1/16" stainless steel tubes and fittings for feeding liquid water and delivering gaseous species, i.e. helium, hydrogen, oxygen and propane. Water was fed to the system with a Jasco PU-2089 Plus HPLC pump at constant flow rate mode. The 1/16" tube, through which water was allowed to flow and the lines between the water inlet and the FPP were kept at approximately 140 °C with 1 m heating tape to enable vaporization of water before contacting gas mixture and entering to the system. A 16-

gauge wire K-type sheathed thermocouple was placed along the heated line and connected to a Shimaden SR91 temperature controller with ± 0.1 K sensitivity. The high purity gases were supplied by pressurized cylinders. The flow rates of the gases were controlled by Brooks 5850E mass flow controllers. The set point values of the flow controllers were adjusted by four-channel Brooks 0154 series control box. At the inlet and the outlet of the mass flow controllers, 1/4" stainless steel tubes were used until the primary mixing zone. On-off valves were placed in front of the mass flow controllers to protect them from possible back-pressure. In order to provide homogeneous mixing, the reactant gases were passed through the primary mixing region before the water feed was introduced. This primary mixing region was constructed using 1/8" stainless steel tubes, whereas the mixing region of steam and gaseous mixture was constructed using 1/16" stainless steel tubes.

The reactants, metered and mixed in the feed section, were allowed to flow through the Fuel Processor prototype (FPP). The feed section and the FPP were connected by 1/4" stainless steel tubes. This section was composed of one main oven with dimensions of 100 cm x 30 cm x 60 cm, three 25 cm x 20 cm OD x 4 cm ID cylindrical ovens whose temperature were controlled to ± 0.1 K sensitivity by Shimaden FP23 programmable temperature controllers and three 1/4" stainless steel fixed-bed micro-reactors constructed in CATREL with a length of 37 cm. The reactors were longer than the oven facilitating the placement of the reactor inside the oven by the help of stainless steel fittings. During the reaction tests, the catalyst bed was placed in the center of the stainless steel reactor. 20-gauge wire K-type sheathed thermocouples (insulation material: ceramic fiber braid) were placed near the center of the catalyst bed just outside the micro-reactor wall in each reactor and were connected to the temperature controllers. In this system, instead of wrapping and fastening the thermocouple around the reactor, the thermocouple was attached to an L-shaped 1/8" stainless steel tube and fastened. After curling the end of the thermocouple actually the measuring part, the tube was attached to the reactor such that curled end points exactly to the center of the catalyst bed. The position of the reactor and hence the catalyst bed were adjusted to coincide with the constant-temperature zone of vertical oven as in Figure 3.3. Silane-treated glass wool was used to hold the catalyst bed in a fixed position. Ceramic glass wool insulations were placed in top and bottom ends of the reactor furnaces to prevent heat loss and to provide a stable temperature profile.

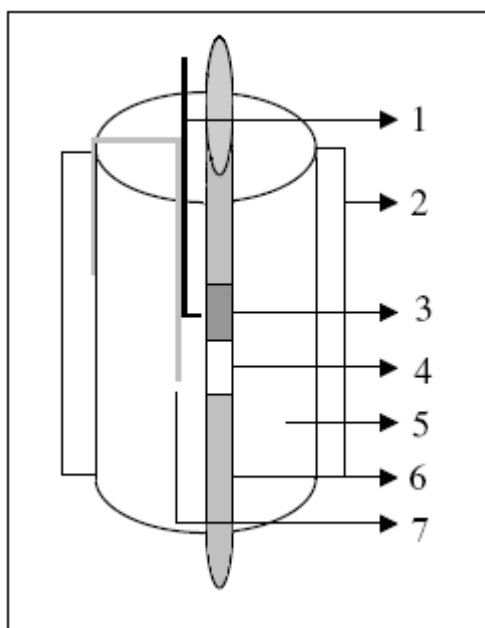


Figure 3.3. The reactor and furnace system: 1. Thermocouple 2. Ceramic wool insulation 3. Catalyst 4. Catalyst bed 5. Oven 6. 1/4" reactor 7. 1/8" stainless steel tube

Before the reaction, the reaction gases and de-ionized water were mixed for 1.5 hour to provide homogeneous mixture and steady state operation. Then the gas-stream mixture was fed to the reactors in FPP. Prior to the feed and product analysis, water should be removed from the streams. Cold traps were placed before the first reactor for feed analysis and after the last reactor for product analysis. The cold trap consisted of an ice box, two series connected stainless steel cylinders and one coiled tubing to increase contact time between the gas flow and cold environment and to guarantee condensation of remaining water vapor. After the removal of the H_2O , the product stream was sent and analyzed by using a Hiden Analytical HPR-20 QIC mass spectrometer connected to a personal computer employing MASsoft software.

The advantages and innovations about the FPP design and construction, its flow sheet and schematic representation are given in detail in the results and discussion section.

3.3. Catalyst Preparation and Pretreatment

3.3.1. OSR Catalyst

3.3.1.1. Support Preparation. The catalytic oxidation and steam reforming of hydrocarbons are known to be high-temperature reactions. Therefore, the catalyst supports should not only have high surface areas, but also possess high thermal stabilities. γ - Al_2O_3 is a commonly used support material due to its high surface area. However, it is reported to have low stability at temperatures higher than 873 K and tends to facilitate carbon formation in the presence of steam due to its high acidity. The most thermally stable version of alumina is obtained when γ -phase is transformed into α -phase at temperatures higher than 1400 K. However, its low surface area being less than $5 \text{ m}^2/\text{g}$, is likely to end up with poor catalytic activities due to the low dispersion of active metals. Hence, using a support such as δ -alumina, an intermediate phase between γ and α , having relatively high thermal stability and an acceptable surface area is optimum in terms of obtaining efficient catalytic performance (Ma, 1995).

The support preparation procedure used in this study involved crushing and sieving γ - Al_2O_3 into 400-200 μm (45-60 mesh) particle size and drying at 423 K for 2h followed by calcination at 1173 K for 4h in a muffle furnace. BET surface area of the δ - Al_2O_3 support obtained was found as $81.6 \text{ m}^2/\text{g}$ (Avci, 2003).

3.3.1.2. Preparation of Pt-Ni/ δ - Al_2O_3 Catalyst. The bimetallic Pt-Ni/ δ - Al_2O_3 catalyst (0.2% Pt-10% Ni) was prepared by a sequential route in which Pt solution was impregnated over initially prepared and calcined Ni/ δ - Al_2O_3 catalyst. Ni/ δ - Al_2O_3 catalyst was prepared by the incipient-to-wetness impregnation technique using aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The aqueous solution was prepared by dissolving a calculated amount of the precursor salt in definite amounts of de-ionized water (ca. 1.1 ml solution/g support). The support, δ - Al_2O_3 , was placed in a Büchner flask, kept under vacuum before, during and after the addition of precursor solutions. Since trapped air in the pores of the support could prevent penetration of the solutions, vacuum pump was used to remove the trapped air and to give a uniform distribution of the active component. Thus, before impregnating the solution, the support material was mixed with ultrasonic mixer for 25 min under

vacuum. A Masterflex computerized-drive peristaltic pump was used to feed the precursor solution to the vacuum flask at a rate of 0.5 mL/min via silicone tubing. The resulting thick slurry formed after ultrasonic mixing of the aqueous solution and the support under vacuum for 1.5 h was then dried overnight at 393 K and calcined at 873 K for 4 h to obtain (NiO/ δ -Al₂O₃). For the impregnation of the second metal, NiO/ δ -Al₂O₃ was placed in a Büchner flask and mixed ultrasonically for 25 min under vacuum. The aqueous Pt solution (Pt(NH₃)₄(NO₃)₂) was then added to NiO/ δ -Al₂O₃ and mixed ultrasonically under vacuum for 1.5 h. The resulting slurry involving two metals was dried overnight at 393 K, and finally, the catalyst was calcined at 773 K for 4 h.

3.3.1.3. Pretreatment of Pt-Ni/ γ -Al₂O₃ Catalyst. In order to obtain high catalytic activities, a pretreatment involving the reduction of the active metals from the oxide state, which is formed during the calcinations, to the metallic state is required prior to the reaction, since catalysts in their oxide forms are usually inactive for the reactions.

TPR studies have shown that reduction using pure hydrogen flow at 773 K for 4 h is a suitable procedure for pretreating the bimetallic Pt-Ni catalyst (Ma, 1995). Ma has also reported that during reduction, the water in the catalysts may cause premature sintering, which may lead to deactivation before the reaction. Considering these issues, the following stepwise reduction procedure was followed for the catalyst used in all of the experiments (Avci, 2003).

After placing the catalyst into the constant temperature zone of the micro-reactor, He was allowed to flow at 50 ml/min for 10 minutes to remove oxygen from the system. The gas flow was switched from He to H₂ and the latter was set to flow at 20 ml/min. Reduction was started by heating the catalyst from room temperature to 423 K at a rate of 10 K/min. The temperature was kept constant at 423 K for 30 min for the removal of adsorbed water. Third step involved heating the sample from 423 K to 573 K at a rate of 5 K/min, followed by a 30 min isothermal segment at 573 K for the removal of crystalline water. The temperature was then increased from 573 K to 773 K at a rate of 2 K/min and finally kept constant at 773 K for 4 h. After reduction, the system was allowed to cool down to ca. 423 K under H₂ flow. Below this temperature, the gas flow was switched from

H₂ to He and the latter was allowed to flow at a small flow rate, e.g. 5 ml/min, overnight to sweep H₂ from the system prior to the tests.

3.3.2. WGS Catalyst

3.3.2.1. Support Preparation. The support preparation procedure used in this study involved crushing and sieving ZrO₂ into 400-200 µm (45-60 mesh) particle size followed by calcination at 923 K for 3 hours in a muffle furnace.

3.3.2.2. Preparation of Au-Re/ZrO₂ Catalyst. The bimetallic Au-Re/ZrO₂ catalyst (2% Au-1% Re) was prepared by a sequential route in which Re precursor solution is added by impregnation method followed by addition of Au solution by deposition precipitation method. Re-ZrO₂ catalyst was prepared by the incipient-to-wetness impregnation technique using aqueous solution of NH₄ReO₄. The aqueous solution was prepared by dissolving a calculated amount of the precursor salt in definite amounts of de-ionized water (ca. 0.7 ml solution/g support). The support, ZrO₂, was placed in a Büchner flask and the impregnation procedure is applied as in Section 3.3.1.2. The resulting thick slurry formed after ultrasonic mixing of the aqueous solution and the support under vacuum for 1.5 h was then dried overnight at 383 K and calcined at 523 K for 1 h.

Re-impregnated support was put in a beaker along with de-ionized water to obtain a suspension, and the suspension's pH was adjusted around 8 using a solution of (NH₄)₂CO₃. The beaker containing the suspension was placed in an ultrasonic bath to carry out the procedure in continuous agitation. The gold precursor was dissolved in de-ionized water to obtain a 10⁻³ M solution and this solution was added to the support suspension drop by drop. The resulting mixture was left in the ultrasonic bath for one more hour and then filtered. The sample was washed with de-ionized water several times and dried overnight at 383 K and calcined at 523 K for 1 h in a muffle furnace.

3.3.2.3. Pretreatment of Au-Re/ZrO₂ Catalyst. After placing the catalyst into the constant temperature zone of the micro-reactor, the sample was heated from room temperature to reduction temperature of 453 K at a rate of 7.5 K/min under 95 ml/min He flow and then 5 ml/min H₂ was introduced to the reactor to clear the catalyst surface from oxygen, which is

present in the metal-oxide form, for 1 hour. After reduction, hydrogen flow is stopped and the system was allowed to cool down under He flow at a small flow rate, e.g. 5 ml/min, overnight to sweep H_2 from the system.

3.4. Reaction Tests

All the reaction tests were performed in the Fuel Processor Prototype (FPP) constructed for catalyst testing. In the tests, first two reactors (i.e. reforming and WGS reactors) of FPP were used in a serial fashion for performing combined OSR and WGS tests.

3.4.1. Blank Tests

Blank tests were conducted to ensure that the material of construction, glass-wool and δ -alumina (used as inert material within the catalyst bed) has no catalytic activity. The results indicated that these items above were inactive under the conditions used in the reaction tests.

3.4.2. OSR of Propane and Water Gas Shift Reactions

The reaction conditions as well as catalyst types and weights were chosen from the optimum conditions reported by Selen (2003) and Güven (2009). However, the dynamic studies required perturbations in the process variables, therefore, besides the optimum condition, various reaction conditions and feed compositions determined in an experimentally designed fashion had to be considered in order to determine that which process variables should be varied in what extent during the on-going experiment. For guaranteeing high performance and controllability Selen (2003) investigated oxidative steam reforming (OSR) of propane over bimetallic Pt-Ni/ δ -Al₂O₃ catalyst. The experiments were conducted according to the assigned carbon:oxygen, steam:carbon and W/F ratios ($1.50 < C/O_2 < 2.70$; $2 < S/C < 3$; $0.51 < W/F < 1.37$) for the temperature range of 623-743 K and for an inflow of 110-293 ml/min. Four types of feed were used during those experiments. In this thesis work, different than Selen's study, total inflow (first feed before the perturbations) was held constant at 100 ml/min and two temperature levels were chosen

as 673 K and 723 K. Selen's experimental conditions (modified according to 100 ml/min total inflow), as well as feed composition with corresponding flow rates of the reactants and the inert gas, are given in Table 3.4. It should be noted that the flow rates also correspond to percentages in the feed due to the 100 ml/min total inflow. She obtained optimum activity and selectivity with steam/carbon ratio of 3, carbon/oxygen ratio of 2.7 and W/F ratio of 0.51.

Table 3.4. A summary of the feed flow compositions

Set #	Flow rate (ml/min)					S/C	C/O ₂	W/F (mgcat* min/ml)
	Total	Propane	Oxygen	Helium	Steam			
1	100	7.3	10.2	38.7	43.8	2	2.12	1.5
2	100	6.0	8.4	31.7	53.9	3	2.12	1.5
3	100	5.1	10.3	38.4	46.2	3	1.50	1.5
4	100	6.6	7.3	27.2	58.9	3	2.70	1.5

Set 4 was chosen as the original feed in this thesis work. All experiments as well as dynamic tests started with this feed composition. Catalyst weight (0.2%Pt-10%Ni/ δ -Al₂O₃) was selected as 150 mg in all experiments. However, modification in total inflow by keeping catalyst weight constant shifted W/F ratio to 1.5, whereas $0.51 < W/F < 1.37$ was the range studied by Selen (2003).

Güven (2009) has studied Au-based, bimetallic WGS catalysts to be used in a fuel processor. She investigated the effect of temperature for a range of 523-623 K, the effect of W/F ratio (0.02, 0.03, and 0.06), H₂O/CO ratio (5, 6 and 7) and also the effect of Re impregnation and composition on the WGS performance of Au based catalysts. The optimum catalyst composition for WGS reaction was found to be 1%Re-2%Au/ZrO₂. Catalyst weight was selected as 170 mg for this catalyst composition.

In this work, OSR and WGS experiments were conducted in serial fashion. 150 mg of fresh catalyst (0.2% Pt-10% Ni/ δ -Al₂O₃) was placed into the constant temperature zone of OSR microreactor and 170 mg of fresh catalyst (1% Re-2% Au/ZrO₂) was placed into

the constant temperature zone of WGS microreactor. The catalysts were pretreated through reduction as described in the previous section. The temperatures of the reactors were raised to the reaction temperatures under inert helium flow of 50 ml/min. After reaching the reaction temperature, flow was decreased and helium was trapped within the reactors by diverting the flow to the bypass vent. Feed gases (propane, oxygen, steam and helium) were allowed to flow through the bypass vent line for one and a half hour to ensure steady-state homogeneous flow. The reaction was started by diverting the feed flow into the reactor. Mass Spectrometer required approximately 2-2.5 hours to reach steady state. After the reaction with the original feed reached steady state, the first perturbation in the feed was given to the system. The system reached steady state in approximately 2-2.5 hours after each perturbation. A total of two perturbations are given into the system, and three steady state profiles (including the original one) were obtained in each experiment.

The feed compositions used in Selen's study (2003) have been a guidance for the perturbations in the dynamic studies. Three types of experiments were conducted at two temperature levels. Propane flow rate, oxygen flow rate and steam flow rate were changed for each type of experiment. In each experiment, perturbations were given to one type of process variable. For example, during the propane tests, first perturbation was given a ramp type increase in propane flow rate, and the second perturbation was given as a ramp type decrease in propane flow rate. In each experiment, the system behavior was observed for one increase and for one decrease in the amount of process variable. By taking the conditions in Table 3.4 into account, propane flow rate, oxygen flow rate and steam flow rate have been changed for flow ranges of 5.1-7.3 ml/min, 7.3-10.3 ml/min and 43.8-58.9 ml/min, respectively. Original feed composition and a summary of the experimental conditions as well as perturbations are given in Table 3.5 and Table 3.6, respectively. Original feed composition had to be modified in terms of steam flow rate due to the HPLC pump rate and significant figures. Steam flow rate in Selen's set # 4 feed was 58.9 ml/min. It was modified in this study, which didn't change S/C significantly. In order to get a total inflow of 100 ml/min, the change was balanced by helium flow rate.

Table 3.5. Original feed flow composition used in each experiment

Flow rate (ml/min)					S/C	C/O ₂
Total	Propane	Oxygen	Helium	Steam		
100	6.6	7.3	26.5	59.6	3	2.70

Table 3.6. A summary of the experimental conditions used during this study

Exp #	T _{OSR} (K)	T _{WGS} (K)	Manipulated variable	Flow rate (ml/min)		
				Original Feed	1 st perturbation	2 nd perturbation
1	723	523	Oxygen	7.3	10.3	8.4
2			Propane	6.6	7.3	5.1
3			Steam	59.6	44.7	59.6
4	673	573	Oxygen	7.3	10.3	8.4
5			Propane	6.6	7.3	5.1
6			Steam	59.6	44.7	59.6

4. RESULTS AND DISCUSSION

The aim of this study is to design, construct and test a fuel processor prototype (FPP) for catalyst performance studies under steady-state and dynamic operation conditions. In this context, the output parameter(s) that can be used in monitoring the system behavior were also tried to be determined. The first part of the thesis work covers the basis of design and general process description. The second part includes inertia tests for system behavior, and steady state and dynamic performance of the catalysts against changes in the process variables.

4.1. Design and Construction of the FPP

An experimental fuel processor prototype (FPP) was designed and constructed. The ultimate aim of the fuel processor is to obtain CO-free hydrogen from hydrocarbons, like methane and propane. In the fuel processor, three catalytic reactions, namely reforming, WGS and PROX are performed in series. Thus, the prototype must include three reactors for these reactions. Accordingly, the prototype consists of a main oven with a controlled heater; three vertical ovens, inside the main oven, having their own temperature controlling system for the reactors, in which each one of the reforming, WGS and PROX reactions can be conducted; a main circulating fan for guaranteeing homogeneous temperature inside the main oven (i.e. around the reactor ovens) and 1/4", 1/8" and 1/16" stainless steel tubes, fittings and valves for transfer lines. Size and design parameters of the test system were determined after a long decision period. The schematics of the main oven with corresponding dimensions are given in Figures 4.1.

Material of construction of the main oven and the reactor ovens is stainless steel. Lids of the main oven can be opened upwards and/or frontwards. Lids and walls of the main oven, except the left and right ones, were constructed by sandwiching glass wool insulations between two stainless steel plates. Rock wool, sometimes referred to stone wool, is used as the insulation material in the left and right walls. The reason for using different insulation materials in the construction part is the fact that valves, fan and resistance that are fastened in the left and right walls, required thinner walls having higher

insulation ability. Using sandwiching technique with these insulation materials provided efficient thermal insulation, less energy consumption, less fluctuations in the temperatures and prevention of hot outside surfaces. Inside the main oven, there are three vertical ovens, each being 25 cm long and having a diameter of 20 cm, as it can be seen in Figure 4.2 (pipelines, valves and fittings are excluded). The driving force for heat flow is the temperature difference between the reactors and main oven, and it has been important in determination of reactor sizing that guarantees constant temperature zones in the reactor ovens during the tests. The insulation material inside the reactor ovens is also glass wool. Cylindrical ovens are preferred rather than cubic ones in order not to impede uniform air and heat circulation inside the main oven, especially around and between the reactor ovens.

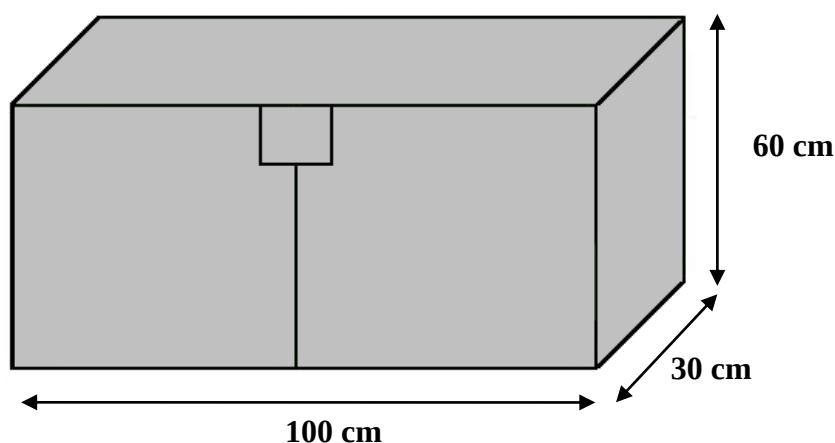


Figure 4.1. Main oven from outside

The reactors are placed inside each of the reactor ovens, whose temperature level is controlled by programmable temperature controllers. Electrical ovens are used in order to heat up the reactors. However, for effective heating of the main oven, a fan-resistance combination is used in the left wall of the system, which is shown schematically in Figure 4.2. Heating is supplied by a resistance with a diameter of 22 cm and the fan is used in order to guarantee effective circulation of air and homogeneous ambient temperature for the reactor ovens and the transfer lines. The fan has a diameter of 15 cm and maximum operating temperature is 350 °C. Main oven keeps liquid reactant(s) and products, (in our case water) vaporized inside the whole system; it eliminates the need of using heating tapes around pipelines, since all the reactor ovens and all their feed and product lines as well as the transfer lines are placed inside the main oven. Therefore, the presence of the main oven

guarantees a perfect ambient temperature control for the reactor ovens and contamination free performance of the system.

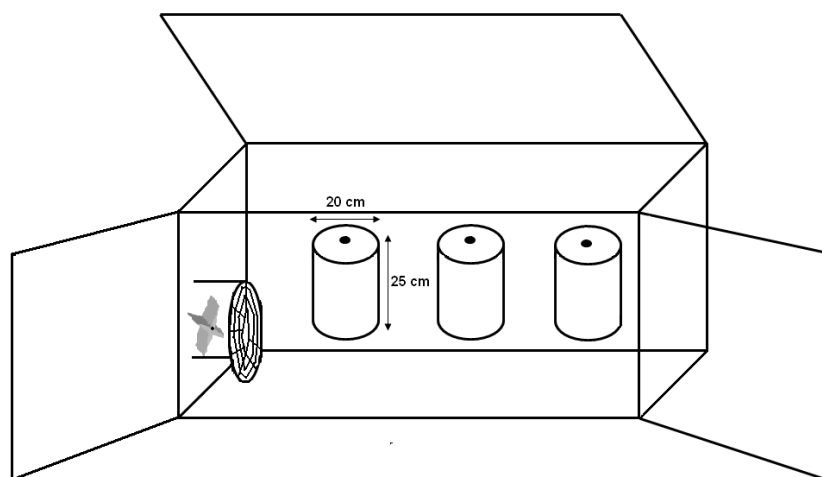


Figure 4.2. Inside the main oven

The Fuel Processors include three reactors in series, in which three reactions, namely reforming, water-gas shift (WGS) and preferential CO oxidation (PROX) are conducted, as it is explained in Chapter 2 in detail. The test system enables to perform these three reactions in a serial operation during which each reactor operates at different temperature levels. The piping/valve combinations are designed such that each reactor has individual feeding block having mass flow controllers for gas and HPLC pump for liquid feed supplies to permit additional streams in order to obtain the desired product concentration at the exit of the system in serial operation mode. Besides the possibility of the additional new streams, this advantage offers parallel use of the reactors, meaning that one can observe the effect of catalyst composition and/or process variables by performing the same experiment in each reactor simultaneously with different reaction conditions and/or catalysts. This design also allows to perform catalyst pretreatment and reduction steps simultaneously, which is a time-saving opportunity before the experiments. The reactor system can be used to simulate different combinations of reactions, meaning that it can be used not only for OSR, WGS and PROX reactions in serial operation, but also for any reactions such as HTWGS, LTWGS and PROX, double combination of OSR and WGS reactions or for individual tests. The design of the system enables to measure the performance of the combined system operating in a serial fashion as well as the performance of each one of the single units.

The feed and product analysis of the fuel processor prototype are conducted by a Mass Spectra equipped with an 8-way manifold/diverter system making simultaneous on-line and real-time analysis of all feeds and product streams, total of 6 lines incoming to/outgoing from the reactors, possible. One can analyze the concentration of the gases in the feed or product stream of any reactor at any time.

It is possible to divert flow using three way valves. There are two three way valves after contacting of the gas mixture with inlet steam, as it can be seen in Figure 4.4. The first one allows two options: Feed analysis or feeding the mixture to the first reactor. After choosing feed analysis, the gases can be diverted so that the concentration of the gases in the feed composition can be analyzed using the mass spectrometer. Another three way valve is used for diverting the flow to the bypass vent line for establishing steady state flow and mixing of the steam and other gaseous reactants prior to the reaction.

One of the challenges of this system was water contamination. As it is known, water has to be removed prior to the analysis. In order to overcome this problem, two stainless steel cylinders and also a 2 m $\frac{1}{4}$ stainless steel tube in spiral shape is used as condensers in an ice bath to guarantee the complete removal of water, as it is shown in Figure 4.3.

After each reactor there is vent option before the transfer to analysis system, which is very useful during catalysts pretreatment and reduction steps. Besides this advantage, possibility of addition of new streams, which can be used not only for regulating the flow compositions for keeping the overall CO & H₂ concentration levels within the preferred limits, but also for making it possible to carry out pretreatment and reduction steps simultaneously.

Five temperature controllers are used in this system, as it is shown in Figure 4.4. Three of them are programmable and are used for the reactors, one of them is used for the main oven and another one is used in the transfer line of the water feed from the HPLC pump to main oven. Heating tape for the water feed was necessary, because it had to be vaporized not only before mixing with the gas mixture, but also before entering to the main oven.

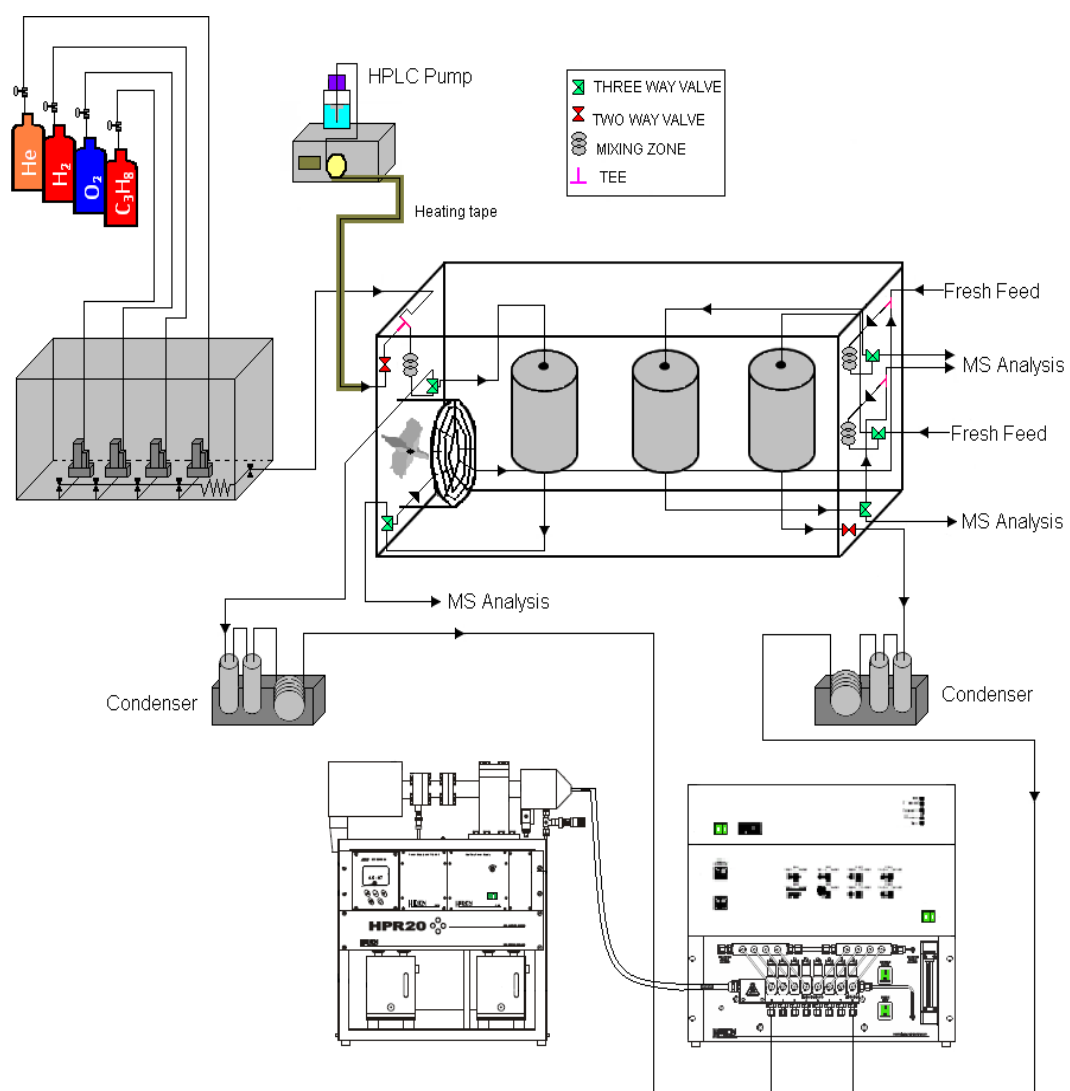


Figure 4.3. The microreactor flow and product analysis system

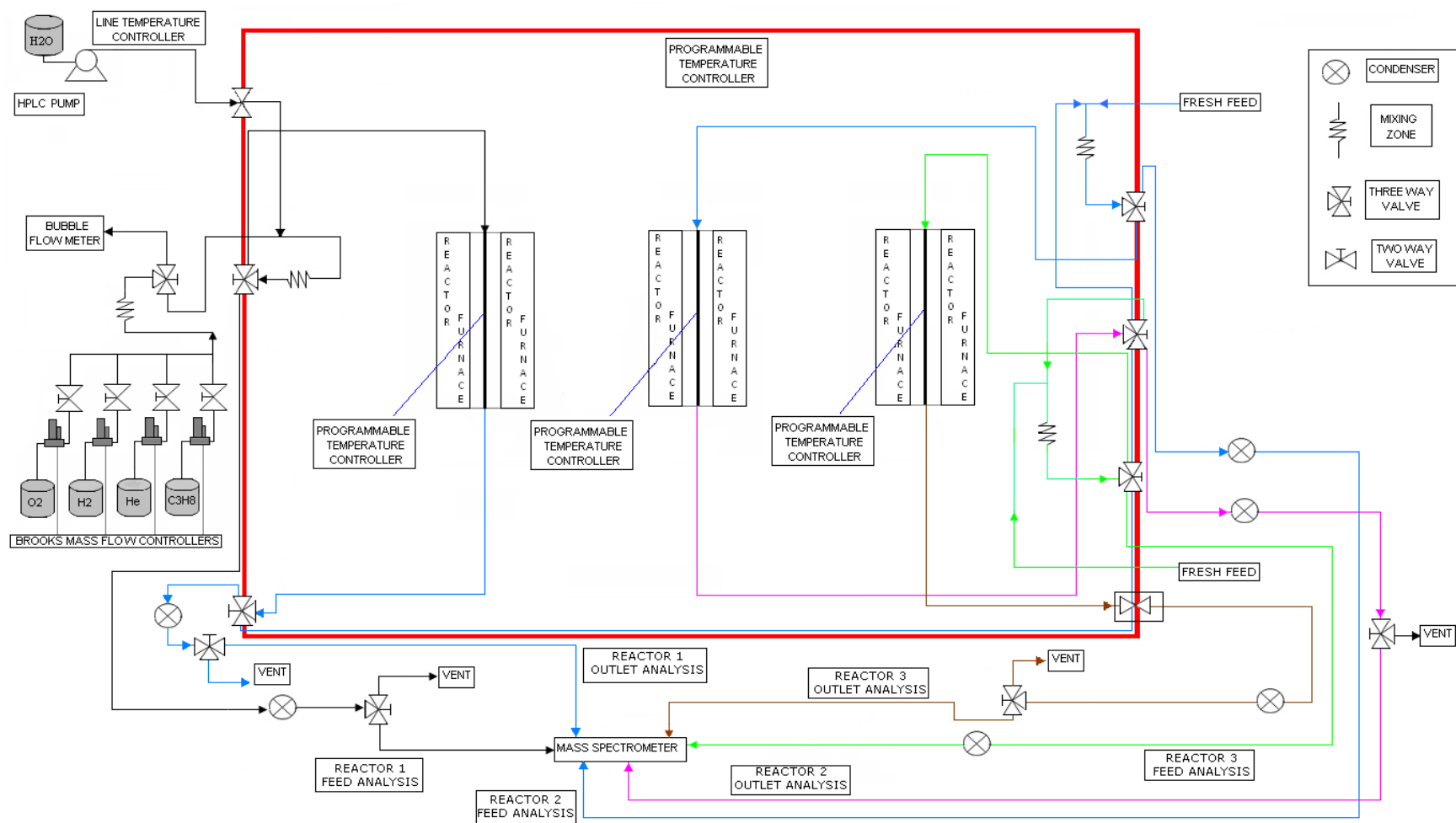


Figure 4.4. Process flowsheet of the fuel processor system

4.2. Tests for Determination of System Inertia

This part of the thesis work includes blank inertia tests made with inactive catalysts for analyzing dynamic behavior of the system when there is no reaction. The aim is to observe when and how the system responds to the changes in the process variables, namely oxygen flow rate and propane flow rate. Unreduced δ -alumina supports with no metal loadings were placed in the reactors in order to take the effect of pressure drop, which may occur with the catalyst bed, into account. Since the velocity of the gases changes when going through the bed, this effect had to be considered in analyzing the response time. As it is mentioned in the previous section, there are a lot of transfer lines with changing diameters and lengths. Inertia tests helped to determine the time that takes mass spectrometer to sense any perturbation (done at the beginning of the system) after gas mixture flows through all reactors, transfer lines and condensers without any reaction occurring.

In the first part of these tests, ramp type perturbations were given to the oxygen flow rate. The temperature of the first reactor (OSR reactor) was set to 723 K, and the temperature of the second reactor (WGS reactor) was set to 523 K. The outlet stream of the WGS reactor passed through condensers before the analysis in MS since water vapor may harm the MS and the analysis. The oxygen flow rate in the original feed was 7.3 ml/min. During these tests, it was changed to 8.4 ml/min and 10.3 ml/min, which were the values Selen (2003) used for different feed streams during her parametric OSR performance tests. Many ramp type perturbations were given to the oxygen flow rate in the direction as an increase and followed by a decrease in order to observe the response time of the system clearly. Figure 4.5 shows propane (pink) and oxygen (dark blue) concentration changes in the outlet of WGS reactor in response to the perturbations given to the oxygen flow rate, which is shown in red. As it is expected, an increase in the oxygen flow rate increased oxygen concentration and decreased propane concentration. Similarly, the opposite effect can be observed for a decrease in oxygen flow rate in the feed.

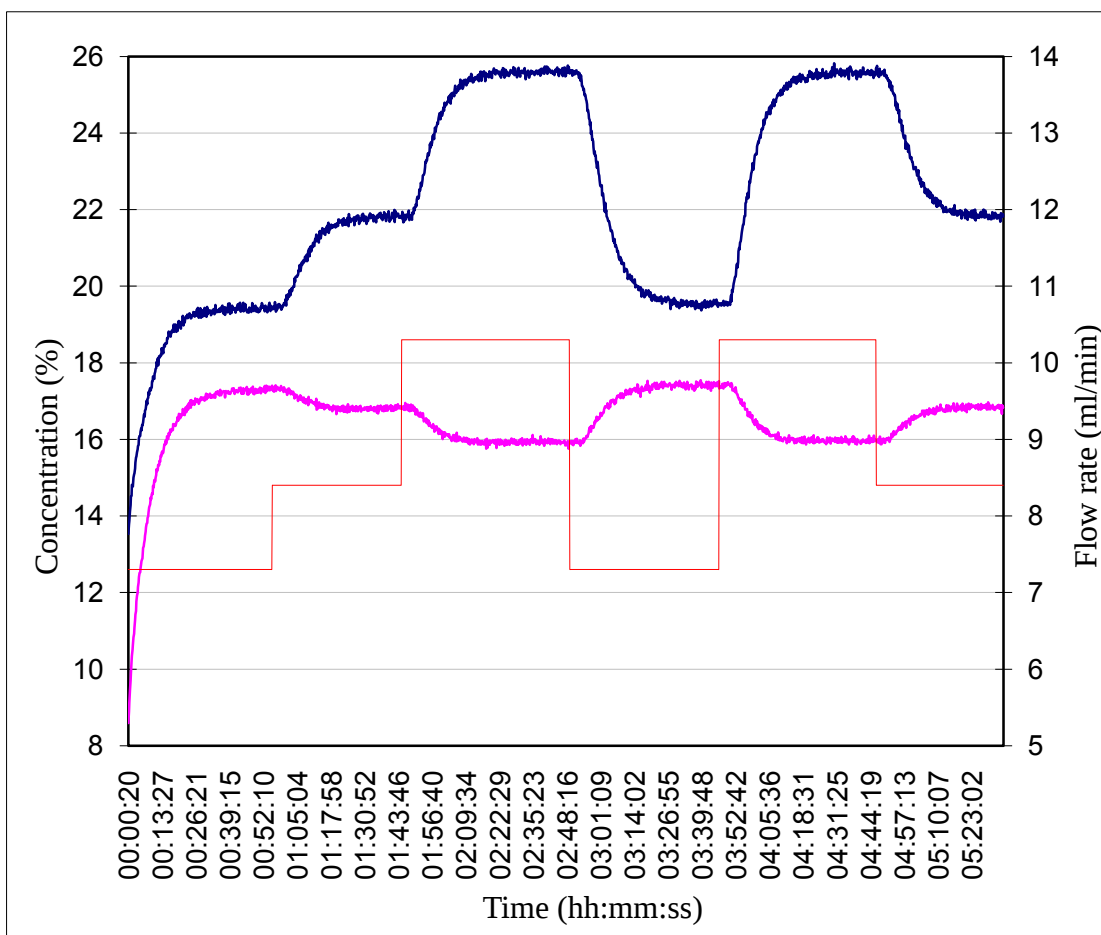


Figure 4.5. System response against perturbations in O₂ flow rate
(— Propane concentration — Oxygen concentration — Oxygen flow rate)

The response time of the system, when there was no reaction can be better seen, if it is zoomed to the moment that the perturbation in the feed was made. Figure 4.6 shows the response of the system, when the flow rate of the oxygen was increased from 7.3 ml/min to 10.3 ml/min. The figure helps to approximate the response time, however, the opportunity of online and real time analysis allowed determining the exact time. First of all, if Figure 4.6 is carefully observed, the time that took mass spectrometer to sense the change in the inlet flow rate after the stream passes through all transfer lines, reactors, etc. was 4-5 minutes. The perturbation was given at 03:46:35 and the steady state concentration profile of the exit stream for the former/original set was disturbed after 4 minutes and 10 seconds, and the steady state was reached at 04:22:22. It can be said that in no reaction condition, the system required approximately 36 minutes for reaching the new steady state after a perturbation in the feed was made.

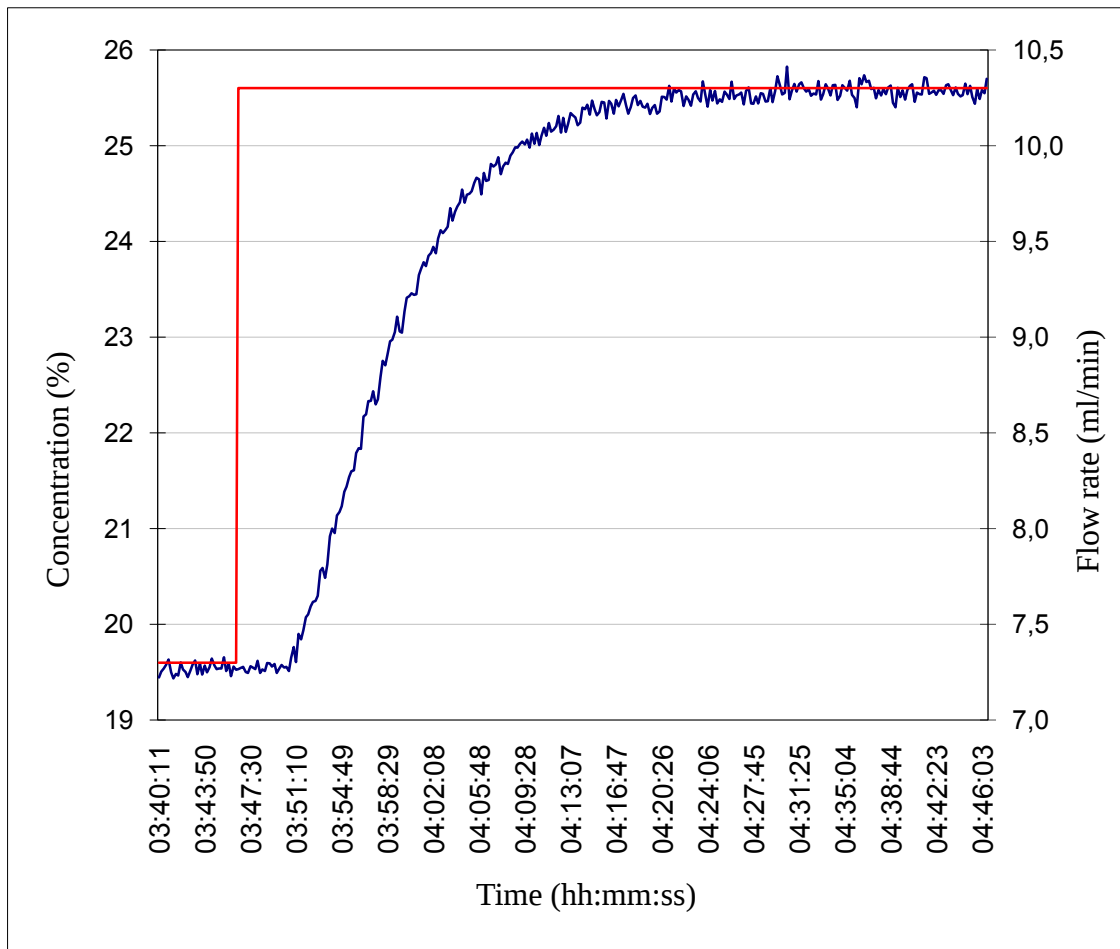


Figure 4.6. System response to an increase in O₂ flow rate
(— Oxygen concentration — Oxygen flow rate)

Figure 4.7 shows the response of the system, when the flow rate of the oxygen was decreased from 10.3 ml/min to 8.4 ml/min. The perturbation was given at 04:46:32 and the steady state profile of the exit stream for the former/original set was disturbed after 3 minutes and 33 seconds; and the steady state was reached at 05:21:41. For this case, the system again required approximately 36 minutes to reach new steady state. Other cases are also observed and the common point was that new steady state was achieved in approximately 36 minutes. What changes was the time necessary for MS to sense the perturbation. It can be said that both sensing time of MS and the shape of the concentration profile depend on the flow rate of the gas stream and the amplitude of the ramp, but the change was limited only in seconds.

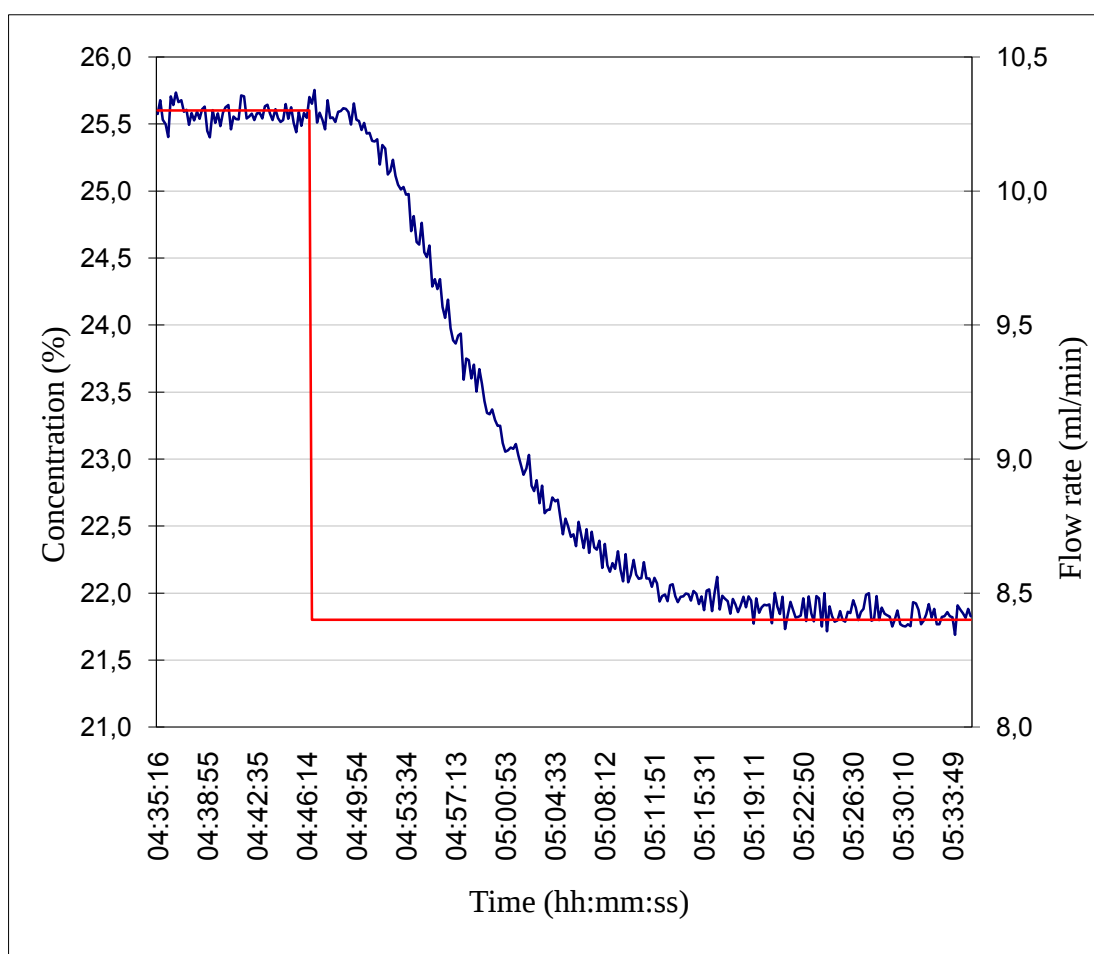


Figure 4.7. System response to a decrease in O₂ flow rate
(— Oxygen concentration — Oxygen flow rate)

In the second part of these tests, perturbations were given to the propane flow rate. The temperature of the OSR reactor was set again to 723 K, and the temperature of the WGS reactor was set to 523 K. The propane flow rate in the original feed was 6.6 ml/min. During these tests, it was changed with ramps to 5.1 ml/min and then to 7.3 ml/min, which were the values Selen (2003) used in her parametric OSR performance tests. Many ramp type perturbations were given to the propane flow rate in the feed stream, as an increase and a decrease in order to observe the response time of the system clearly. Figure 4.8 shows propane (pink) and oxygen (dark blue) concentration profiles in the exit stream which changes in response to the ramps in propane flow rate (green) in the feed stream. As it is expected, an increase in the propane flow rate in the feed increased propane concentration of the exit stream and, at the same time, decreased oxygen concentration. Similarly, the opposite effect can be observed for a decrease in propane flow rate.

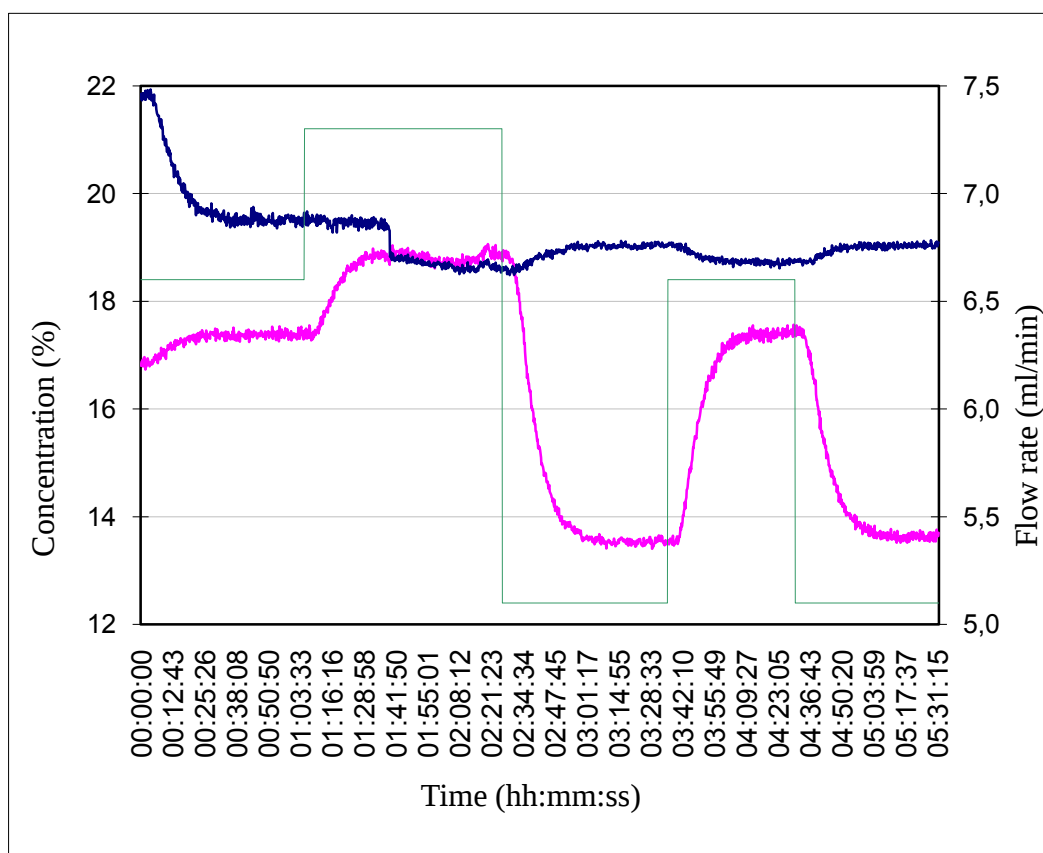


Figure 4.8. System response against perturbations in C_3H_8 flow rate
(— Propane concentration — Oxygen concentration — Propane flow rate)

Flammability limits, carbon to oxygen ratio and steam to carbon ratio were important parameters in designing the experiments and defining the test limits. In order to stay around S/C of 3 and C/O_2 of 2.7, propane flow rate should not be changed in large amounts. Since propane flow rate was small, the perturbations in propane flow rate resulted in remarkable changes in propane concentration, however, only slight changes in the oxygen concentration was observed. One can easily observe that any ramp change in the feed results in opposite responses in oxygen and propane concentration profiles. Figure 4.9 shows the response of the system, when the flow rate of the propane in the feed was increased from 5.1 ml/min to 6.6 ml/min. The perturbation was given at 03:36:07 and the steady state concentration profile of the former/original set was disturbed after 4 minutes and 37 seconds; and the new steady state was reached at 04:12:08. This result confirms the previous ones that in no reaction condition, the system required approximately 36 minutes for reaching the new steady state.

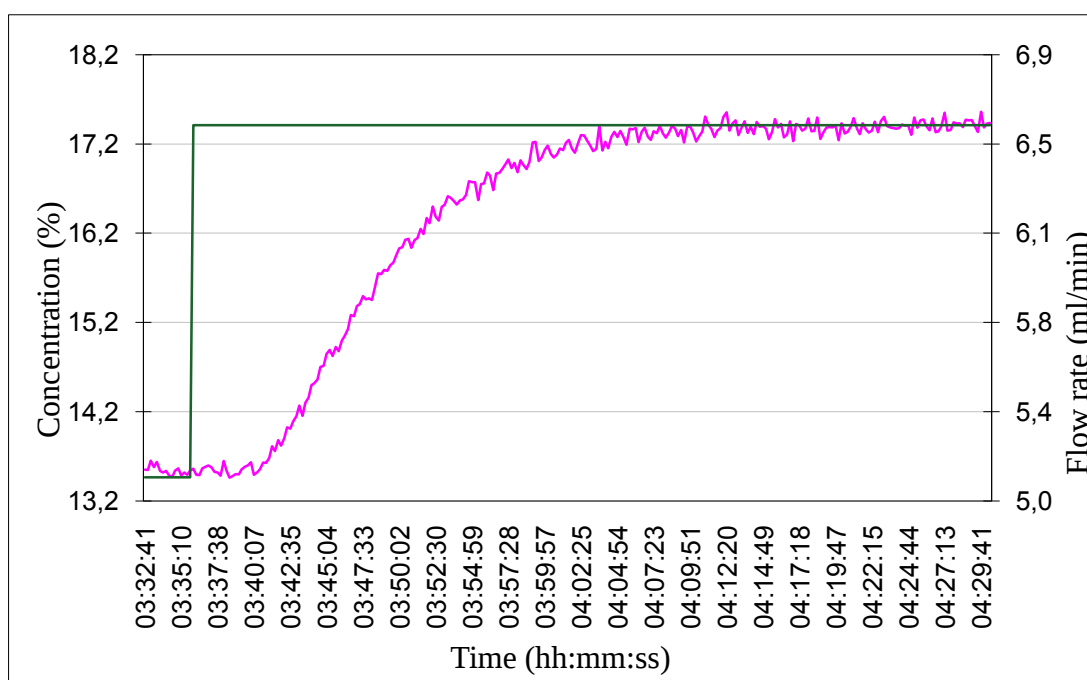


Figure 4.9. System response against an increase in C_3H_8 flow rate

(— Propane concentration — Propane flow rate)

Figure 4.10 shows the response of the system, when the flow rate of the propane in the feed was decreased from 6.6 ml/min to 5.1 ml/min. For this case, the system again required approximately 37 minutes to reach new steady state in no reaction condition.

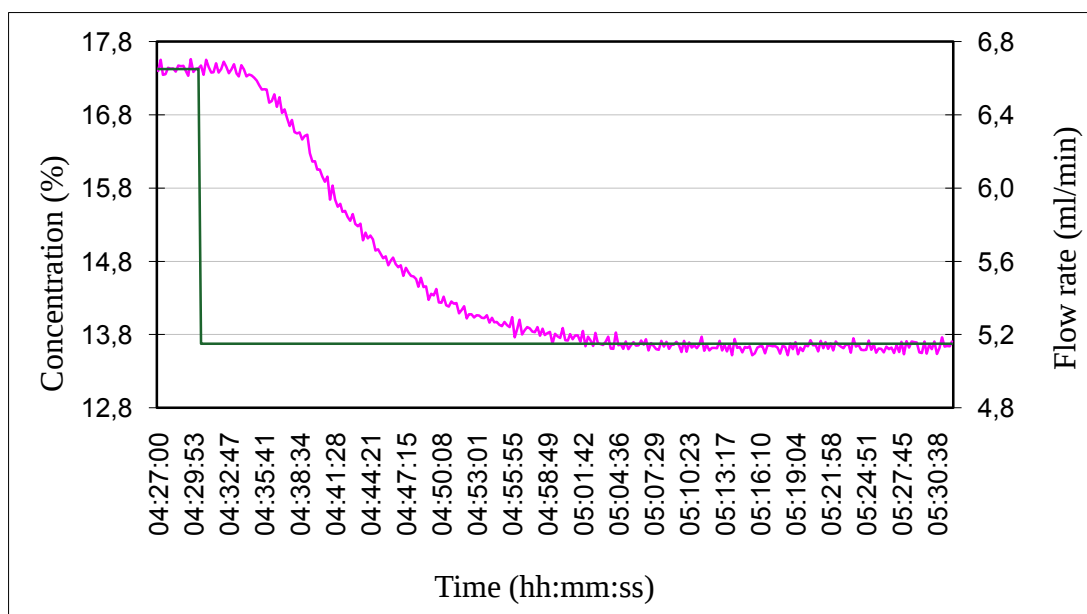


Figure 4.10. System response against a decrease in C_3H_8 flow rate

(— Propane concentration — Propane flow rate)

Dynamic tests also included perturbations in water flow rate, however, since water must be removed before analysis, inertia tests for water did not performed.

Inertia tests showed that the system reached the new steady state after a perturbation in approximately 36 minutes, when there was no reaction. It can be predicted that in dynamic tests reaching a new steady state will take longer than 36 minutes because of the time required to bring both reactors, in which many side reactions occur beside the main reaction, to the new steady state. Knowing the inertia of the system, one can study the dynamic response of the system to any perturbation in a detailed fashion and can model the system response. The blank test models can be used in analyzing the system dynamics during real operation helping to form the control structure.

4.3. Catalyst Performance Tests

Suitable activity and selectivity characteristics are important parameters in catalyst design and development. The dynamic response of the fuel processor prototype highly depends on the characteristics and performance of its catalysts. In this part of the study, the dynamic and steady state performance of the serial OSR and WGS reactors are studied. In the tests, 0.2%Pt-10%Ni/ γ -Al₂O₃ catalyst was used in OSR and 2%Au-1%Re/ZrO₂ was used in WGS reactor. Oxygen flow rate, propane flow rate, steam flow rate and reactor temperatures were used as the test parameters.

The oxidative steam reforming activity is proportional to the C₃H₈ conversion; the activity of the catalysts was expressed as C₃H₈ conversion percent defined as follows:

$$C_3H_8 \text{ conversion } (\%) = \frac{[C_3H_8]_{in} - [C_3H_8]_{out}}{[C_3H_8]_{in}} \times 100 \quad (4.1)$$

In all sets, hydrocarbon and oxygen conversions were nearly 100 percent throughout the experiments. The flow rate of liquid water used in the experiments was calculated by the formula:

$$\dot{V}_{(steam)H_2O} = \frac{\dot{V}_{(liquid)H_2O} \times \rho_{H_2O} \times R \times T}{MW_{H_2O} \times P} \quad (4.2)$$

where $\rho=1000$ g/L; $P=1$ atm; $R=0.082$ L.atm / (mol.K); $T=298$ K and $MW_{H_2O}=18$ g/mol.

The ramp type perturbations given to oxygen flow rate, propane flow rate and steam flow rate can also be expressed as perturbations given to the steam to carbon ratio and carbon to oxygen ratio. Modified version of the experimental conditions listed in Table 3.6 is given in the following table.

Table 4.1. Experimental conditions in terms of S/C ratio and C/O₂ ratio

Exp #	T _{OSR} (K)	T _{WGS} (K)	Manipulated variable	Original Feed		1 st perturbation		2 nd perturbation	
				S/C	C/O ₂	S/C	C/O ₂	S/C	C/O ₂
1	723	523	Oxygen	3.0	2.7	3.0	1.9	3.0	2.4
2			Propane	3.0	2.7	2.7	3.0	3.9	2.1
3			Steam	3.0	2.7	2.3	2.7	3.0	2.7
4	673	573	Oxygen	3.0	2.7	3.0	1.9	3.0	2.4
5			Propane	3.0	2.7	2.7	3.0	3.9	2.1
6			Steam	3.0	2.7	2.3	2.7	3.0	2.7

4.3.1. Effect of Oxygen Flow rate

In this part of the study, the effect of oxygen flow rate in the feed (or C/O₂ ratio) on the steady state performance of serial OSR and WGS reactors was investigated. The experimental conditions are given in Table 4.1. As can be followed from the table, the effect of C/O₂ ratio in the feed was tested comparing the results of C/O₂=2.7 (original feed), C/O₂=1.9 and C/O₂=2.4 for two different temperature level combinations for OSR & WGS reactors (Exp. 1 & 4). Steady state concentrations of H₂, CH₄ and CO₂ gases in the product stream are given in Figure 4.11 and 4.12, CO gas concentration in the exit stream is given in Figure 4.13 and selectivity of the catalysts, as H₂/CO ratio in the product stream, is given in Figure 4.14 for sets 1 & 4. The comparison between the results of the sets indicates that all variables mentioned above lead to responses in similar directions. A decrease in the C/O₂ ratio increased H₂, CO₂ and CO concentrations, while decreased the concentrations of CH₄ and C₃H₈ in the exit of WGS reactor. Increase in the oxygen flow

rate resulted in a decrease in the selectivity of the OSR & WGS system, as shown in Figure 4.14. Decreased methane concentration can be explained by suppressed methanation side reaction, indicating higher concentrations of CO and CO₂ gases at the outlet of the oxidative steam reforming reactor. Feeding additional O₂ to the system, which favor rapid TOX of propane, resulted in less C₃H₈ concentration in the product stream. The selectivity of the system, defined as H₂/CO in the product, is of extreme importance; the results indicate that an increase in C/O₂ ratio in the feed led to an increase in the H₂/CO ratio at the exit of OSR and WGS system.

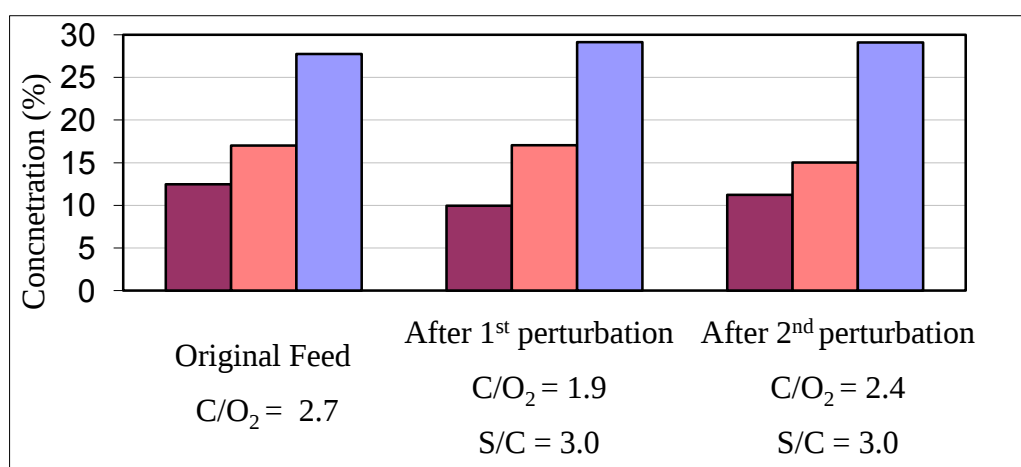


Figure 4.11. Changes in concentration against perturbations in O₂ flow rate for exp. # 1

(■ CH₄ ■ CO₂ ■ H₂)

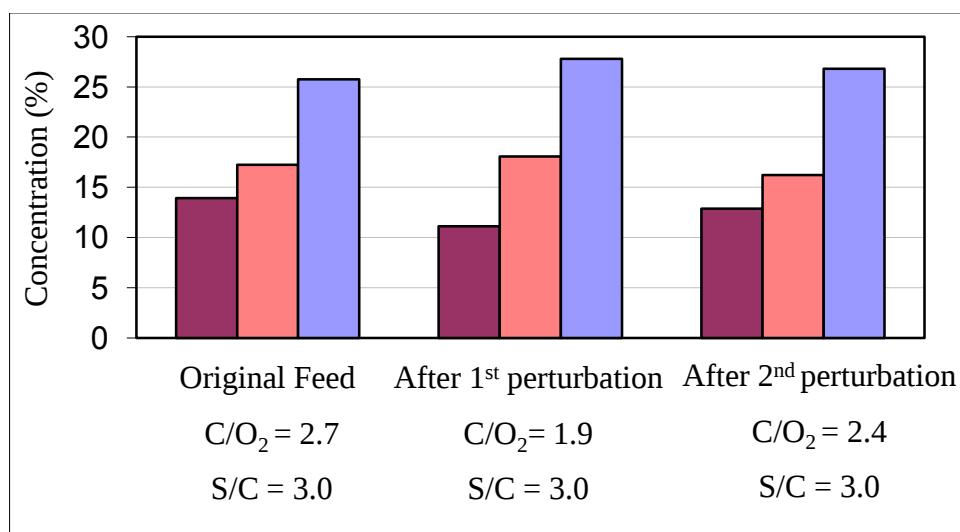


Figure 4.12. Changes in concentration against perturbations in O₂ flow rate for exp. # 4

(■ CH₄ ■ CO₂ ■ H₂)

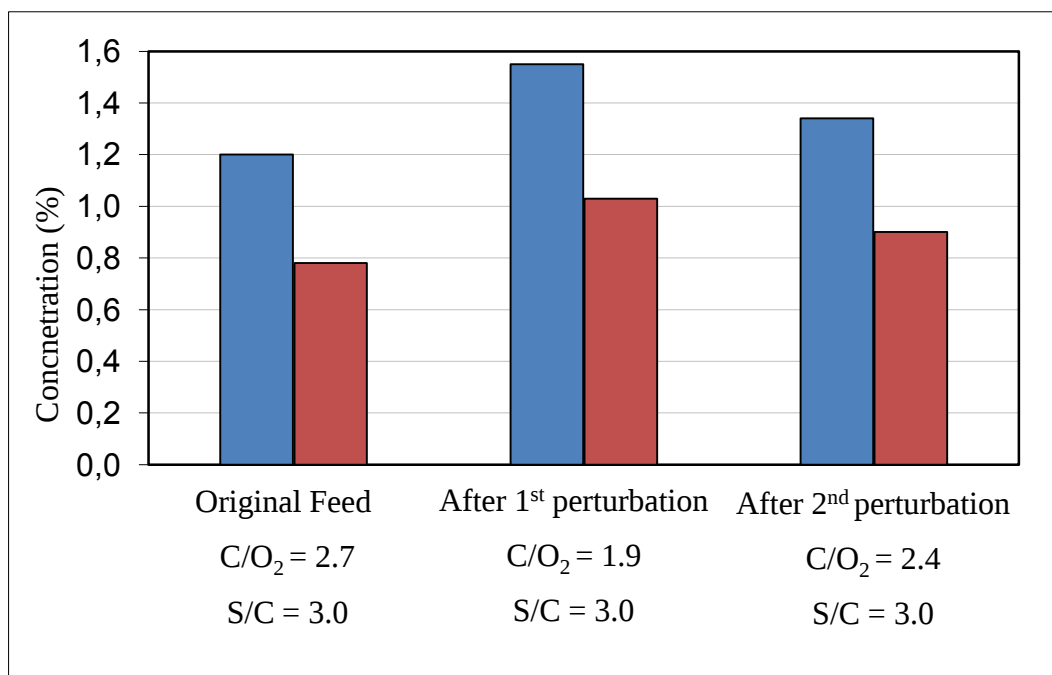


Figure 4.13. Effect of O_2 flow rate on CO concentration

(■ Experiment # 1 ■ Experiment # 4)

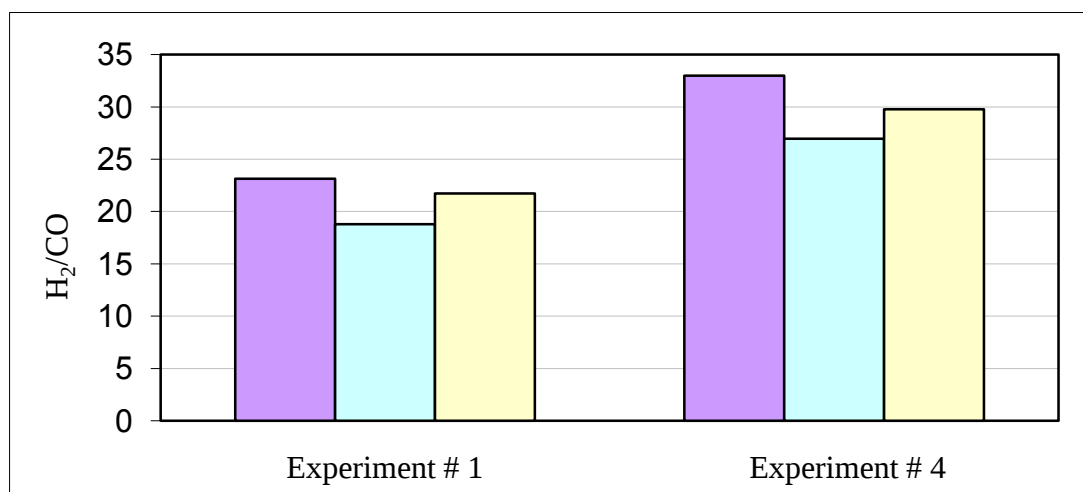


Figure 4.14. Selectivity of the catalyst for experiments # 1 & # 4

(■ Original Feed $C/O_2 = 2.7$ $S/C = 3.0$ ■ After 1st perturbation $C/O_2 = 1.9$ $S/C = 3.0$
 ■ After 2nd perturbation $C/O_2 = 2.4$ $S/C = 3.0$)

4.3.2. Effect of Propane Flow rate

In this part of the study, the effect of propane flow rate in the feed on the steady state performance of serial OSR and WGS reactors was investigated. When the propane flow rate was increased from 6.6 ml/min to 7.3 ml/min (1st perturbation) keeping the steam flow rate constant, S/C ratio decreased, while C/O₂ ratio increased. Greater hydrogen production would be expected, since the amount of hydrocarbon in the feed stream was increased. If Figure 4.15 and 4.16 are analyzed, very slight increase or even a decrease in H₂ concentrations can be observed. This may be resulted from the enhanced methanation in OSR reactor and/or suppressed WGS reaction by limited steam. Increase in methane concentration in the product for higher propane flow rate can be seen in Figures 4.15 and 4.16 (purple). During these tests, propane flow rate were adjusted so that S/C ratio was close to 3 in order to prevent coke formation in OSR reactor. Furthermore, increase in propane flow rate increased CO concentration and decreased H₂/CO ratio.

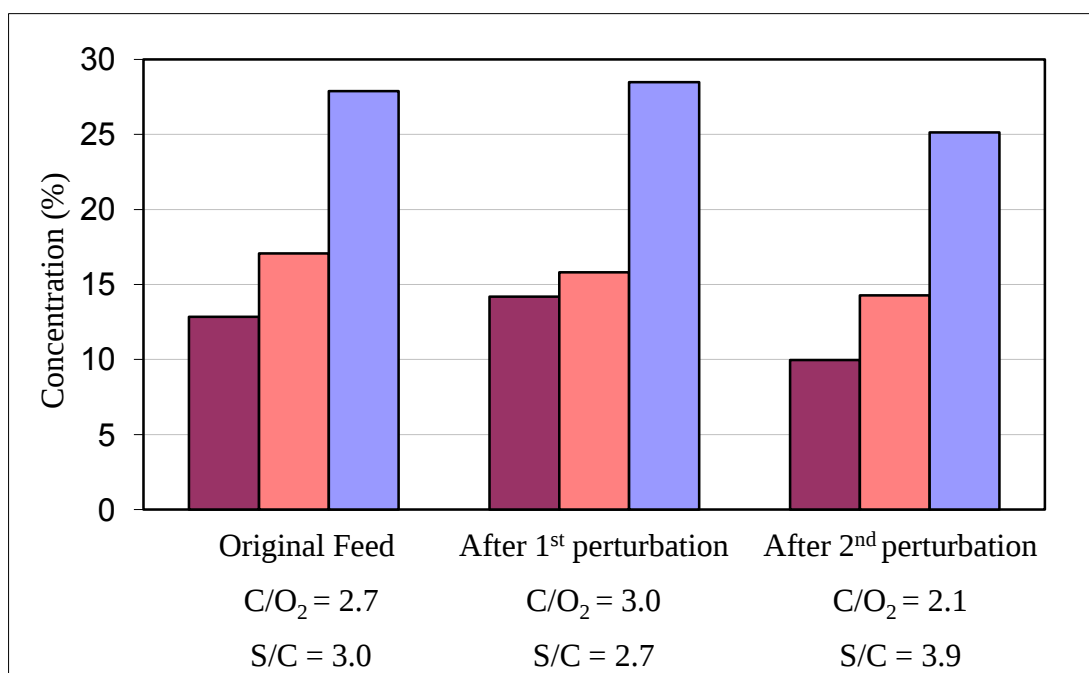


Figure 4.15. Changes in concentration against perturbations in C₃H₈ flow rate for exp. # 2
(■ CH₄ ■ CO₂ ■ H₂)

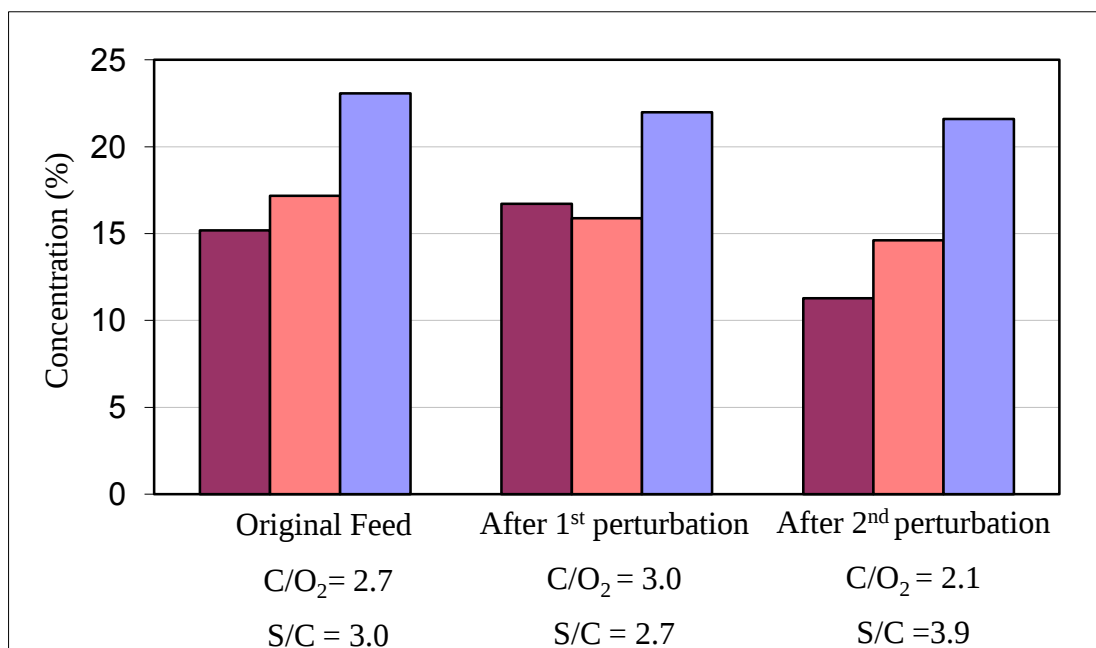


Figure 4.16. Changes in concentration against perturbations in C₃H₈ flow rate for exp. # 5
(■ CH₄ ■ CO₂ ■ H₂)

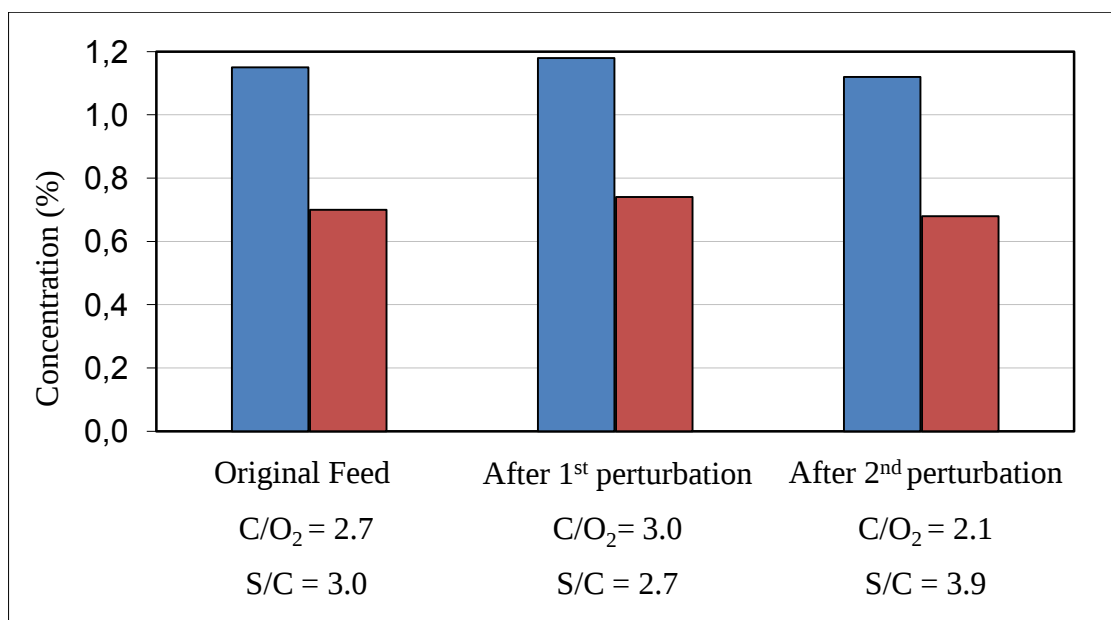


Figure 4.17. Effect of C₃H₈ flow rate on CO concentration
(■ Experiment # 2 ■ Experiment # 5)

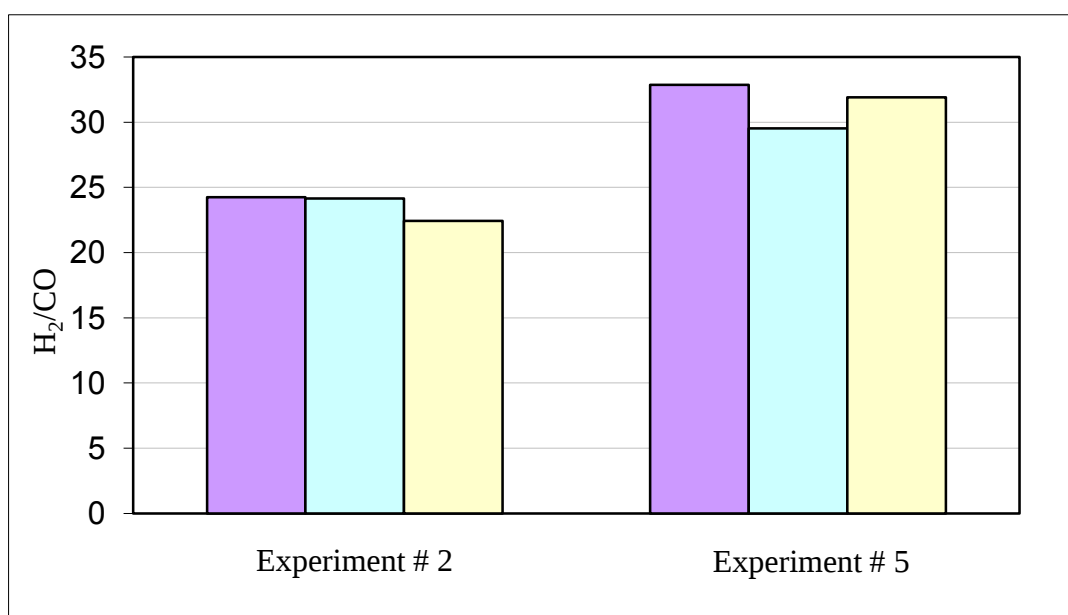


Figure 4.18. Selectivity of the catalyst for experiments # 2 & # 5

(■ Original Feed C/O₂ = 2.7 S/C = 3.0 ■ After 1st perturbation C/O₂ = 3.0 S/C = 2.7
■ After 2nd perturbation C/O₂ = 2.1 S/C = 3.9)

4.3.3. Effect of Steam Flow rate

Steam reforming reaction is directly related to the amount of water fed or S/C ratio. This reaction contributes mostly to the H₂ amount produced. That's why, when water flow rate was decreased, there existed remarkable decrease in H₂ concentration, as it can be seen in Figure 4.19 and 4.20. A decrease in steam flow rate (or in S/C) enhanced methanation and led to an increase in CO concentration while suppressing CO₂ production. All of these findings indicated that a decrease in steam concentration in the feed stream did not favor WGS reaction as well. The decrease in water flow rate shifted the WGS reaction in reverse direction resulting in an increase in CO concentration and, at the same time, led to a decrease in CO₂ and H₂ concentrations.

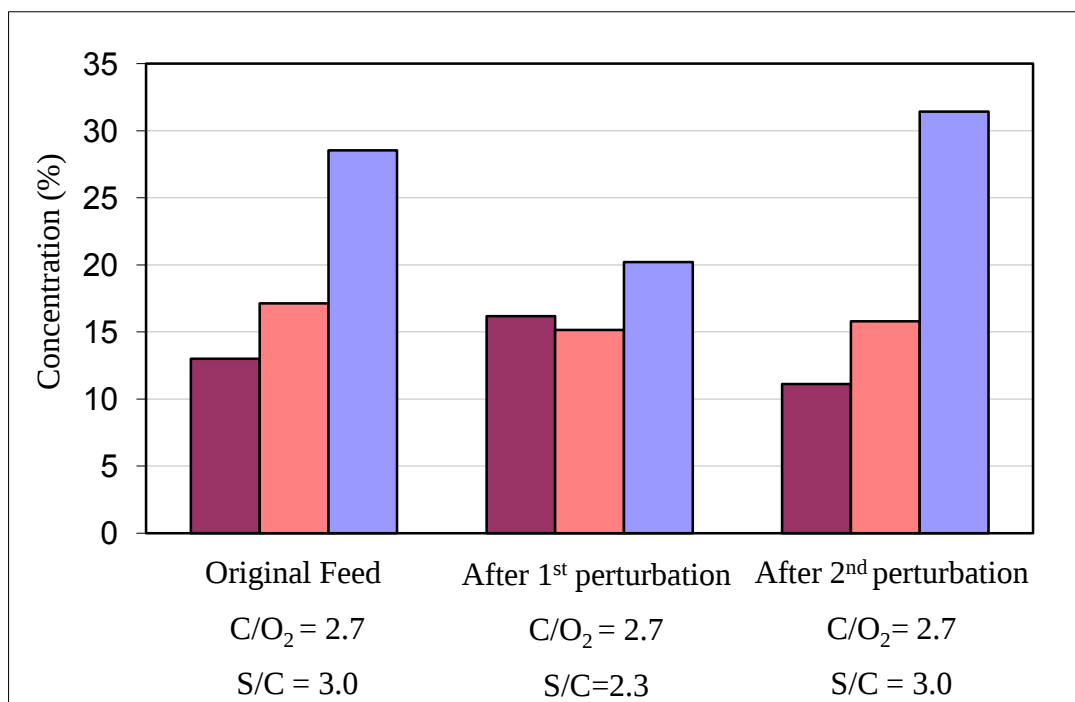


Figure 4.19. Changes in concentration against perturbations in steam flow rate for exp. # 3
(■ CH₄ ■ CO₂ ■ H₂)

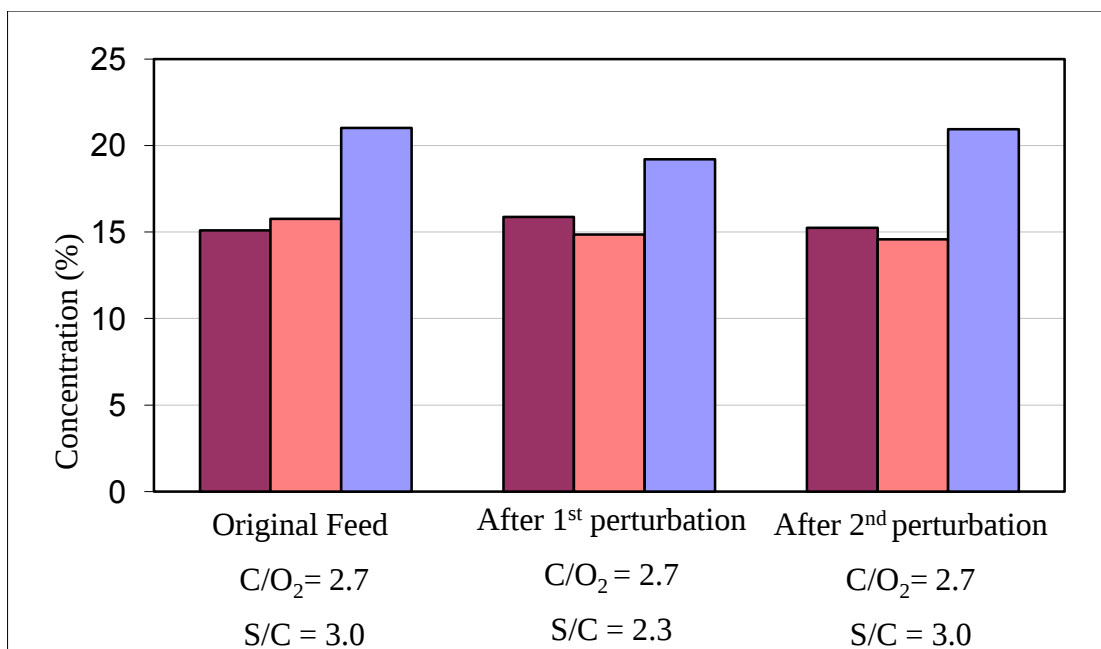


Figure 4.20. Changes in concentration against perturbations in steam flow rate for exp. # 6
(■ CH₄ ■ CO₂ ■ H₂)

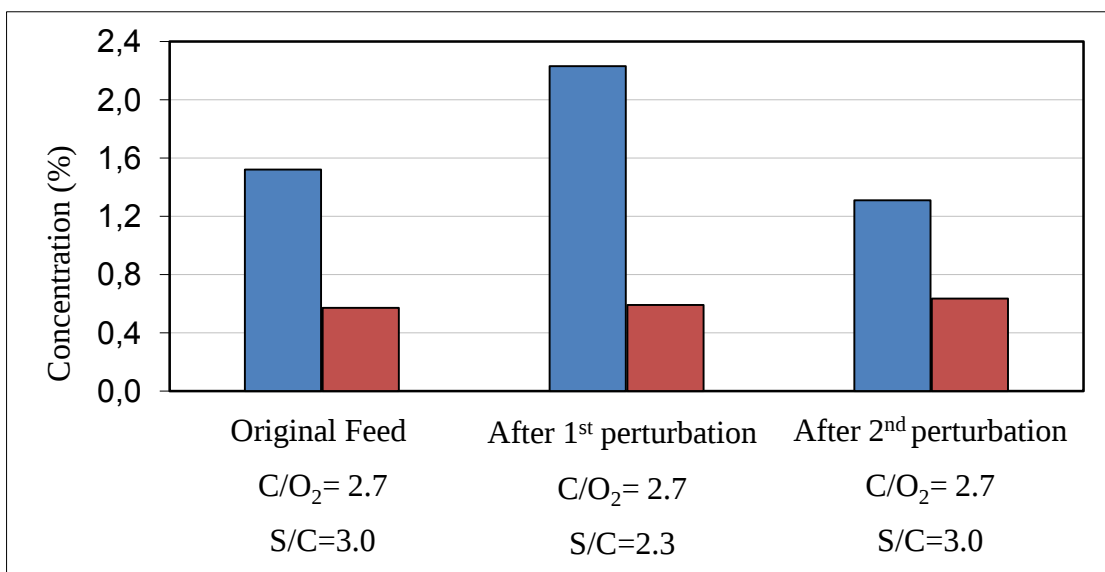


Figure 4.21. Effect of steam flow rate on CO concentration

(■ Experiment # 3 ■ Experiment # 6)

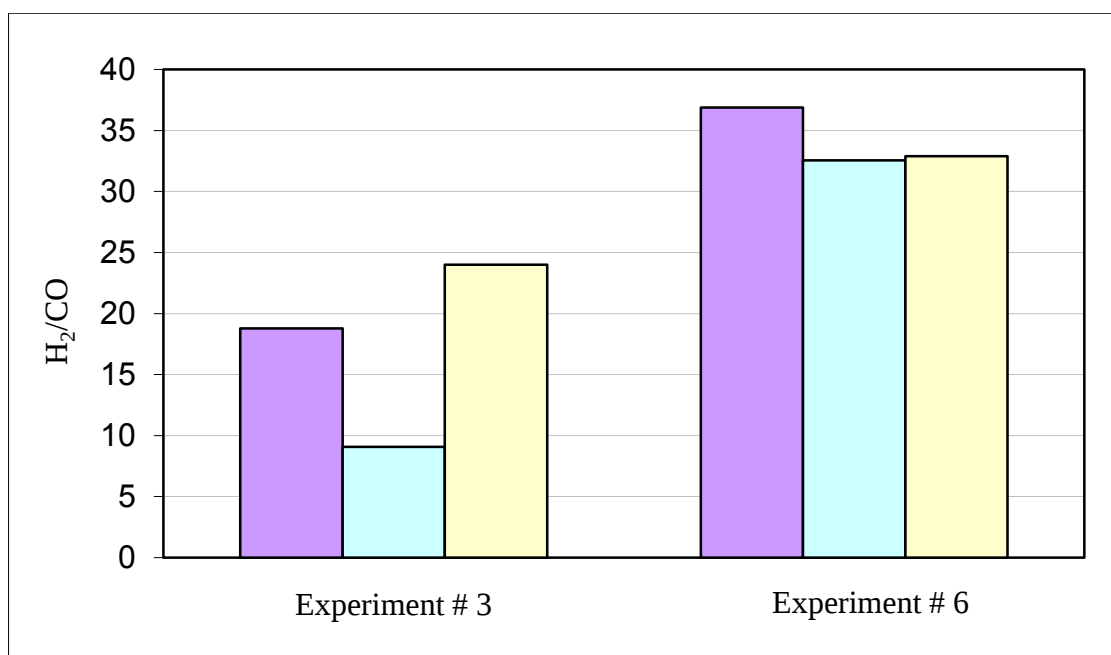


Figure 4.22. Selectivity of the catalyst for experiments # 3 & # 6

(■ Original Feed $C/O_2 = 2.7$ $S/C = 3.0$ ■ After 1st perturbation $C/O_2 = 2.7$ $S/C = 2.3$
 ■ After 2nd perturbation $C/O_2 = 2.7$ $S/C = 3.0$)

4.3.4. Effect of Temperature

Two temperature combinations were used for serial OSR and WGS reactors in order to study the effect of temperature on serial OSR and WGS system performance. In the first set (see Exp. 1-3), oxidative steam reforming reaction was conducted at 723 K and WGS reaction at 523 K, whereas in the second set (see Exp. 4-6) 673 K and 573 K temperature levels, respectively, were used. The comparison between the results of the sets indicated that decreasing OSR temperature while increasing WGS temperature has decreased H_2 production rate in the first reactor, increased methanation reactions in the first reactor (lower temperatures in OSR favors methanation reactions) and increased CO conversion in the second reactor. The results of the Güven's (2009) performance tests on Au-Re/ZrO₂ WGS catalysts confirmed the improvement effect of temperature increase on CO conversion. CO₂ concentration at the exit was slightly affected. The comparison of H_2 /CO ratios indicated the remarkable increase in selectivity for the second set though the H_2 production was rather limited for this set. Enhanced H_2 /CO selectivity came from the enhanced activity of WGS catalyst at 573 K (Figure 4.23).

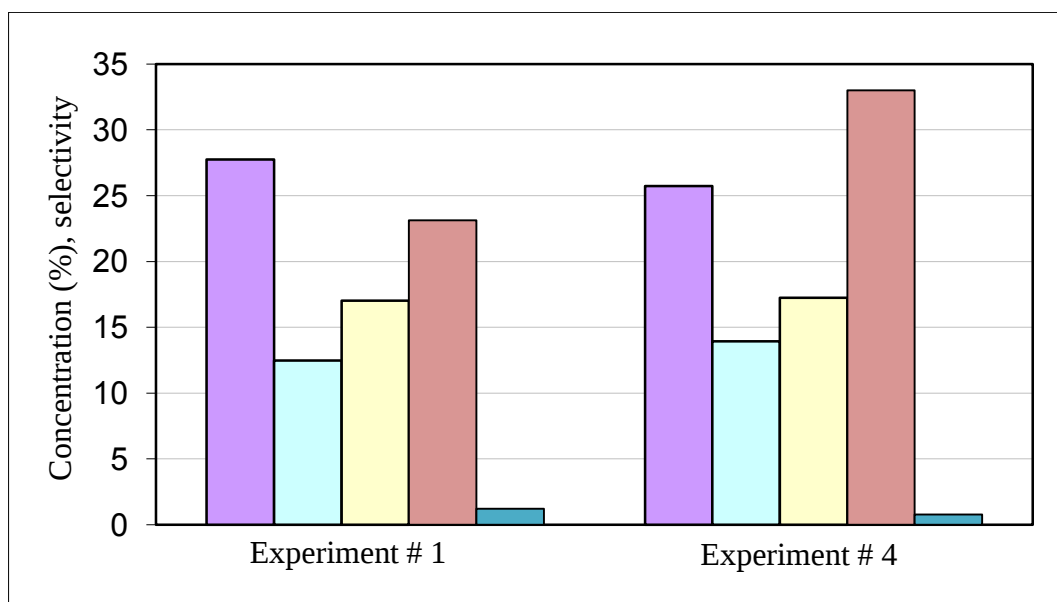


Figure 4.23. Effect of temperature on gas concentrations

($\square$ H_2 $\square$ CH_4 $\square$ CO_2 $\square$ H_2/CO $\square$ CO)

4.4. Dynamic Tests

Determination of dynamic response of the system to the perturbations given to the flow rates of the feed gases required the analysis of the exit concentration profiles till the new steady state was reached upon the perturbation. The system performance was analyzed through the real time changes in H_2 and CO concentrations. However, since steady state profile in H_2 was reached very hardly because of the fluctuations led by the fact that H_2 was consumed and produced by several different reactions in OSR and WGS reactors, the analysis of dynamic response of the system was made on the basis of the changes in CO , CO_2 , C_3H_8 and O_2 concentration in the product stream.

Figure 4.24 shows system's dynamic response, when the propane flow rate was decreased from 7.3 ml/min to 5.1 ml/min. The perturbation was given at 04:01:33. As in the inertia tests, MS signal change upon perturbation started 4-5 minutes after the perturbation was given. As it can be remembered, in inertia tests steady state profiles were achieved in 36 minutes in no reaction condition. As it is expected, steady states with reactions were achieved in a lot longer time; for example, in this experiment, 1 hour and 20 minutes was needed, since different time on stream durations are necessary for each OSR and WGS reactors to reach steady state. CO_2 concentration showed a good S-typed profile for the period till system reaches steady state.

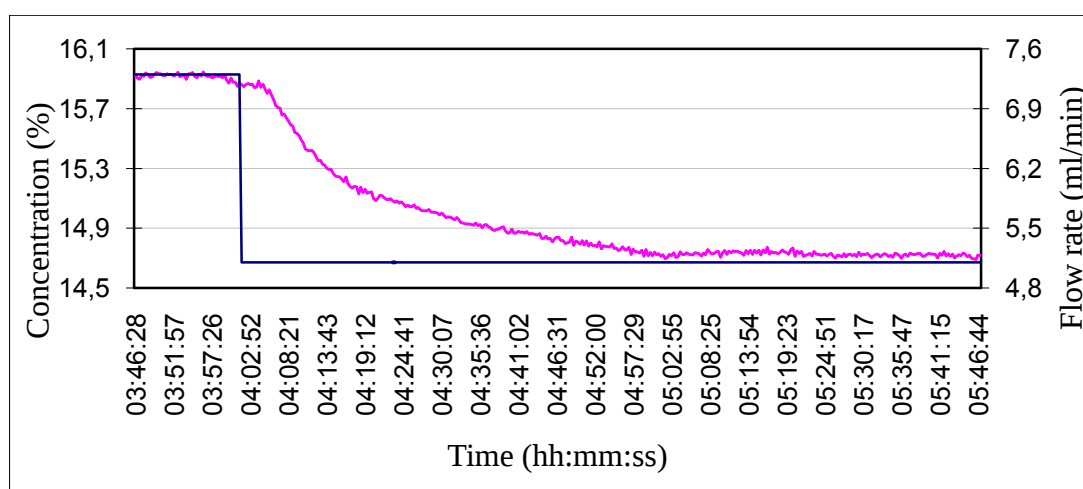


Figure 4.24. System dynamic response in CO_2 % (pink) with respect to perturbation in propane flow rate (blue) in experiment # 5

The result of the same experiment was also analyzed in terms of CO concentration change at the exit. The perturbation was given at 04:01:33 to the OSR inlet as in the previous analysis. Here, the steady state was achieved after 1 hour 20 minutes. CO profile was fluctuated during transition state, but steady state was achieved eventually.

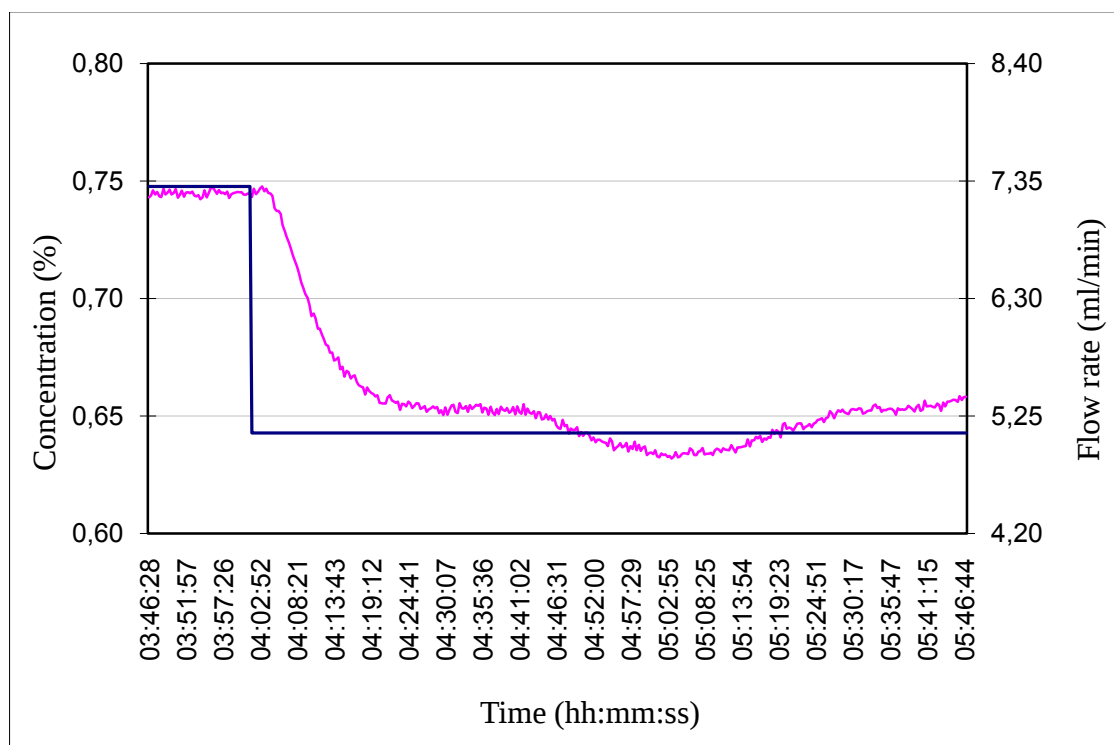


Figure 4.25. System dynamic response in CO % (pink) with respect to perturbation in propane flow rate (blue) in experiment # 5

Figure 4.26 shows system dynamic response of the OSR and WGS system in terms of propane exit concentration to the perturbation in propane flow rate. The experimental conditions were the same as in Figure 4.24 and 4.25. In propane case, steady state was achieved 10 minutes before CO₂ and CO steady state condition prevails. This might be explained by nearly 100% conversion of propane. Because of the very high conversions of propane, the concentration of propane at the outlet of the second reactor was 0.15%. Additionally, once propane was converted, there was no possibility of its reproduction. Therefore, steady state for propane concentration was reached faster. However, since CO₂ and CO were consumed and produced through different reactions/reaction paths simultaneously, the time needed for their steady state was longer.

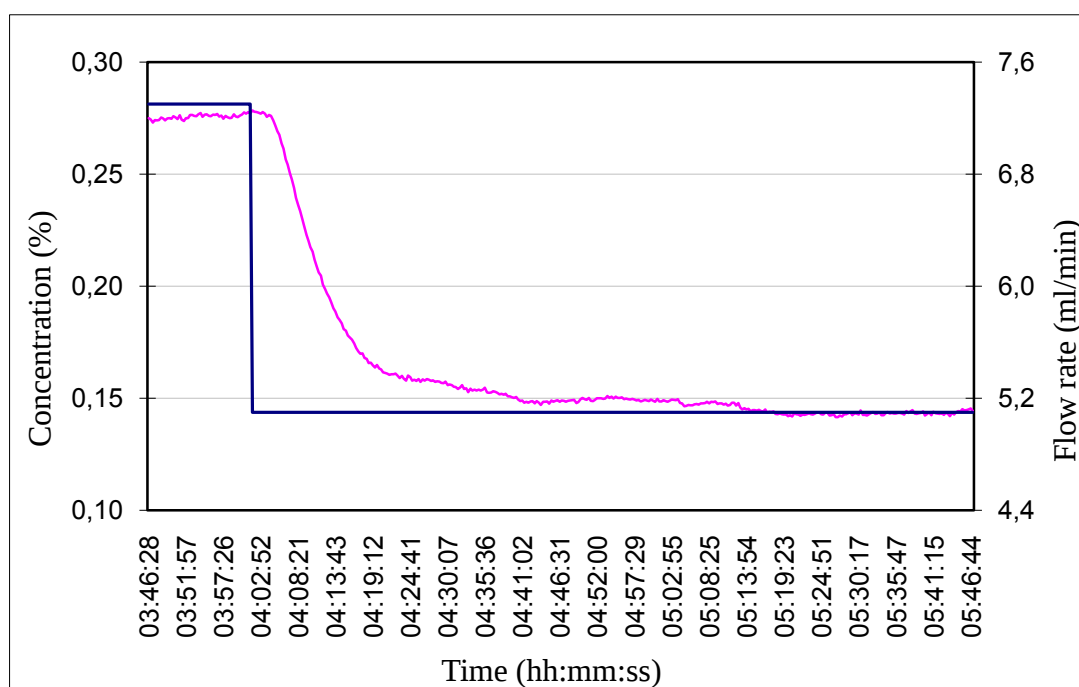


Figure 4.26. System dynamic response in C_3H_8 % (pink) with respect to perturbation in propane flow rate (blue) in experiment # 5

Similarly, the dynamic response of the OSR and WGS system in O_2 concentration with respect to perturbation in oxygen flow rate is given in Figure 4.27. The perturbations were given at 2:29:57 and 4:29:35 time on stream. During tests, O_2 concentrations were smaller than propane concentrations. Therefore, steady state was reached in a shorter time than that of propane. Under these experimental conditions, it took 1 hour to reach steady state. S-type profiles were again achieved in this case. Note that the seesaw shape profile was the result of magnification.

The same perturbations were observed in terms of CO concentration as in Figure 4.28. In the case of a positive ramp in oxygen inlet flow, CO outlet concentration was reached steady state in 1 hour, whereas the steady state was achieved in half an hour, when the perturbation was a negative ramp in O_2 inlet flow.

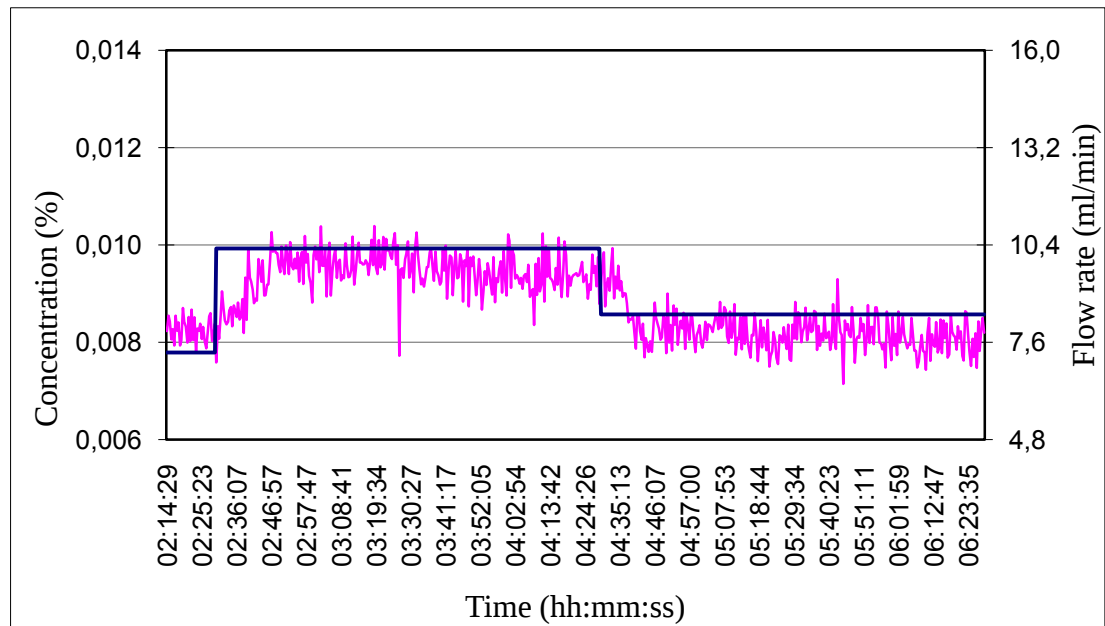


Figure 4.27. System dynamic response in O_2 % (pink) with respect to perturbation in oxygen flow rate (blue) in experiment # 4

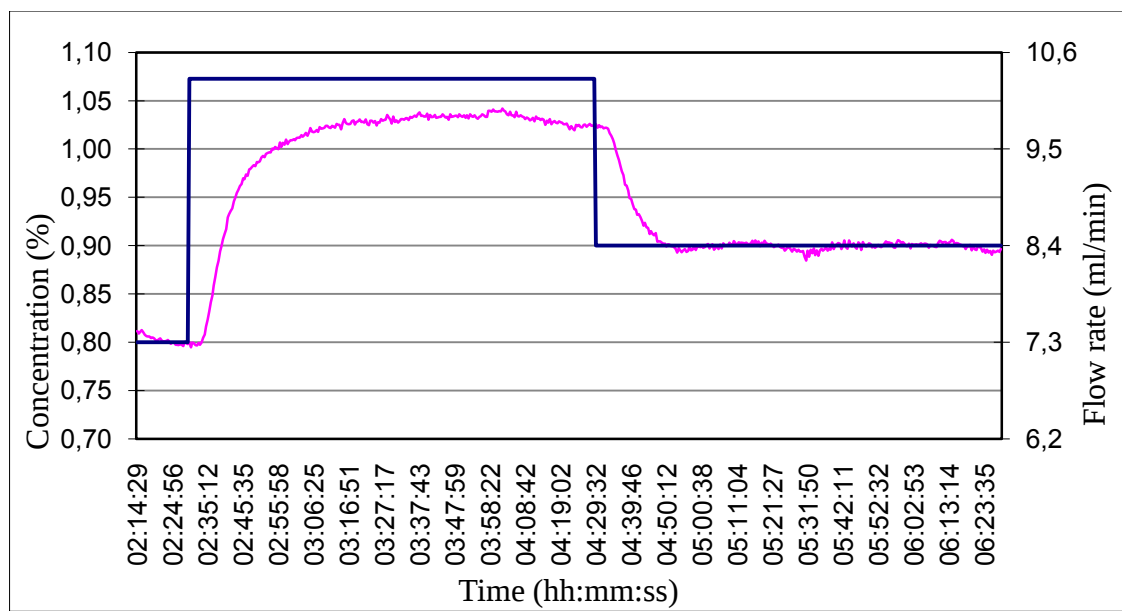


Figure 4.28. System dynamic response in CO % (pink) with respect to perturbation in oxygen flow rate (blue) in experiment # 4

Table 4.2. Summary of all experimental results performed in this study

	Exp #	1	2	3	4	5	6
H ₂ %	Original feed	27.76	27.88	28.54	25.74	23.07	21.02
	After 1 st perturbation	29.13	28.49	20.22	27.78	21.98	19.21
	After 2 nd perturbation	29.10	25.13	31.43	26.81	21.59	20.95
CH ₄ %	Original feed	12.47	12.84	13.01	13.94	15.19	15.10
	After 1 st perturbation	9.97	14.19	16.18	11.13	16.71	15.88
	After 2 nd perturbation	11.23	9.96	11.11	12.88	11.28	15.24
CO ₂ %	Original feed	17.02	17.08	17.14	17.25	17.17	15.76
	After 1 st perturbation	17.06	15.82	15.16	18.08	15.88	14.85
	After 2 nd perturbation	15.04	14.28	15.79	16.21	14.61	14.57
CO %	Original feed	1.20	1.15	1.52	0.78	0.70	0.57
	After 1 st perturbation	1.55	1.18	2.23	1.03	0.74	0.59
	After 2 nd perturbation	1.34	1.12	1.31	0.90	0.68	0.64
C ₃ H ₈ %	Original feed	0.041	0.040	0.045	0.041	0.180	0.048
	After 1 st perturbation	0.033	0.046	0.116	0.031	0.280	0.049
	After 2 nd perturbation	0.036	0.030	0.056	0.037	0.140	0.047
O ₂ %	Original feed	0.008	0.008	0.008	0.008	0.010	0.007
	After 1 st perturbation	0.009	0.008	0.007	0.009	0.010	0.007
	After 2 nd perturbation	0.007	0.007	0.008	0.008	0.010	0.007
H ₂ /CO	Original feed	23.13	27.88	28.54	33.00	32.86	36.88
	After 1 st perturbation	18.79	28.49	20.22	26.97	29.51	32.56
	After 2 nd perturbation	21.72	25.13	31.43	29.79	31.90	32.90
X _{C₃H₈}	Original feed	99.76	99.77	99.74	99.77	98.99	99.73
	After 1 st perturbation	99.79	99.76	99.31	99.80	98.56	99.73
	After 2 nd perturbation	99.79	99.79	99.68	99.78	98.98	99.73
X _{O₂}	Original feed	99.96	99.96	99.96	99.96	99.96	99.96
	After 1 st perturbation	99.97	99.96	99.96	99.96	99.96	99.97
	After 2 nd perturbation	99.97	99.96	99.96	99.96	99.96	99.97

5. CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

A fuel processor prototype used in measuring the combined performance of the catalysts used in fuel processing reactions was designed, constructed and tested. Blank tests and preliminary tests showed that this system is working properly. Existence of main oven instead of using heating tapes ensured the contamination free performance of the system. The opportunity of additional streams into each reactor enables parallel operation and/or simultaneous catalyst pretreatment, besides performance tests for serial reactions.

Blank inertia tests showed that any ramp type perturbation made by the user in the flow rate of any gas in the feed stream is sensed by the MS after 4-5 minutes. The steady state was reached in 36 minutes.

The most important part of this study was to conduct serial OSR and WGS performance tests with novel catalysts developed in our lab. Six tests each including two ramp type perturbations were performed. Perturbations were given to oxygen, propane and steam flow rates. Propane and oxygen conversions of nearly 100 % were achieved in all experiments. H_2/CO ratio parameter has been chosen as the selectivity of the combined catalysts. Any increase in the oxygen, propane and steam flow rate in the feed stream has increased CO exit concentration. Increase in oxygen and steam flow rate, and decrease in propane flow rate increased H_2 concentration at the exit stream.

In the dynamic tests including ramp type perturbations given to propane and oxygen flow rate, S-type concentration profiles for gases in the exit WGS exit stream were achieved. Fluctuations in H_2 and CO concentration profiles, being key gases of both reactors, made it harder to observe a steady state profile. However, CO_2 and CH_4 concentrations showed the best S-type concentration profiles, because their steady state profiles were very stable after reaching steady state. Oxygen and propane perturbation tests showed better steady state profiles, than these of the water tests, with requirement of 1 hour 20 minutes to reach steady state.

Highest achieved selectivity (H_2/CO) was 37 for OSR temperature of 673 K and WGS temperature of 573 K, S/C ratio of 3 and C/O₂ ratio of 2.7 and for a total inflow of 100 ml/min, where the perturbation variable is steam flow rate. The test also showed the lowest CO concentration obtained at the WGS outlet as 0.57%.

5.2. Recommendations

Considering the system design and results obtained in this study, following ideas are suggested for future studies.

- In serial operation, system was considered as a single unit, i.e. product analysis is done only at the outlet of the second reactor. In future work, a splitter can be placed at the outlet of the first reactor, dividing the outlet stream of the first reactor into two. By this way, the product of the first reactor can be sent continuously to the second reactor, while a portion of it to MS for analysis, which will enable the analysis of the reactor 1 outlet without interrupting the serial operation.
- Besides the serial operations, individual tests of each reactor will be required in order to determine system response, e.g., OSR individual tests and combined tests of OSR and WGS reactions will help to predict system response and to derive model for the system aiming to determine control action parameters.
- Various serial tests can be conducted to determine the optimum experimental conditions for the highest hydrogen to carbon monoxide ratio in the product.
- PROX reactor as a third reactor can be included into the system in order to produce carbon monoxide free hydrogen stream to be used in fuel cell applications.
- The design of the system allows introducing additional streams into the system. Water feed for the WGS reaction and oxygen feed for the PROX reaction will definitely improve product quality.

- Replacing of the 1/4" reactors with 1/2" reactors and increasing catalyst weight and total inflow will allow conducting experiments under conditions close to the industrial scale.
- Besides the serial operation of OSR, WGS and PROX reactions, different combinations such as HTWGS, LTWGS and PROX can also be conducted.

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