# STEAM REFORMING AND INDIRECT PARTIAL OXIDATION OF LIGHT HYDROCARBONS OVER BIMETALLIC CATALYSTS

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# ABSTRACT

## STEAM REFORMING AND INDIRECT PARTIAL OXIDATION OF LIGHT HYDROCARBONS OVER BIMETALLIC CATALYSTS

This experimental work involves the investigation of power law type kinetic study of ethanol steam reforming and indirect partial oxidation of propane/*n*-butane mixture with the purpose of hydrogen production over a bimetallic 0.2wt%Pt-15wt%Ni/δ-$Al_2O_3$ catalyst. The kinetic investigation of ethanol steam reforming gave reaction orders of 1.18 and -0.18 with respect to ethanol and steam, respectively and an activation energy of 39.3 kJ $mol^{-1}$. Indirect partial oxidation tests (i.e. combined total oxidation and steam reforming) were conducted for a hydrocarbon feed of a 1:1 propane/*n*-butane mixture. The effects of temperature, steam/carbon ratio, carbon/oxygen ratio and residence time on the activity and selectivity of the catalyst were investigated. The experimental conditions were adjusted such that the effect of two parameters, namely steam/carbon ratio and the propane/*n*-butane ratio in LPG, can be studied through direct comparison with the literature. The parameter that determines the selectivity of the process, namely hydrogen/carbon monoxide ratio, tended to increase with higher steam/carbon, $W/F_{Total}$ and $C/O_2$ ratios. A decrease in residence time, i.e. increase in the total flowrate, led to a considerable increase in the hydrogen production due to the limited residence time of carbon monoxide and hydrogen on the catalyst surface that prevents methanation. .The composition that represents LPG fuel in this study, with a propane/*n*-butane ratio of 1:1, seems to be superior to the previously tested composition, a ratio of 3:1, considering the hydrogen production rate (151 $\mu mol\, H_2 / g.cat \times s$ versus 70 $\mu mol\, H_2 / g.cat \times s$); and the hydrogen/carbon monoxide ratio (49 versus 46). Optimum activity and selectivity for IPOX of propane/n-butane mixture was obtained with steam/carbon ratio of 7, carbon/oxygen ratio of 2.70 and W/F ratio of 0.51 for the experimental conditions tested.

# ÖZET

## HAFİF HİDROKARBON YAKITLARININ ÇİFT METALLİ KATALİZÖRLER ÜZERİNDE BUHAR REFORMLAMASI VE DOLAYLI KISMİ OKSİDASYONU

Bu deneysel çalışma çift metalli Pt-Ni/δ-$Al_2O_3$ katalizörü üzerinde hidrojen elde etme amacı ile etanol buhar reformlama reaksiyonun üssel tip kinetik incelemesini ve propan ve n-bütan karışımının dolaylı kısmi oksidasyon araştırmasını içerir. Etanol buhar reformlama reaksiyonun kinetik incelemesi sonucunda etanol ve buhar reaksiyon dereceleri sırasıyla 1,18 ve -0,18 olarak bulunmuştur; aktivasyon enerjisi ise 39,3 kJ $mol^{-1}$ olarak belirlenmiştir. Dolaylı kısmi oksidasyon (toplam oksidasyon + buhar reformlama) deneyleri bire bir oranında eklenmiş propan ve n-bütan karışımı için yapılmıştır. Testlerde sıcaklığın, buhar/karbon oranının, karbon/oksijen oranının ve kalış süresinin ($W/F_{total}$) katalizörün aktivitesine ve seçimliliğine etkileri incelenmiştir. Deney şartları, buhar/karbon ve LPG yakıtı içindeki propan/n-bütan oranlarının etkilerinin önceki çalışmalarla karşılaştırarak belirlenebilmesi amacı ile oluşturulmuştur. Seçimliliğin belirlenmesinde önemli olan hidrojen/karbon monoksit oranının; buhar/karbon oranı, karbon/oksijen oranı ve kalış süresi ile doğru orantılı olarak değiştiği gözlenmiştir. Kalış süresindeki düşüş, yani toplam akış hızının artışı, karbon monoksitin hidrojenle metan oluşturmasını engellemek sureti ile hidrojen üretimini arttırmıştır. Bire bir oranında karıştırılan propan ve n-bütan'dan oluşan LPG yakıtının, 70 $\mu mol\, H_2 / gr.kat \times sn$ yerine 151 $\mu mol\, H_2 / gr.kat \times sn$ üretmesi ve hidrojen/karbon monoksit oranını 49'dan 46'a düşürmesi nedenleri ile üçe bir oranında propan ve n-bütan karıştırılarak hazırlanan LPG yakıtından daha üstün olduğu saptanmıştır. Propan/n-bütan karışımının dolaylı kısmi oksidasyonunda belirlenmiş optimal koşullar buhar/karbon oranı için 7, karbon/oksijen oranı için 2,70 ve $W/F_{total}$ oranı için ise 0,51'dir.

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| | |
|---|---|
| $E_A$ | Activation energy |
| $k_0$ | Specific rate of reaction |
| $P_i$ | Partial pressure of component i |
| $-r$ | Reaction rate |
| $R$ | Gas constant |
| $T$ | Temperature |
| $X_i$ | Conversion of component i |

| | |
|---|---|
| $\alpha$ | Order of ethanol steam reforming with respect to ethanol |
| $\beta$ | Order of ethanol steam reforming with respect to steam |

| | |
|---|---|
| AC | Activated carbon |
| ATR | Autothermal reforming |
| BET | Brunauer-Emmett-Teller |
| $C/O_2$ | Carbon/oxygen ratio |
| CATREL | Catalyst technology and reaction engineering laboratory |
| CHP | Combined heat and power |
| EDAX | Energy dispersive X-ray |
| ESEM | Environmental scanning electron microscopy |
| GC | Gas chromatograph |
| GHG | Greenhouse gas |
| HC | Hydrocarbon |
| ID | Internal diameter |
| IPOX | Indirect partial oxidation |
| ITP | Increasing temperature program |
| LPG | Liquefied petroleum gas |
| MS | Molecular sieve |
| S/C | Steam/carbon ratio |
| SEM | Scanning electron microscopy |

| | |
|---|---|
| SR | Steam reforming |
| TCD | Thermal conductivity detector |
| W/F | Residence time |
| XRD | X-ray diffraction |

# 1. INTRODUCTION

All communities, industrialized or developing, tend to use large amounts of energy in order to maintain their standard of living. The environmental problem here stems from the fact that the energy is mostly produced from hydrocarbon fuels via conventional methods, like combustion, which lead to accumulation of $CO_2$ - a well known greenhouse gas whose increasing amount in the atmosphere is predicted to result in climate change - as well as environmental pollution due to the emission of other pollutants such as CO, $SO_x$, $NO_x$ etc. Apart from environmental issues, the fast depletion of fossil fuels brings other problems into consideration associated with sustainable development objectives. The dependency on the lessened amount of fossil fuels is predicted to provoke new conflicts among oil imported and exported countries. For all these reasons new power generation systems are considered for the past few decades by scientists and researchers.

Fuel cells are electrochemical devices that combine the fuel and the oxidant to produce electricity. Their use will diminish the fossil fuel dependency, as they can be fuelled by man-made secondary energy sources. Fuel cells are known to be more efficient than internal combustion engines in two ways, (i) they generate energy electrochemically instead of combustion and (ii) they do not contain any moving parts which increase operational costs. Besides, fuel cells generate harmless water vapor and lower amounts of carbon dioxide as by-product per unit power produced compared to conventional power production methods.

Proton Exchange Membrane Fuel Cells (PEMFCs) are being seen as the most promising fuel cell type for small power generators suitable for residential units and for automobiles (Ahmed and Krumpelt, 2001). Although PEMFCs can be fuelled with methanol, methanol's toxic nature makes hydrogen a better fuel candidate for this type of fuel cells. Due to the obstacles faced with hydrogen storage, on-board hydrogen production has became to be the key factor for these small power generators.

Recent studies performed on on-board hydrogen production focus on three production routes; (i) steam reforming, (ii) partial oxidation, and (iii) indirect partial oxidation (IPOX). The latter is seen to be more propitious than the first two as it combines the endothermic and exothermic characteristics of both steam reforming and partial oxidation thereby increasing the overall efficiency of the process (Trimm and Onsan, 2001). Further investigations of indirect partial oxidation are being performed mostly related to alternative fuel choices, new catalyst types and effects of different parameters on the process. However recent efforts are deficient of kinetic studies on IPOX as the process consists of two basic and many other side reactions. For this reason, the understanding of kinetic details will be attainable only if it is approached by the kinetic study of steam reforming and partial oxidation separately.

The aim of the current study is to gain more detailed information on catalytic hydrogen production from various hydrocarbon feeds. Firstly, the kinetic study on ethanol steam reforming was brought into completion including determination of the rate constant, rate parameters with respect to ethanol and steam, and the activation energy. The second part consisted of the investigation of hydrogen production from LPG having a composition of 50 per cent propane and 50 per cent *n*-butane via indirect partial oxidation. Both reactions were catalyzed by a sequentially impregnated Pt-Ni/δ-$Al_2O_3$ catalyst. The effects of steam/carbon ratio, residence time and carbon/oxygen ratio were examined using on-line analysis system. Section 2 composes of a literature survey including the development in the hydrogen energy system and its related technologies. The details of the experimental ingredients, the catalyst preparation and the reaction system are presented in Section 3. Results of the study and their related discussions can be found in Section 4. The research is ceased with Section 5 which includes the conclusions drawn and recommendations about the future works.

# 2. LITERATURE SURVEY

## 2.1. Fuel Cell

### 2.1.1. Fuel Cell Operation

A fuel cell is an electrochemical device that combines fuel and an oxidant to produce electricity. The fuel is typically hydrogen and oxygen the oxidant, with water and heat as the by-product. A fuel cell is similar in structure to a battery but it does not run down, nor does it require recharging-as long as fuel is supplied it will continue to operate. The conversion of the fuel (hydrogen) to energy takes place without combustion; therefore, the process is highly efficient, clean and quiet (Fuel Cells and Hydrogen, 2002).

A fuel cell consists of two electrodes separated by an electrolyte. In most cases, hydrogen fuel is fed into the anode of the fuel cell. Oxygen (air) enters the fuel cell at the cathode. Every hydrogen molecule splits into two $H^+$ ions and two electrons by a catalytic reaction. The electrons are conducted through the anode, thereby creating a separate circuit, and return to the cathode side. Similarly, two negatively charged oxygen ions are formed from every oxygen molecule by the catalyst at the cathode. The negative charge at the cathode attracts the hydrogen ions through the membrane, where two hydrogen ions combine with an oxygen atom and two of the electrons from the external circuit to form a water molecule.

The reaction in a single fuel cell produces about 0.7 volts. In order to increase the voltage, many separate fuel cells are combined to form a fuel-cell stack.

### 2.1.2. Types and Applications of Fuel Cells

Five major types of fuel cells are being developed, characterized by their electrolytes: Proton Exchange Membrane (PEMFC), Alkaline (AFC), Phosphoric Acid (PAFC), Molten Carbonate (MCFC), and Solid Oxide (SOFC). In general, higher temperature systems (MCFC, SOFC) tend to be best suited for larger applications, while low temperature systems (PEMFC, PAFC, AFC) are currently best suited for smaller applications. Major differences between the various cells are shown in Table 2.1 (Fuel Cell Handbook, 2000).

Table 2.1. Summary of the major differences of the fuel cell types

| | PEMFC | AFC | PAFC | MCFC | SOFC |
|---|---|---|---|---|---|
| Electrolyte | Ion Exchange Membranes | Mobilized or Immobilized Potassium Hydroxide | Immobilized Liquid Phosphoric Acid | Immobilized Liquid Molten Carbonate | Ceramic |
| Operating Temperature | 80°C | 65°C - 220°C | 150°C - 220°C | 650°C | 600 - 1000°C |
| Charge Carrier | $H^+$ | $OH^-$ | $H^+$ | $CO_3^-$ | $O^-$ |
| External Reformer for $CH_4$ (below) | Yes | Yes | Yes | No | No |
| Prime Cell Components | Carbon-based | Carbon-based | Graphite-based | Stainless-based | Ceramic |
| Catalyst | Platinum | Platinum | Platinum | Nickel | Perovskiters |
| Product Water Management | Evaporative | Evaporative | Evaporative | Gaseous Product | Gaseous Product |
| Product Heat Management | Process Gas + Independent Cooling Medium | Process Gas + Electrolyte Calculation | Process Gas + Independent Cooling Medium | Internal Reforming + Process Gas | Internal Reforming + Process Gas |

2.1.2.1. Proton Exchange Membrane Fuel Cell (PEMFC). The electrolyte in this fuel cell is an ion exchange membrane that is an excellent proton conductor. Because of this solid electrolyte, the cell is known to exhibit good resistance to gas crossover. The only liquid in this fuel cell is water; thus, corrosion problems are minimal. Water management in the membrane is critical for efficient performance; the fuel cell must operate under conditions where the byproduct water does not evaporate faster than it is produced because the membrane must be hydrated. Because of the limitation on the operating temperature imposed by the polymer, usually less than 120°C, and because of problems with water balance, a $H_2$-rich gas with minimal or no CO (acts as a poison at low temperatures) is used (Fuel Cell Handbook, 2000). However, this low operation temperature is not a disadvantage as it makes the cell suitable for quick start-ups.

2.1.2.2. Alkaline Fuel Cell (AFC). The electrolyte in this fuel cell type is concentrated (85 wt %) KOH in fuel cells operated at high temperature (~250°C), or less concentrated (35-50 wt %) KOH for lower temperatures (<120°C). The electrolyte is retained in a matrix (usually asbestos), and a wide range of electrocatalysts can be used such as Ni, Ag, metal oxides, spinels, and noble metals. The fuel supply is limited to non-reactive constituents except for hydrogen. CO is a poison, and $CO_2$ will react with the KOH to form $K_2CO_3$, thus altering the electrolyte (Fuel Cell Handbook, 2000).

2.1.2.3. Phosphoric Acid Fuel Cell (PAFC). Phosphoric acid concentrated to 100% is used for the electrolyte in this fuel cell, which operates at 150 - 220°C. At lower temperatures, phosphoric acid is a poor ionic conductor, and CO poisoning of the Pt electrocatalyst in the anode becomes severe. As the relative stability of concentrated phosphoric acid is higher than the other common acids, PAFCs are able to operate at the high end of the acid temperature range (100 to 220°C). The matrix universally used to retain the acid is silicon carbide, and the electroctalyst in both the anode and the cathode is Pt (Fuel Cell Handbook, 2000).

2.1.2.4. Molten Carbonate Fuel Cell (MCFC). The electrolyte in this fuel cell is usually a combination of alkali carbonates, which is retained in a ceramic matrix of $LiAlO_2$. The fuel cell operates between 600 and 700°C where the alkali carbonates form a highly conductive molten salt, with carbonate ions providing the ionic conduction. At high temperatures in MCFCs, Ni and nickel oxide catalysts are suited for anode and cathode to promote reaction (Fuel Cell Handbook, 2000).

2.1.2.5. Solid Oxide Fuel Cell (SOFC). The electrolyte in this fuel cell is a solid, nonporous metal oxide, usually $Y_2O_3$-stabilized $ZrO_2$. The cell operates between 600 and 1000°C where ionic conduction by oxygen atoms takes place. Typically, the anode is Co-$ZrO_2$ or Ni-$ZrO_2$ cermets, and the cathode is Sr-doped $LaMnO_3$ (Fuel Cell Handbook, 2000).

### 2.1.3. Benefits of Fuel Cells

No other energy generating technology holds the combination of benefits that fuel cells offer. Benefits include high efficiency, unmatched environmental performance, high quality power, fuel flexibility, quiet operation, simplicity (no moving parts), modularity/scalability, and adaptability to specialized applications.

2.1.3.1. Energy Security. Because they are efficient, modular and fuel flexible, fuel cells can enable a transition to a secure, renewable energy future, based on the use of hydrogen. Fuel cell systems include a fuel reformer which can produce the hydrogen from any hydrocarbon or alcohol fuel, or by using electricity or biomass. The various possibilities for different hydrogen production raw materials provides the path for global energy independence and also hope for imported oil dependent countries (Fuel Cells and Hydrogen, 2002).

2.1.3.2. High Efficiency. Because fuel cells make energy electrochemically, and do not burn a fuel, they are on the average 30-40% more efficient than internal combustion engines, depending on the energy source chosen. When waste heat is put to use for heating and cooling, overall system efficiencies may exceed 85% (Fuel Cells and Hydrogen, 2002).

2.1.3.3. Environmental Benefits. Fuel cells offer good environmental performance compared to power generation technologies that rely on combustion. It is reported that a fuel cell power plant may create less than one ounce of pollution per 1,000 kW-hours of electricity produced – compared to the 25 pounds of pollutants in conventional combustion generating systems (First Fuel Cell installed under New Jersey Clean Energy program, 2002). Also, fuel cell vehicles operating on stored hydrogen produce zero pollution as they emit neither conventional pollutants nor greenhouse gases. Systems that rely on a reformer on board produce small amounts of emission, but would still reduce smog-forming pollution by up to 90% compared to traditional combustion engines, depending on the choice of fuel. Additionally, as the reaction inside the fuel cell is highly efficient, fuel cell vehicles can reduce emissions of $CO_2$ by more than half even if the hydrogen is produced from fossil fuels (Fuel Cells and Hydrogen, 2002).

2.1.3.4. Operating Flexibility. Fuel cell systems can ease the strain on the existing centralized power grid and reduce inefficiencies due to transmission losses. Their ability to be used in combined heat and power applications increases efficiencies over central station power significantly, thereby reducing GHG emissions. The potential total efficiency of these Combined Heat and Power (CHP) systems can exceed 85%. Also, the modularity of fuel cell stacks allows for incremental buildup of capacity at the peak electric demand at a very low cost compared to additional centralized power plants (Fuel Cells and Hydrogen, 2002).

## 2.2. Hydrogen

### 2.2.1. Properties of Hydrogen

Hydrogen is the simplest element, an atom consisting of only one proton and one electron. This colorless and odorless gas is also the most plentiful element in the universe as it accounts for 75% of the universe mass. Despite its simplicity and abundance, hydrogen does not occur naturally as a gas on the Earth – it is always combined with other elements. Other than water, hydrogen is also found in many organic compounds, notably the "hydrocarbons" that make up many of the conventional fuels such as gasoline, natural gas, propane, methanol, ethanol, etc.

Hydrogen can be made by separating it from hydrocarbons by applying heat, a process known as reforming hydrogen. An electrical current can also be used to separate water into its components of oxygen and hydrogen. Some algae and bacteria, using sunlight as their energy source, can give off hydrogen under certain conditions (Momirlan and Veziroğlu, 2005).

### 2.2.2. On-Board Hydrogen Storage

Hydrogen is the only choice of fuel for fuel cell powered vehicles that run at zero emission levels. Storage basically implies to reduce the enormous volume of the hydrogen gas at normal conditions, and it should be noted that 4 kg of hydrogen which is required for a practical driving distance occupies nearly 49 $m^3$. The reversibility of the hydrogen uptake and release excludes all covalent hydrocarbon compounds as hydrogen carriers, because hydrogen is only released from the compounds if being heated to temperatures above 800°C. The methods of hydrogen storage include compression, liquefaction, physisorption and metallic hydrides (Zhou, 2005).

Compression might be the simplest way to store hydrogen in a cylinder of pressure up to 20 MPa; however, the energy density is too low to satisfy the fuel demand of driving practice. About four times higher pressure is needed to meet the driving purpose; but, such industrial cylinders are not commercially available. Additionally, the cost of hydrogen compression is much higher than the cost of liquid hydrogen. Furthermore, the explosion risk of pressurized cylinders is of big concern in the populated regions (Zhou, 2005).

Liquefaction faces two challenges: the efficiency of the process and the boil-off of the liquid. The technical work required to liquefy hydrogen is about 15.2 kW-h/kg, which is almost half of the lower heating value of hydrogen. The critical temperature of hydrogen is very low (33.2 K) and liquid hydrogen above this temperature evaporates continuously. Therefore, liquid hydrogen can only be stored in an open system otherwise the pressure inside the closed system can be as high as 1000 MPa. Thus, beside the high cost of liquefaction, the inevitable boil-off of hydrogen to the atmosphere makes this method unpractical (Zhou, 2005).

The storage of hydrogen can rely on physisorption because the adsorbed gas can be released reversibly. However, a major flaw arises from the fact that the different mechanisms proposed -such as multilayer mechanism or capillary condensation – assume the possibility of condensation of the adsorbed adsorbates. As condensation is not possible at above-critical temperatures, monolayer surface coverage is the only plausible mechanism for physisorption. In this mechanism, however, as long as the interaction between hydrogen molecules and the surface atoms of the material remains the Van der Waals force; specific surface area of the material, which is the decisive factor of the storage capacity, will not allow high storage volumes. Therefore, physisorption of hydrogen on nanotubes/nanofibers of any materials seems hopeless for enhancing the hydrogen density due to its small surface area (Zhou, 2005).

Recently, it is known that some metals absorb hydrogen and form hydrides. Some metal hydrides absorb and desorb hydrogen at ambient temperature and near the atmospheric pressure. However, in these hydrides the gravimetric hydrogen density (i.e. mass ratio of hydrogen to the material) is limited to less than 3 wt% which eventually reduces the storage capacity (Zhou, 2005).

For all the reasons explained above, hydrogen storage does not seem to be a practical solution for hydrogen fuelled vehicles in the short and mid-long term. Therefore, efficient devices called fuel-processors that can convert hydrocarbon fuels into hydrogen on board are seen as the most promising way for fuel cell powered vehicles.

### 2.2.3. On-board Hydrogen Production

2.2.3.1. Fuels. A primary fuel is a fuel available in large commercial quantities and not immediately or necessarily derived from another fuel (Brown, 2001). Zero emission levels can be obtained only by hydrogen fed fuel-cell-powered vehicles; however, hydrogen must be produced from one of the primary fuels such as methanol, natural gas, gasoline, diesel fuel, ethanol or liquefied petroleum gas (LPG).

Methanol currently appears to be the preferred primary fuel for prototype fuel-cell-driven automobiles. It is a single chemical compound commercially produced in large quantities via synthesis gas from the steam reforming of natural gas (Brown, 2001). Methanol has some advantages over other fuel alternatives, such that it is the only compound that produces no carbon monoxide in the exit stream during hydrogen production or high hydrogen yields can be obtained by steam reforming of methanol. However, methanol has some significant drawbacks such as current lack of infrastructure leading to distribution problems and low efficiency in its production from natural gas which brings about no practical advantage in global warming aspects. In addition its toxicity combined with its water solubility may lead to leakage and spillage that would threaten drinking water supplies (Brown, 2001).

Unlike methanol, gasoline and diesel fuel are not single compounds. These are obtained by processing crude oil and therefore contain some impurities. Despite the readily available distribution network for gasoline and diesel fuel, their numerous compounds possess impurity related obstacles. Diesel fuel is a heavier compound than gasoline, deposits coke too easily and, therefore, is not an attractive alternative for on-board conversion (Avcı, 2003). Gasoline has high sulphur content which may lead to deactivation of catalyst and is a complex fuel that contains a lot of undesired aromatics. However, substantial research is being conducted on the use of both fuels for on-board processors, since they are important for transportational and military applications.

As natural gas comes from the ground, it can consist of many individual components. The major constituent is usually methane. Nevertheless, water, other hydrocarbons, hydrogen sulphide, nitrogen, and carbon dioxide can be present in large amounts (Brown, 2001). Methane produces the highest percentage of hydrogen in the exit stream. Due to a very strong C-H bond (440 kJ/mol), methane is one of the most stable organic molecules; hydrogen production would require temperatures of 1000°C which makes methane not suitable for on-board hydrogen production. Even so, it is considered to be the ultimate fuel for processing in small or large-scale stationary applications (Avcı, 2003).

Ethanol appears as an attractive alternative to methanol since it is much less toxic, offers a high octane number, a high heat of vaporization and a low photochemical reactivity (Fierro *et al.*, 2005). The current production route forms ethanol by hydrating ethylene, which is obtained from thermal cracking of petroleum naphthas (Brown, 2001). In addition, bio-ethanol is being produced in large quantities from biomass fermentation recently; hence, ethanol is now seen as a renewable energy source. Furthermore, the infrastructure needed for ethanol production and distribution is already established in some countries including North and South Americas, since ethanol is currently distributed and used as an octane enhancer or oxygenate blended with gasoline (Mattos and Noronha, 2005).

Another alternative fuel is LPG which is a mixture of propane and *n*-butane, whose relative amounts depend on the region from which crude oil is obtained. LPG is a typical widespread fuel, since it can be easily transported and be stored in liquid form in pressurized vessels for mobile and portable use (Selen, 2003). The propane storage vessels range from 425 g for small gas canisters up to 33 kg for mobile and portable use. It is an important byproduct of oil exploration and of crude oil processing in refineries. In general, its sulphur content is very low, so it is an environmentally beneficial fuel (Ledjeff-Hey *et al.*, 2000). Not only its present distribution network (as it had been already used as a fuel in certain countries for over 40 years); but also its low sulphur content, in contrast to other hydrocarbons, brings LPG into consideration as an attractive alternative for on-board hydrogen production especially for short and mid term periods.

2.2.3.2. Processes. Hydrogen production from hydrocarbons can be achieved via four different processes, namely pyrolysis, steam reforming, partial oxidation and autothermal reforming.

Pyrolysis is mainly the decomposition or cracking of hydrocarbons to hydrogen and carbon at high temperatures according to Reaction 2.1.

$$C_nH_m \Rightarrow nC + \frac{1}{2} m H_2 \tag{2.1}$$

The main gaseous product is hydrogen. As no carbon oxides are generated, extra reactions such as water gas shift (further reaction of carbon monoxide with steam in order to form additional hydrogen and carbon dioxide) and preferential oxidation are not required. The basic advantages of pyrolysis include fuel flexibility, production of clean carbon byproduct, and significant reduction in $CO_X$ emissions. Temperatures above 675°C are required, but the use of transition metal catalysts such as Ni, Fe, or Co reduces the operation temperature (Muradov, 2003). High heat requirement problem can also be solved with the use of solar energy, however this solution will possibly not influence the near-to-medium term (Abanades and Flamant, 2005). The catalyst deactivation problem associated with the carbon build-up on the catalyst surface remains to be a major problem which prevents extensive use of pyrolysis for on-board fuel conversion.

The steam reforming process consists of reaction of the hydrocarbon with steam to produce carbon monoxide and hydrogen (Reaction 2.2).

$$C_nH_m + nH_2O \Rightarrow nCO + \left(\frac{1}{2} m + n\right) H_2 \tag{2.2}$$

The reaction usually takes place over a nickel catalyst at temperatures in the region of 725 - 925°C. The reaction is equilibrium limited and highly endothermic requiring considerable heat input, therefore steam reforming is not suitable by itself for on-board hydrogen production for vehicular applications (Joensen and Rostrup-Nielsen, 2002).

In partial oxidation, the hydrocarbon reacts directly with air at carefully balanced oxygen to fuel ratio in order to prevent complete combustion of the fuel. This reaction is highly exothermic; hence, the overall process becomes net heat producing (Reaction 2.3).

$$C_nH_m + \tfrac{1}{2} m O_2 \Rightarrow n CO + \tfrac{1}{2} m H_2 \qquad (2.3)$$

In either steam reforming or partial oxidation heat management, thermal integration of the fuel processor and the fuel cell becomes key to achieve high efficiencies (Joensen and Rostrup-Nielsen, 2002). Autothermal reforming (also known as indirect partial oxidation) combines the thermal effects of partial oxidation and steam reforming. Fuel, air and steam are fed at proper amounts, and the partial oxidation supplies heat for the subsequent endothermic steam reforming and water gas shift reaction which eventually decreases the operation temperature. The net result is a slightly exothermic process. Therefore, indirect partial oxidation is accepted to be the most promising route to produce hydrogen from hydrocarbon fuels for mobile applications (Ahmed and Krumpelt, 2001).

## 2.3. Steam Reforming

Steam reforming (Reaction 2.2) is an endothermic process leading to hydrogen and carbon monoxide and is catalyzed usually by nickel or noble metal catalysts.

$$C_nH_m + n H_2O \Rightarrow n CO + \left(\tfrac{1}{2} m + n\right) H_2 \qquad (2.2)$$

Depending on the amount of steam used, carbon dioxide may also be produced (Reaction 2.4). The equilibrium amounts of carbon monoxide, carbon dioxide and hydrogen depend strongly on temperature, less strongly on pressure. The higher the temperature, the more carbon monoxide is found in the product (Brown, 2001).

$$C_nH_m + 2n\,H_2O \Rightarrow n\,CO_2 + \left(\tfrac{1}{2}m + 2n\right)H_2 \tag{2.4}$$

Methane can be formed as a side product (Reaction 2.5 and 2.6). At low temperatures methane-formation is thermodynamically favored, but may be kinetically suppressed by appropriate catalysts (Springmann *et al.*, 2002).

$$CO + 3H_2 \Rightarrow CH_4 + H_2O \tag{2.5}$$

$$CO_2 + 4H_2 \Rightarrow CH_4 + 2H_2O \tag{2.6}$$

Another main reaction of the steam reforming process is the water gas shift reaction (Reaction 2.7) which simultaneously eliminates CO and enhances hydrogen production.

$$CO + H_2O \Rightarrow CO_2 + H_2 \tag{2.7}$$

Steam reforming is basically an interaction of the catalyst support with the metal. The support provides the sites for water activation into hydroxyl groups, while the active metal provides the sites for the dissociative chemisorption of the fuel (Kolb *et al.*, 2004). For many years, nickel has been the most suitable metal for steam reforming of hydrocarbons. The current steam reforming catalysts are mainly nickel supported on refractory alumina and ceramic magnesium aluminate. These supports are reported to provide high crush strength and stability (Ming e*t al.*, 2002). Despite its low cost, coke formation and sulphur poisoning are two major problems associated with nickel catalysts. The formation of coke during the steam reforming of hydrocarbons results mainly from catalytic side reactions. For nickel catalysts, filamentous carbon is formed at the surface of the metal particle by a consecutive process of formation, diffusion, and dissolution. Coking is an even more serious problem when reforming heavy hydrocarbons such as gasoline or diesel fuel (Ming e*t al.*, 2002). Ruthenium or rhodium based catalysts are known to be more effective catalysts for steam reforming by preventing carbon deposition (Ming e*t al.*, 2002; Trimm and Önsan, 2001), and they may replace the cost-effective nickel catalyst in fuel cell applications. These precious metals, namely Rh, Ru, Pt, Pd, Re, are usually supported on alumina or on rare-earth oxides, particularly ceria. Nickel catalysts are usually promoted with alkali or alkali-earth compounds to accelerate carbon removal from the surface, but these promoters seem to suffer from the drawback of having increased volatility in high temperature steam environments (Ghenciu, 2002).

Recent efforts are put on developing new catalysts which are resistant to coke formation while sustaining the price advantage of nickel. Urasaki *et al.* (2005) have studied the catalytic activity and resistance to coking of nickel catalysts supported on a variety of the perovskite-type oxides ($LaAlO_3$, $LaFeO_3$, $SrTiO_3$, $BaTiO_3$, $La_{0.4}Ba_{0.6}Co_{0.2}Fe_{0.8}O_{3\_\delta}$) which are compared to those of the conventional Ni/$\alpha$-$Al_2O_3$ catalyst for steam reforming of methane. They reported that the lattice oxygen in $LaAlO_3$ and $SrTiO_3$ helped to increase methane conversion and catalyst stability compared to the $\alpha$-$Al_2O_3$ support, as the lattice oxygen promoted the $CH_x$ fragments adsorbed on metallic nickel and hindered the production of inactive carbon species.

In another recent study, Kolb *et al.* (2004) have investigated the steam reforming of propane over rhodium, platinum, and palladium catalysts in the absence and presence of ceria. The highest activity was found for platinum at 450°C; but as temperature increased, the carbon species formed leads to catalyst deactivation. Rhodium was identified as the best catalyst in terms of both selectivity and stability. The bimetallic Rh-Pt/$\gamma$-$Al_2O_3$ catalyst showed similar activity compared to rhodium, but the stability of the bimetallic catalyst was better. Ceria addition to the bimetallic catalyst showed no measurable deactivation even at 650°C.

Typical catalysts for methanol steam reforming are based on Cu-ZnO-$Al_2O_3$ (Ghenciu, 2002). Effect of CuZnAl(Zr)-oxide catalysts on methanol steam reforming was investigated by Velu *et al.*(2001), and they concluded that the CuZrZn-oxide catalyst was more active compared to the CuZnAl-oxide catalyst because of the inverse effect of aliminum on the reducibility, surface area and dispersion of cupper. Basile *et al.* (2005) have reported that Lenarda *et al.* also studied this reaction system over Pd based catalysts supported on Zn/$ZnAl_2O_4$; the reported high performance of this catalyst has been assigned to the formation of PdZn alloys.

It is reported by Sun *et al.* (2005) that Haga *et al.* have investigated the steam reforming of ethanol and it was found that Co/$Al_2O_3$ exhibited the highest selectivity by suppression of methanation of carbon monoxide and decomposition of ethanol. Ethanol is a compound that easily becomes dehydrated, forming ethylene which leads to carbon formation. Therefore efforts are devoted to not only maximizing hydrogen production but also discouraging the reactions leading to undesirable products, such as methane, acetaldehyde, diethly ether or acetic acid, that compete with hydrogen atoms. Marino *et al.* (2001) have considered Cu-Ni-K/$\gamma$-$Al_2O_3$ catalysts for ethanol steam reforming and concluded that the catalyst is able to produce acceptable amounts of hydrogen at atmospheric pressures and 300°C. Also, the effect of nickel was explained by the enhancement of ethanol gasification resulting in increased gas yield and reduced acetaldehyde and acetic acid production. In a recent study Sun *et al.* (2005) have investigated the activities of Ni/$Y_2O_3$, Ni/$La_2O_3$ and Ni/$Al_2O_3$ catalysts. They concluded that Ni/$La_2O_3$ catalyst exhibits high activity for ethanol steam reforming with a conversion of 80.7% ethanol with 49.5% hydrogen selectivity at 250°C. At 320°C the ethanol conversion increased to 99.5% and the hydrogen selectivity was 48.5%.

## 2.4. Partial Oxidation

Hydrogen production from hydrocarbons may be carried out either by direct partial oxidation or by indirect partial oxidation (autothermal reforming), the latter being a combination of direct partial oxidation and steam reforming.

### 2.4.1. Direct Partial Oxidation

Direct partial oxidation (Reaction 2.3) is the reaction of the fuel with an oxygen quantity inadequate for complete combustion (Brown, 2001).

$$C_nH_m + \frac{1}{2}m\,O_2 \Rightarrow n\,CO + \frac{1}{2}m\,H_2 \qquad (2.3)$$

It is a much faster reaction than steam reforming, offering therefore the advantage of smaller reactors and higher outputs (Ghenciu, 2002). Among the virtues of catalytic partial oxidation is that the reaction is virtually thermoneutral and has a low energy demand. However, these advantages may easily be offset by the competing total oxidation reactions which significantly enhance process exothermicity. Despite the fact that the process is essentially adiabatic, it is characterized by high catalyst surface temperatures which lead to thermal non-equilibrium between the solid and the gaseous phase. Therefore, heat and mass transfer play a decisive role in determining the entire product spectrum (Joensen and Rostrup-Nielsen, 2002). Microfabricated silicon reactors are reported to be effective for overcoming the high temperature differences between the reaction medium and the catalyst surface (Younes-Metzler *et al.*, 2005).

The catalysts widely employed in catalytic partial oxidation include supported nickel (NiO-MgO), nickel-modified hexa-aluminates; platinum group metals Pt, Pd, Rh on alumina, on ceria containing supports, or on titania, and also supported metallic clusters (Ghenciu, 2002).

Choudhary *et al.* (1998) have investigated the partial oxidation of methane on $Ni/AlPO_4$ catalysts between a temperature range of 500 - 900°C and observed high activity and selectivity at high temperatures (>800°C).

Liguras *et al.* (2004a) have employed cordierite monoliths, ceramic foams made from mullite and zirconia-alumina as well as $\gamma$-$Al_2O_3$ pellets as supports for $Ni/La_2O_3$ catalysts for the production of hydrogen by catalytic partial oxidation of ethanol. Catalysts supported on four different materials provided good activity and selectivity; however, the one supported on the zirconia-alumina ceramic foam produced slightly better results. In another publication, they examined effects of the same supports for Ru catalysts, and decided that this time the catalyst supported on a cordierite monolith exhibited excellent catalytic performance for a wide variety of process conditions and had excellent long-term stability (Liguras *et al.*, 2004b).

### 2.4.2. Indirect Partial Oxidation

Steam reforming is endothermic and partial oxidation is exothermic, as mentioned above. It is possible to react the fuels with a mixture of steam and oxygen or air and carry out both reactions simultaneously. The exothermic oxidation (Reaction 2.3) supplies the energy for the endothermic reforming (Reaction 2.2). This process is referred to as indirect partial oxidation (IPOX) or autothermal reforming (ATR) and produces a mixture of carbon monoxide, carbon dioxide and hydrogen.

$$C_nH_m + nH_2O \Rightarrow nCO + \left(\tfrac{1}{2}m + n\right)H_2 \tag{2.2}$$

$$C_nH_m + \tfrac{1}{2}mO_2 \Rightarrow nCO + \tfrac{1}{2}mH_2 \tag{2.3}$$

IPOX catalysts have to be active for both steam reforming and partial oxidation, be robust at high temperature and resistant to sulphur and coke formation, especially in the catalytic zone that has limited oxygen. Catalyst formulations for IPOX fuel processors depend on the fuel choice and operating temperature. For methanol, Cu-based formulations can be used wile IPOX of higher hydrocarbons usually utilizes metals catalysts such as Pt, Ru, Rh and Ni deposited or incorporated into oxide supports such as ceria-containing oxides (Ghenciu, 2002).

Reitz *et al.* (2000) have investigated the activity of CuO / ZnO / $Al_2O_3$ catalyst for indirect partial oxidation of methanol and concluded that copper oxide catalysts are highly active for this reaction. One year later, Velu *et al.* (2001) have compared the catalytic performances of a series of CuZnAl-, CuZnZr-, and CuZnAlZr-oxide catalysts. They have indicated that among CuZn-based catalysts, those containing Zr were the most active and those containing Al were the least active ones. In another study, Liu *et al.* (2003) have studied catalytic performances of Pd/ZnO in IPOX of methanol as a function of Pd loading and compared to Cu/ZnO catalysts; and they have deduced that selectivity of the reaction was greatly increased by increasing Pd loading on ZnO. The increased selectivity was attributed to the formation of Pd-Zn alloy on the catalyst. In their following study, it was validated that Pd/ZnO is highly active and selective in IPOX of methanol and is more stable than Co-ZnO catalyst; however they admitted that CO formation on Pd/ZnO is higher than that on Cu-ZnO based catalysts and high Pd loading is required to decrease the CO formation. Therefore, they modified the catalyst using a co-precipitation method by introducing a third metal component: Mg, Al, Zr, Ce, La, Ru or a first row transition metal element. The catalysts Pd/ZnO-$Cr_2O_3$, PdZnO-$Fe_3O_4$, and Pd-ZnO-CuO gave good results, and it was inferred that the doping of a small amount of Cr, Fe, and Cu into Pd/ZnO was found to decrease CO formation and increase the selectivity of the reaction for hydrogen production (Liu *et al.*, 2004). *Shan et al.* (2004) have tested $Ce_{0.9}Cu_{0.1}O_Y$ catalyst for hydrogen production from methanol. The catalyst prepared by complexation-combustion method led to methanol conversions higher than 85% with 90% hydrogen yield at 240°C.

Unlike methanol, studies on the IPOX of ethanol for $H_2$ production have not progressed well and hardly few reports exist. Velu *et al.* (2005) have investigated $Cu_{1-x}Ni_xZnAl$-mixed metal oxide catalyst in oxidative steam reforming of bio-ethanol. In their study, introduction of Ni to a Cu-rich catalyst suppressed the dehydrogenation of ethanol to acetaldehyde and led to an increase in $H_2$ yield. Fierro *et al.* (2005) have considered the IPOX of ethanol over Ni-based catalysts; and they have concluded that the best activity was shown by $Ni_{19.4}Cu_{0.6}Al$ at 923K and by $Ni_{20.1}Zn_{0.7}Al$ at 750°C.

Qi *et al.* (2005) have developed a $La_{0.8}Ce_{0.2}NiO_3$ catalyst with a crystal structure of perovskite, and investigated the autothermal reforming of gasoline or its surrogate *n*-octane carried out on either bulk perovskite pellets or monolithic perovskite catalyst. The catalyst, obtained by partially substituting La with Ce at the A-site of $LaNiO_3$, showed mechanical and thermal stabilities. It possessed fairly good sulphur tolerance and was almost immune to 5 ppmw sulphur. Moreover, compared with noble-metal-based catalysts, $La_{0.8}Ce_{0.2}NiO_3$ monolithic catalyst showed superior behavior for the gasoline ATR system especially at low temperature.

Takehira *et al.* (2004) examined the effect of preparation method of Ni/MgAl catalysts in autothermal reforming of methane. spc-Ni/MgAl (spc: solid-phase crystallization method) catalysts had been prepared from Mg-Al hydrotalcite-like containing Ni at the Mg site as the precursors, and highly dispersed and stable Ni metals were found on these catalysts after the reduction. In partial oxidation of methane, spc-$Ni_{0.5}/Mg_{2.5}Al$ afforded high enough methane conversion even at the high space velocity ($9\times10^5$ ml $h^{-1}$ $g_{cat}^{-1}$), exceeding the value obtained over 1wt% Rh/MgO. As spc-$Ni_{0.5}/Mg_{2.5}Al$ has showed a high and stable activity for ATR of methane, it was denoted as a hopeful candidate for ATR of methane which can feed a fuel cell continuously. Souza and Schmal (2005) have investigated the IPOX of methane with Pt –based catalysts on three different supports, $Pt/Al_2O_3$, $Pt/ZrO_2$ and $Pt/ZrO_2/Al_2O_3$ in the temperature range of 400-900°C. The $Pt/ZrO_2/Al_2O_3$ catalyst was found to be the most active and stable at 800°C.

Whittington *et al.* (1995) have compared the activity of a monolithic three-way catalyst containing 0.3 wt% Pt, Pd and Rh promoted with various oxides supported on a ceria-alumina washcoat with the performance of the monometallic Pt, Pd, Ph catalysts for direct and indirect partial oxidation, steam reforming of propane and water-gas shift reactions. The orders of activity for the indirect partial oxidation of propane is Pt > three-way catalyst > Pd > Rh in the absence and presence of ceria. Ayabe *et al.* (2003) have investigated the IPOX of methane and propane separately over supported metal catalysts. The sequence of the activities of the 2wt% metal on alumina for methane was in the order of Rh > Pd > Ni > Pt > Co. The catalytic activity of $10wt\%Ni/Al_2O_3$ was higher than that of Rh-based catalyst. The IPOX of propane was studied with $10wt\%Ni/Al_2O_3$ catalyst for different space velocities. They observed a large amount of carbon deposition for propane compared to methane even under the steam rich conditions.

In one of the rare studies over propane, Aartun *et al.* (2004) have examined POX and IPOX of propane in a microstructured reactor from Fecralloy (Fe-Cr-Al) oxidized at high temperature to form a porous layer of $\alpha$-$Al_2O_3$ impregnated with Rh. Beside the benefits of microstructured reactor which contains dispersed catalysts on the porous layer, they have also observed no coke formation as opposed to Ni/ $Al_2O_3$/Fecralloy reactor.

In recent years, the activity of bimetallic catalysts is being investigated for IPOX of methane or propane. Nagaoka *et al.* (2005) have studied ATR of methane over Ni and/or Rh catalyst prepared from hydrotalcites. They reported that the catalytic activity decreased in the order NiRh/MgAl > Ni/MgAl > Rh/MgAl. The bimetallic catalyst was found to be very stable propably due to the hydrogen spillover from Rh in the NiRh alloy. Tomishige *et al.* (2003) have investigated the indirect partial oxidation of methane on bimetallic Pt(0.3)-Ni(10)/alumina and monometallic Ni(10)/alumina and Pt(0.3)/alumina. They observed a high temperature for Ni/alumina catalyst, indicating that methane oxidation proceeded near the catalyst bed inlet and then methane reforming proceeded. On the other hand, for the bimetallic catalyst, a flat temperature profile was observed, providing autothermicity, indicating that oxidation and steam reforming proceeded simultaneously.

One year later, Dias and Assaf (2004) have confirmed the enhancement effect of introducing small amounts of Pt, Pd and Ir (<0.3% by weight) into Ni/$\gamma$-$Al_2O_3$ catalysts (15%Ni w/w) for IPOX of methane. They further studied the possible reason for this enhancement and concluded that the effect of promoter is neither to catalyze partial oxidation nor to alter the metal site. As it is known that the addition of noble metals to nickel catalysts favors the reduction of this metal, they proposed that the increased activity of the bimetallic catalysts was due to the expansion of the metal surface area resulting from the mentioned increase in reduction. In their following study, they examined the possibility of autoreduction of these bimetallic catalysts with the aim of making the reaction ignite without previous reduction of the catalyst with $H_2$. It was deduced that platinum and iridium were good promoters for the ignition of the reaction on the nickel catalyst, without previous reduction with hydrogen. In the temperature-programmed-reduction with methane, the reduction start temperatures were found to be 460°C and 480°C for Pt and Ir. Palladium, a cheaper metal than Pt and Ir, did not favor the autoreduction when added as chloride to the nickel-catalyst. However, when added to alumina as nitrate, catalyst reduction occurred at around 460 °C for Pd/Ni-Al. It is concluded that bimetallic Pt, Ir, and Pd-Ni/Al catalysts are promising candidates for the production of hydrogen for portable or small-scale fuel cells where quick start-up is necessary (Dias and Assaf, 2005).

Selen (2003) has studied the IPOX of propane and propane/*n*-butane mixture (LPG) over bimetallic 0.2wt%Pt-15wt%Ni/$\delta$-$Al_2O_3$ catalysts, where the effects of temperature, stream/carbon ratio (S/C), carbon/oxygen ratio ($C/O_2$) and residence time on the catalytic activity and selectivity were investigated. The bed temperatures were controlled in a decreasing or increasing temperature program within the range of 350 - 470°C. The superior performance of the Pt-Ni/$\delta$-$Al_2O_3$ system was attributed to the formation of distinct but very close Pt and Ni sites and to the utilization of the catalyst particles as micro heat exchangers during IPOX. It was concluded that this performance was due to the transfer of the heat produced by total oxidation on Pt sites through the catalyst particles to Ni sites which catalyze the simultaneous steam reforming reaction. For IPOX of propane, the effect of S/C was validated in terms of the amount of hydrogen produced per amount of propane used. An increase in S/C ratio led to an increase in the amount of hydrogen produced per amount of hydrocarbon consumed. A rise in $C/O_2$ resulted in higher hydrogen production rate and the hydrogen selectivity was verified by the ratio of produced hydrogen over carbon monoxide. The effect of residence time was investigated for three parameters: hydrogen production, methane production and $H_2/CO$ ratio. A decrease in residence time, which equally means an increase in total flow rate with the same catalyst loading (150 mg), led to a considerable increase in the hydrogen production at all temperatures along with higher methane production rates. Lower residence times, which led to higher hydrogen production rates, also caused lower $H_2/CO$ ratios. At the end of the study, the optimum conditions were found to be a steam to carbon ratio of 3.00, carbon to oxygen ratio of 2.70 and residence time of 0.51 $g_{cat}$ h $mol^{-1}$ hydrocarbon.

For LPG experiments, Selen (2003) has fixed the ratio of *n*-butane to one-third of propane. Effect of S/C ratio was not investigated for LPG due to the coke deposition problems and was fixed at 5. For fixed S/C and $C/O_2$ ratios, a decrease in residence time led to a considerable increase in hydrogen production as it was the case for IPOX of propane. This phenomenon is thought to be caused by the limited residence time of carbon monoxide and hydrogen on the catalyst surface which eventually prevents methanation. Addition of *n*-butane to the feed led to a decrease in hydrogen production with increasing $C/O_2$ ratio which was in contrast with the results of pure propane. For LPG, highest hydrogen production was achieved with lowest $C/O_2$ ratio for fixed S/C ratio and residence time. The results indicate that low residence times should be preferred for higher activities. This investigation also expressed that the presence of *n*-butane in the feed stream led to higher production and higher $H_2/CO$ ratio in spite of higher amounts of CO produced.

In a recent study, Recupero *et al.* (2005) have studied IPOX of propane on a proprietary ceria-supported platinum catalyst which actually represents the first step of a project oriented for the development of a compact and reliable fuel processor fed by LPG. Generally 1.0 g of the precious Pt-catalyst was used and the catalyst remained stable for about 100 hrs at 100°C. The experimental $H_2$ values were found to be very close to the thermodynamically predicted results, and some pressure drop was recorded in the reactor due to carbon deposition which was found to be completely invariant during the experiments, suggesting that no carbon deposition occurs.

## 2.5. Water-Gas Shift

Besides steam reforming or partial oxidation, a separate reaction appears in most of the processing schemes. The water-gas shift reaction (Reaction 2.7) is a critical step in fuel processors for preliminary carbon monoxide clean up and additional hydrogen generation prior to the further elimination of carbon monoxide (Ghenciu, 2002).

$$CO + H_2O \Rightarrow CO_2 + H_2 \tag{2.7}$$

The reaction is moderately exothermic, with low carbon monoxide levels resulting at low temperatures, however with favorable kinetics at higher temperatures. As the flow contains carbon monoxide, carbon dioxide, steam and hydrogen, additional reactions such as methanation, carbon monoxide disproportionation or decomposition may occur (Ghenciu, 2002). Water-gas shift reaction running simultaneously with steam reforming not only produces hydrogen and reduces carbon monoxide but also gasifies the carbon deposited on the surface of the catalyst (Selen, 2003).

Water-gas shift is usually carried out in two stages. The classical catalyst formulations employed are Fe-Cr oxide for the first stage (high-temperature shift, at around 400°C) and Cu-ZnO-$Al_2O_3$ for subsequent stages (low-temperature shift, at around 200°C) (Ghenciu, 2002).

Junior *et al.* (2005) have investigated the substitution of chromium by vanadium as dopant in the iron based water-gas shift catalyst. The doping with vanadium led to magniteti richer in Fe(III) and with a higher surface area. The vanadium not only delayed the sintering of the particle but also stabilized more Fe(III) in the structure and thus avoided the formation of metallic iron which cause catalyst deactivation.

In addition to the catalysts mentioned above, part of the recent effort is devoted to the use of gold or platinum based catalysts for water-gas shift reaction. Fu *et al.* (2005)

have reported the high activity and stability of low-content-gold-cerium oxide catalysts at temperatures as high as 400°C which are non-pyrophoric, i.e. do not spontaneously generate heat when exposed to air, unlike Cu/Zn-oxide catalyst. Luengnaruemitchai *et al.* (2003) studied the water-gas shift reaction over Pt/$CeO_2$, Au/$CeO_2$ and Au/$Fe_2O_3$ catalysts and found out that the platinum based catalyst was more active than the gold based catalysts. In a recent study, the addition of Re to Pt catalyst supported on $Ce_{0.46}Zr_{0.54}O_2$ was investigated, and it was concluded that the bimetallic catalyst increased the water-gas shift reaction rate significantly (Choung *et al.*, 2005).

## 2.6. Carbon Monoxide Clean-Up

Water-gas shift reaction is an equilibrium reaction; therefore, complete removal of carbon monoxide is not achievable. As PEMFC's can only tolerate 4 ppm carbon monoxide, further elimination of carbon monoxide is necessary. There are three techniques for carbon monoxide removal: preferential oxidation, selective methanation and the use of hydrogen-selective Pd-alloy membranes. Currently, preferential oxidation of carbon monoxide appears to be the preferred solution as it is the lowest cost method without excessive hydrogen consumption (Ghenciu, 2002).

### 2.6.1. Preferential Oxidation of Carbon Monoxide

Preferential oxidation (Reaction 2.8) catalysts need to be active and selective; the catalyst should oxidize CO to less than 4 ppm without oxidizing a large amount of hydrogen (Reaction 2.9).

$$CO + O_2 \Rightarrow CO_2 \tag{2.8}$$

$$H_2 + \frac{1}{2}O_2 \Rightarrow H_2O \tag{2.9}$$

Catalyst formulations comprise of Pt or promoted Pt, Ru, Pd, alloys of Pt-Sn or Pt-Ru, or Rh on alumina or on molecular sieves, or Au catalysts, or more recently Cu catalysts on alternative supports (Ghenciu, 2002).

Özkara and Aksoylu (2003) have studied the selective oxidation of CO in $H_2$-rich gas stream over a series of Pt-Ce and Pt-Sn catalysts supported on three different types of activated carbon (AC). The highest activity and selectivity was observed for Pt-Sn catalyst prepared on air-oxidized AC. Rossignol *et al* (2005) have studied preferential oxidation of carbon monoxide of Au based catalysts supported on $Al_2O_3$, $ZrO_2$ and $TiO_2$ and concluded that the catalytic activity of these three catalysts does not change significantly with the support in hydrogen rich steams. Luengnaruemitchai *et al.* (2004) examined the effects of preparation method, $O_2$, water vapor, and $CO_2$ concentration in the feed stream on the selective carbon monoxide oxidation over Au/$CeO_2$ catalysts in a temperature range of 50-190°C. According to the study, presence of the water vapor lowered the CO conversion only at low temperatures, higher $CO_2$ concentration significantly reduced CO conversion; but, neither the water vapor nor the $CO_2$ concentration significantly affected the CO selectivity. The most dramatic effect was due to the preparation method, namely the catalyst prepared with co-precipitation showed a much better activity.

As for the noble metal catalysts, Marino *et al.* (2004) have investigated platinum, iridium, and palladium catalysts over a range of different physical and chemical properties supports; they found out that Pt and Ir gave better results than Pd for preferential oxidation of CO. Also, they observed that the higher the molar ratio in ceria in the support, the higher the activity and the selectivity in the reaction. In another study, Tanaka *et al.* (2003) have reported that the addition of potassium to another precious catalyst Rh supported on zeolite, particularly USY, increased the catalyst's activity so that the CO concentration in the exit stream was below 10 ppm.

In a recent study, Marino *et al.* (2005) tested supported base metal catalysts covering a wide range of transition metals (Co, Cu, Cr, Zn, Ni) supported on oxides such as MgO, $La_2O_3$, $SiO_2$-$Al_2O_3$, $CeO_2$, $Ce_{0.63}Zr_{0.37}O_2$. They noted that the activity of ceria and ceria-zirconia supported copper catalyst was comparable to the performance of noble metal samples classically used for preferential oxidation of CO.

# 3. EXPERIMENTAL

## 3.1. Materials

### 3.1.1. Chemicals

All the chemicals used for catalyst preparation are presented in Table 3.1 (Avcı, 2003).

Table 3.1. Chemicals used for catalyst preparation

| Chemicals | Specification | Source | Molecular weight |
|---|---|---|---|
| Nickel nitrate | $Ni(NO_3)_2.6H_2O$ extra pure | Merck | 290.81 |
| Tetraammineplatinum(II) nitrate | $Pt(NH_3)_4(NO_3)_2$ 50.4 % Pt | Aldrich | 387.22 |
| Gamma alumina | $\gamma$-$Al_2O_3$ | Alcoa | - |

### 3.1.2. Gases and Liquids

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

Table 3.2. Specifications and applications of the liquids used

| Liquid | Specification | Application |
|---|---|---|
| Water | Distilled | Aqueous solutions, Reactant |
| Ethanol | 99.8 vol. %(Riedel-deHaën) | Aqueous solutions, Reactant |

Table 3.3. Specifications and applications of the gases used

| Gas | Specification | Application |
|---|---|---|
| Hydrogen | 99.99 % (BOS) | GC calibration*, Reduction |
| Carbon Monoxide | 99.999 % (BOS) | GC calibration* |
| Helium | 99.999 % (BOS) | GC carrier gas |
| Nitrogen | 99.998 % (BOS) | Inert |
| Dry Air | 78.4 % $N_2$ + 21.5 % $O_2$ (BOS) | GC calibration*, Reactant |
| Methane | 99.9 % (BOS) | GC calibration* |
| Argon | 99.999 % (BOS) | GC carrier gas |
| Propane | 99.5 % (BOS) | GC calibration*, Reactant |
| *n*-Butane | 99.5 % (BOS) | GC calibration*, Reactant |

* (Avcı, 2003)

## 3.2. Experimental Systems

The experimental systems used in this research can be classified into four groups:

- Catalyst Preparation Systems: The set-up used for preparing catalysts by incipient-to-wetness impregnation technique represents this group of experimental systems.
- Catalyst Characterization Systems: This group of systems involves ESEM-EDAX and X-Ray Diffraction techniques used to characterize the physical and structural properties of the catalyst samples prepared as well as the changes occur on their surfaces during the reaction tests.
- Catalytic Reaction System: This continuous flow microreactor system includes gas and liquid flow controllers, temperature controlled heated lines, gas/liquid mixer, reaction chamber placed in a vertical oven whose temperature is controlled by a programmable temperature controller, and feed and product sampling sections. This system is used for measuring reaction kinetics of ethanol steam reforming and for assessing catalytic activity/selectivity of IPOX of LPG.

- Product Analysis Systems: The quantitative determination of the composition of the feed and product streams is conducted by using two different gas chromatographs operating in parallel.

### 3.2.1. Catalyst Preparation System

The system used for catalyst preparation by incipient-to-wetness impregnation technique includes a Retsch UR1 ultrasonic mixer, a vacuum pump, a buchner flask and a MasterFlex computerized-drive peristaltic pump.

### 3.2.2. Catalyst Characterization Systems

The structural analyses of the catalyst samples were carried out at Boğaziçi University Advanced Technologies R&D Center through Environmental Scanning Electron Microscopy-Backscattered Composition Imaging (ESEM-BCI), Energy Dispersive X-ray Analysis (EDAX) and particle size analysis techniques, using a Philips XL30 ESEM-FEG system which has a maximum resolution of 2 nm. In EDAX analyses, the minimum detection limit was 50 ppm.

The phase identification of the catalyst samples were carried out at Boğaziçi University Advanced Technologies R&D Center, using a Rigaku D/MAX-Ultima+/PC X-ray diffraction equipment.

### 3.2.3. Catalytic Reaction System

The catalytic reaction system designed and constructed in CATREL has three sections (Figure 3.1) :

- Feed section
- Reaction section
- Product analysis section

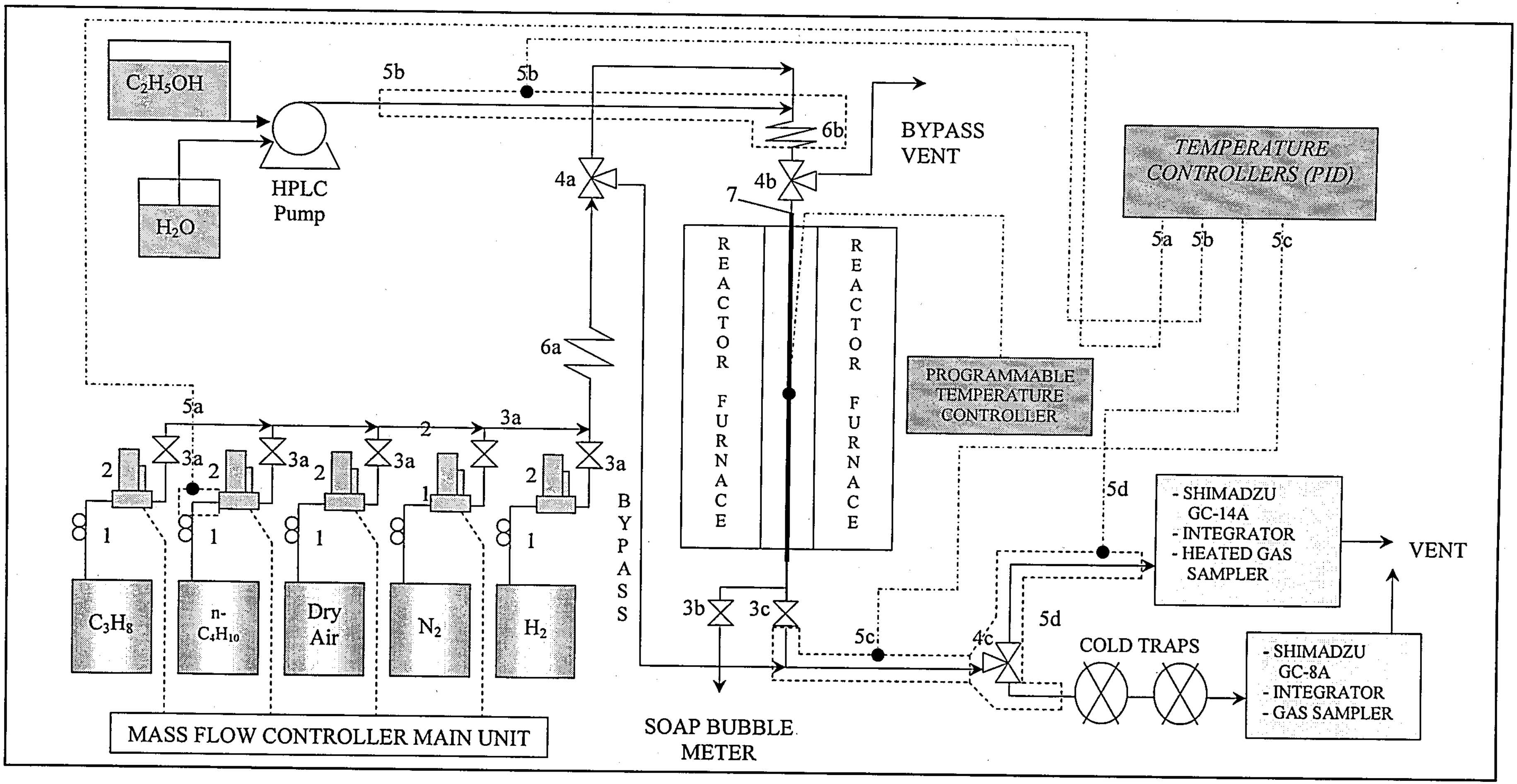

Figure 3.1. Schematic diagram of the flow microreactor system (adapted from the system of Avcı, 2003)

1. Gas regulator; 2. Mass flow controller; 3. On-off valve; 4. Three-way valve; 5. Heated zone; 6. Mixing zone; 7. Differential reactor

The feed section includes mass flow control systems, 1/4", 1/8" and 1/16" stainless steel tubes and fittings for feeding liquid water, ethanol and gaseous species, i.e. propane, n-butane, dry air, nitrogen and hydrogen at desired quantities. The gases that were present in pressurized cylinders were passed through the gas flow regulators and the calibrated Omega Model 5878 mass flow controllers. An Aalborg GFC171S series standalone controller was used to regulate hydrogen flow. On-off valves were placed in front of the mass flow controllers to protect them from possible back-pressure fluctuations. In order to eliminate possible condensation of *n*-butane, the zone between the pressure regulator and the mass flow controller was kept at 150 ± 5 °C using a 0.6 m heating tape and the temperature controller. All the reactants excluding liquid water and ethanol were then passed through a primary mixing zone to ensure the flow of a homogeneous gas mixture into the reactor.

Water or ethanol-water mixture was introduced into the reaction system at constant flow rates using a Jasco PU-1580 intelligent HPLC pump. The 1/16" tube through which the liquid reactant was allowed to flow was kept at 175 ± 5 °C by a 1.4 m heating tape whose temperature is controlled by the temperature controller to feed the liquid reactant in the form of gas. Steam or the vapour mixture and the homogeneous gas mixture were mixed in a secondary mixing zone.

It was possible to divert flow using three way valves: The feed gases could be diverted to the bypass line, so that feed composition could be analyzed using gas chromatographs. Another three way valve was 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.

The reactants, metered and mixed in the feed section, were allowed to flow through the reaction section. This section was composed of a 40 cm x 2.4 cm ID tube furnace controlled to ± 0.5 °C by a Shimaden FP-21 programmable temperature controller and a 1/4" stainless steel fixed-bed microreactor. The reactor was also constructed in CATREL and its length was selected to be 50 cm so that it was longer than the furnace.

During the reaction tests, the catalyst bed was placed in the center of the reactor. The reaction temperature was controlled and measured by a 20-gauge wire K type sheathed thermocouple (insulation material: ceramic fiber braid) that was placed in the center of the furnace around the microreactor. The position of the reactor and hence catalyst bed was adjusted to coincide with the constant-temperature zone of tube furnace. Silane-treated glass wool (Alltech Associates Inc.) 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 furnace to prevent heat loss from the furnace and to provide a good temperature profile.

In order to prevent the condensation of vapor in the product stream, the line from the reactor to the to both gas chromatographs were both kept heated at 175 ± 5 °C using a 1.4 m and a 2.5 m heating tape whose temperature is controlled by the temperature controller. The product stream was analyzed qualitatively and quantitatively using two separate gas chromatographs operating in a parallel scheme.

Four different temperature controllers are employed to control the temperature of the four different zones independently. 16-gauge wire K type sheathed thermocouples (insulation material: fiberglass) were placed at the middle point of each heated zone to measure and control the temperatures. The degree of power input of the heating tapes was adjusted by the controller. The heating tapes were covered with ceramic wool insulation to prevent heat losses.

### 3.2.4. Product Analysis Systems

The product mixture contains groups of species with different characteristics, i.e. hydrocarbons involving methane, ethane, propane, *n*-butane, acetone, acetaldehyde, ethanol, fixed gases involving hydrogen, oxygen, nitrogen, and others involving carbon monoxide, carbon dioxide and water. Considering that all these species excluding water were needed to be analyzed quantitatively, use of two different gas chromatographs was essential; hydrocarbons were effectively analyzed using a Porapak Q column with He carrier gas whereas quantitative detection of hydrogen and other fixed gases were analyzed using a Molecular Sieve column with Ar carrier.

A Shimadzu GC-14A gas chromatograph equipped with a Thermal Conductivity Detector (TCD) and a Shimadzu CR-4A Chromatopac data processor was used interactively to analyze hydrocarbons and carbon dioxide. In order to analyze fixed gases, carbon monoxide and methane, a Shimadzu GC-8A gas chromatograph equipped with a Thermal Conductivity Detector (TCD) and a Shimadzu CR-1B Chromatopac data processor involving a Molecular Sieve (MS) column was employed. Since the analysis column can easily be deactivated if it is contacted with a stream containing liquid species, water and ethanol vapors existing in the product stream was removed by placing two salt-ice cold traps held in Dewar flasks at 0°C before GC-8A inlet. The parallel operation of these gas chromatographs was achieved by diverting the product flow by a three-way valve. The analysis conditions are presented in Table 3.4. For both chromotographs, the previously optimized conditions by Aksoylu (1999) and Avcı (2003) were used whereas analysis reports provided by the manufacturer were employed to finalize the operating conditions used in GC-8A. The calibration curves may be found elsewhere (Avcı, 2003).

Table 3.4. Product analysis conditions

| GC Parameter | GC 1 – Shimadzu GC-14A | GC 1 – Shimadzu GC-8A |
|---|---|---|
| Detector type | TCD | TCD |
| Column temperature, °C | 90 | 60 |
| Injector temperature, °C | 150 | 90 |
| Detector temperature, °C | 150 | 90 |
| TCD temperature, °C | 150 | 90 |
| TCD current, μA | 120 | 60 |
| Carrier Gas (CG) | He | Ar |
| CG flow rate, ml min$^{-1}$ | 25 | 50 |
| Column packing material | Porapak Q, 80-100 mesh | MS 5A, 60-80 mesh |
| Column tubing material | Stainless steel | Stainless steel |
| Column length & ID | 3 m x 3mm | 2 m x 3mm |
| Sample loop | 1 ml kept at 125°C | 1 ml kept at 25°C |

## 3.3. Catalyst Preparation and Pretreatment

### 3.3.1. 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. $\gamma$-$Al_2O_3$ is a commonly used support material due to its high surface area. However it is reported to have low stabilities at temperatures higher than 600°C and tends to facilitate carbon formation in the presence of steam due to its high acidity (Ma, 1995). The most thermally stable version of alumina is obtained when $\gamma$-phase is transformed into $\alpha$-phase at temperatures higher than 1123°C. However, its low surface area, which is less than 5 $m^2\ g^{-1}$, is likely to end up with poor catalytic activities due to the low dispersion of active metals. Hence using a support such as $\delta$-alumina – an intermediate phase between $\gamma$ and $\alpha$ - having relatively high thermal stability and an acceptable surface area can be optimum in terms of obtaining an efficient catalytic performance (Ma, 1995).

The support preparation procedure used in this study was involved drying of $\gamma$-$Al_2O_3$ at 150°C for 2h followed by calcinations at 900°C for 4h in a muffle furnace. BET surface area of the $\delta$ -$Al_2O_3$ support obtained was found as 81.6 $m^2\ g^{-1}$ (Avcı, 2003).

### 3.3.2. Preparation of Pt-Ni/$\delta$-$Al_2O_3$ Catalyst

The bimetallic Pt-Ni/$\delta$-$Al_2O_3$ catalyst (metal loadings were 0.2 weight per cent for Pt and 15 weight per cent for Ni) was prepared through a sequential route, in which Pt solution was impregnated over initially prepared and calcined Ni/$\delta$-$Al_2O_3$ catalyst. Ni/$\delta$-$Al_2O_3$ catalysts were prepared by the incipient-to-wetness impregnation technique using aqueous solution of $Ni(NO_3)_2.6H_2O$. The aqueous solutions were prepared by dissolving the calculated amount of the precursor salt in definite amounts of distilled water (ca. 1 ml solution/g support). The support, $\delta$-$Al_2O_3$, was placed in a Buchner flask and mixed ultrasonically for 25 min. under vacuum. The aqueous solution was then impregnated on the support via a peristaltic pump. The resulting slurries that were formed after ultrasonic mixing of the aqueous solutions and the support under vacuum for 1.5 h were then dried overnight at 120°C and calcined at 600°C for 4 h to obtain ($NiO/\delta\text{-}Al_2O_3$). The aqueous Pt solution was then added to $NiO/\delta\text{-}Al_2O_3$ and mixed ultrasonically under vacuum for 1.5 h. The resulting slurry involving two metals was dried overnight at 120°C and finally calcined at 500°C for 4 h.

### 3.3.3. Pretreatment

In order to obtain high catalytic activities, a pretreatment involving the reduction of the active metals from the oxide state –which is formed while 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 500°C for 4 h is a suitable procedure for pretreating the bimetallic catalyst Pt-Ni (Ma, 1995). Ma (1995) 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 used for the catalyst used in all of the experiments (Avcı, 2003).

After placing the catalyst into the constant temperature zone of the microreactor, $N_2$ was allowed to flow at 50 ml $min^{-1}$ for 10 min. to remove oxygen from the system. The gas flow was switched from $N_2$ to $H_2$ and the latter was set to flow at 20 ml $min^{-1}$. Reduction was started by heating the catalyst from room temperature to 150°C at a rate of 10°C $min^{-1}$. The temperature was kept constant at 150°C for 30 min. for the removal of adsorbed water. Third step was involved heating the sample from 150°C to 300°C at a rate of 5°C $min^{-1}$, followed by a 30 min isothermal segment at 300°C for the removal of crystalline water. The temperature was then increased from 300°C to 500°C at a rate of 2°C $min^{-1}$ and finally kept constant at 500°C for 4 h. After reduction, the system was allowed to cool down to ca. 150°C under $H_2$ flow. Below this temperature, the gas flow was switched from $H_2$ to $N_2$ and the latter was allowed to flow at a small flow rate, e.g. 3 ml $min^{-1}$ overnight to sweep $H_2$ from the system.

## 3.4. Reaction 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) did not interfere with the reaction test outputs. The results indicated that these items above were inactive under the conditions used in the reaction experiments.

### 3.4.2. Kinetic Study of Ethanol Steam Reforming over Pt-Ni/δ–$Al_2O_3$ Catalysts

Reaction experiments were conducted using stainless steel tubular down-flow microreactors. The temperature of the catalyst bed was controlled by a programmable temperature controller with ±0.5°C sensitivity. The catalysts were pretreated through reduction by 20 ml $min^{-1}$ pure hydrogen flow at 500°C for 4 h. After reduction, the temperature of reactor was raised to the reaction temperature that is 400°C, under inert nitrogen flow and nitrogen was trapped within the reactor for 1.5 h in order to allow ethanol, steam and nitrogen to reach steady-state.

In order to investigate the effects of ethanol and water on intrinsic reaction rates, the flowrates of the reactants and inert nitrogen were adjusted so that external and internal heat/mass transfer resistances could be minimized and the conversions could be kept at low values, e.g. nearly 20 per cent (Table 3.5). With the intention of keeping conversions at low values, small amounts of catalyst (20 or 25 mg) diluted with inert δ-$Al_2O_3$ were put into the reactor such that the total bed weighed 250 mg. The total inlet flow was changed between 240 ml $min^{-1}$ and 270 ml $min^{-1}$ and a 45-60 mesh (250-425 μm) particle size was selected. The temperature of the catalyst bed increased to 425°C and 450°C separately, in order to investigate the effect of temperature on intrinsic reaction rate for each experiment set.

Table 3.5. Conditions for the kinetic study of steam reforming of ethanol

| Set # | W (mg) | $C_2H_5OH$ (ml min$^{-1}$) | $H_2O$ (ml min$^{-1}$) | $N_2$ (ml min$^{-1}$) | S/C | W/$F_{HC}$ (mg sec ml$^{-1}$) |
|---|---|---|---|---|---|---|
| 1 | 20 | 25 | 110 | 135 | 2.2 | 0.074 |
| 2 | 25 | 25 | 110 | 135 | 2.2 | 0.093 |
| 3 | 20 | 25 | 75 | 140 | 1.5 | 0.083 |
| 4 | 25 | 25 | 75 | 140 | 1.5 | 0.104 |

### 3.4.3. Indirect Partial Oxidation of Propane and *n*-Butane Mixture over Pt-Ni/δ–$Al_2O_3$ Catalysts

Reaction experiments were conducted using stainless steel tubular down-flow microreactors. In all experiments, fresh catalysts varying between 65 and 150 mg depending on the total flow rates were used without any dilution of the bed. The temperature of the catalyst bed was controlled by a programmable temperature controller with ±0.5°C sensitivity. The catalysts were pretreated through reduction by 20 ml min$^{-1}$ pure hydrogen flow at 500°C for 4 h. The employed temperature program was of increasing temperature progression (ITP) type. It is worth noting that 500°C was not exceeded in the temperature programs due to the high possibility of coke formation via thermal cracking of the hydrocarbons. In all experiments, propane, dry air and water flows were adjusted according to the assigned carbon/oxygen, steam/carbon and W/F ratios ($1.50 < C{:}O_2 < 2.70$; $5 < S{:}C < 7$; $0.51 < W/F < 1.37$). High flowrates were preferred to eliminate temperature rises and hot-spots that may occur due to the exothermicity of the oxidation reaction. Propane/*n*-butane ratio was kept constant at 1:1 for all runs conducted. The details of the experimental conditions are given in Table 3.6.

Table 3.6. Conditions for IPOX of propane and *n*-butane mixture

| Set # | $C/O_2$ | S/C | $W/F_{Total}$ (mg sec $ml^{-1}$) | Total Flowrate (ml $min^{-1}$) | $C_3H_8$ (ml $min^{-1}$) | $C_4H_{10}$ (ml $min^{-1}$) |
|---|---|---|---|---|---|---|
| 1 | 2.12 | 5 | 1.12 | 133.7 | 2.54 | 2.54 |
| 2 | 2.12 | 5 | 1.37 | 109.7 | 2.08 | 2.08 |
| 3 | 2.12 | 6 | 1.37 | 107.1 | 1.79 | 1.79 |
| 4 | 2.12 | 5 | 0.51 | 137.6 | 2.61 | 2.61 |
| 5 | 2.12 | 6 | 0.51 | 126.8 | 2.12 | 2.12 |
| 6 | 1.50 | 5 | 0.51 | 126.8 | 2.14 | 2.14 |
| 7 | 2.70 | 5 | 0.51 | 126.8 | 2.57 | 2.57 |
| 8 | 2.12 | 7 | 1.37 | 109.7 | 1.64 | 1.64 |
| 9 | 2.12 | 7 | 0.51 | 126.8 | 1.90 | 1.90 |
| 10 | 2.70 | 7 | 0.51 | 126.8 | 2.00 | 2.00 |
| 11 | 1.50 | 7 | 0.51 | 126.8 | 1.73 | 1.73 |
| 12 | 2.12 | 7 | 1.12 | 133.7 | 2.00 | 2.00 |

For all experimental sets, the catalyst bed temperature was brought to 350°C under inert nitrogen flow and nitrogen was trapped in the reactor and the reactants were allowed to reach steady-state for 2 h. Then, the reactants are allowed to pass through the reactor at 350°C at first, and after the analyses of the products via the two chromatographs in parallel, the temperature increased to 370°C at a rate of 2 °C/min. Same procedure is repeated until 470°C and analyses of the products were conducted at temperatures 350°C, 370°C, 390°C, 410°C, 430°C, 450°C and 470°C.

# 4. RESULTS AND DISCUSSION

## 4.1. Introduction

Apart from the fast depletion of fossil fuels, the increasing amount of their combustion by-product gas, carbon dioxide, is a very big concern of the scientific community for the past few decades. Efforts are being devoted to replace the existing conventional fossil energy system by a hydrogen energized system. Within the framework of utilizing hydrogen in energy production, there is an increasing interest in the research areas including studies on hydrogen storage, hydrogen production from renewable sources e.g. solar sources, wind or bio-ethanol, and on-board hydrogen production for mobile applications. In order to increase the overall efficiency of the future hydrogen energy systems, both the kinetics of the chemical processes occurring during hydrogen production and the effects of various parameters on the quality and the quantity of hydrogen produced have been investigated.

This study focuses on the determination of power law kinetics of ethanol steam reforming and on the investigation of the effects of reaction parameters on hydrogen production via indirect partial oxidation of LPG. In IPOX studies, 50 per cent propane and 50 per cent *n*-butane mixture was used as a model LPG feed. This study is basically a continuation of previous works conducted by Selen (2003) and Örücü (2005). The catalyst chosen is a bimetallic Pt-Ni catalyst on δ-alumina support.

## 4.2. Catalyst Characterization

Selen (2003) has analyzed the sequentially impregnated bimetallic Pt-Ni/δ-$Al_2O_3$ catalysts by ESEM to obtain information on their textural and metal dispersion properties, and by XRD to determine the crystal phases that exist on the catalyst surface. Two catalyst samples, unreduced and freshly reduced, were analyzed to point out the changes on the catalyst surface and active metallic sites due to reduction.

### 4.2.1. ESEM Analyses

The SEM micrograph of the unreduced bimetallic Pt-Ni catalyst shown in Figure 4.1 indicates that nickel oxide, the gray region in the image, has well distributed over the alumina surface, the dark region in the image, which is hard to see. Platinum species on the surface, bright regions on the two sides of the micrograph, seem agglomerated on the nickel oxide clusters. Upon the EDAX studies, very little metallic nickel formation has been determined (Selen, 2003).

Figure 4.1. SEM micrograph of the bimetallic unreduced catalyst

The effect of the reduction procedure is shown in Figure 4.2. In the SEM micrograph of the freshly reduced bimetallic catalyst, platinum agglomerates (bright regions) are well distributed on reduced nickel (gray region in the background) which covers the alumina surface completely. From EDAX results it was concluded that the nickel oxides formed after the calcination of the catalyst have transformed into metallic nickel upon reduction (Selen, 2003).

Figure 4.2. SEM micrograph of the bimetallic fresh, reduced catalyst

Not only the composition image obtained from SEM but also the EDAX and XRD results indicated that there was no Pt-Ni alloy formation on the catalyst surface. Therefore, Selen (2003) has concluded that the reason for the enhanced catalytic properties of Pt-Ni system may be the synergistic interactions between distinct Pt and Ni sites which are formed very close to each other as shown in Figure 4.3. In that structure, there is enhanced heat transfer between the active metallic sites either directly or through the $Al_2O_3$ support. The energy transfer is from Pt sites catalyzing exothermic total oxidation to Ni sites catalyzing endothermic steam reforming, and this was thought to be the main cause for the improved activity of the bimetallic catalyst at low temperatures compared to monometallic Ni catalyst (Selen Çağlayan *et al.*, 2005).

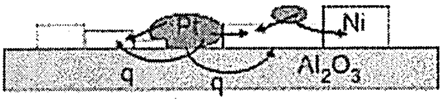

Figure 4.3. The possible use of the bimetallic catalyst as a micro heat exchanger (Selen-Çağlayan *et al.*, 2005)

A carbon deposited catalyst sample is shown in Figure 4.4. In this micrograph, no fibrous morphology of carbon was detected; surface was covered with clusters of deposited carbon which led to zero catalyst activity and blockage of the reactor.

Figure 4.4. SEM micrograph of the carbon deposited bimetallic catalyst

### 4.2.1. XRD Analyses

Selen (2003) has also conducted X-ray diffraction analyses on reduced and unreduced Pt-Ni/δ-$Al_2O_3$ catalyst samples. The transformation of nickel oxides to metallic nickel by reduction are shown in Figures 4.5 and 4.6. XRD results of the reduced sample confirmed the results obtained from EDAX as there were no indication of any Pt-Ni alloy formation.

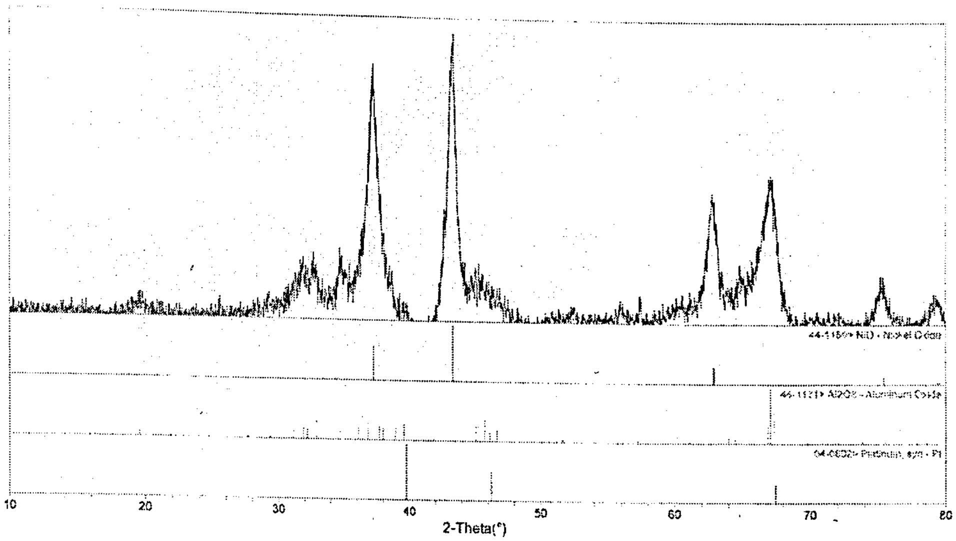

Figure 4.5. XRD pattern of the bimetallic, unreduced catalyst

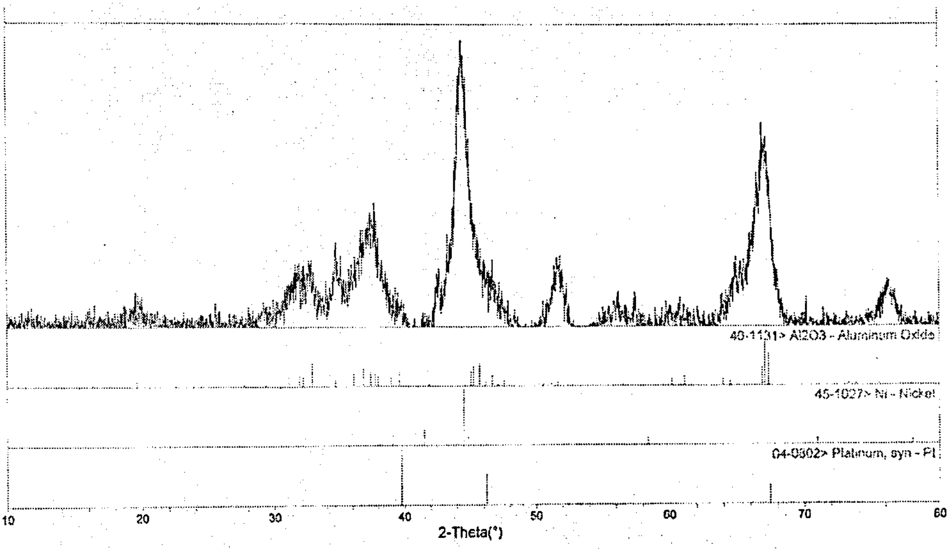

Figure 4.6. XRD pattern of the bimetallic, fresh, reduced catalyst

## 4.3. Kinetic Study of Ethanol Steam Reforming

### 4.3.1. Design of the Experimental Conditions

Experimental conditions for kinetic study of ethanol steam reforming process were determined in accordance with the academic work conducted by Örücü (2005). The research was carried on in order to complement results of the mentioned study. The conditions (Table 4.1) were fixed to keep the ethanol conversions at low values, e.g. ca 20 per cent. The parameters to be evaluated were the activation energy along with the orders of reaction with respect to ethanol and steam.

Table 4.1. Conditions for the kinetic study of steam reforming of ethanol

| Set # | W (mg) | $C_2H_5OH$ (ml min$^{-1}$) | $H_2O$ (ml min$^{-1}$) | $N_2$ (ml min$^{-1}$) | S/C | W/$F_{HC}$ (mg s ml$^{-1}$) |
|---|---|---|---|---|---|---|
| 1 | 20 | 25 | 110 | 135 | 2.2 | 0.074 |
| 2 | 25 | 25 | 110 | 135 | 2.2 | 0.093 |
| 3 | 20 | 25 | 75 | 140 | 1.5 | 0.083 |
| 4 | 25 | 25 | 75 | 140 | 1.5 | 0.104 |

### 4.3.2. Evaluation of Rate Parameters of Ethanol Steam Reforming

The power-law type rate expression for ethanol steam reforming reaction is given by Equation 4.1.

$$-r = \left[k_0 \exp\left(-\frac{E_A}{RT}\right)\right]\left(P_{C_2H_5OH}\right)^{\alpha}\left(P_{H_2O}\right)^{\beta} \qquad (4.1)$$

Evaluation of the rate parameters requires first the determination of the reaction rates on the left-hand side of Equation 4.1. The reaction rates were calculated from the slopes of the conversion versus residence time graphs. Figure 4.7 displays the conversion levels of Set 1 and Set 2, which involve experiments at constant flow and constant feed composition with different catalyst loadings, and hence, different residence times. In the same manner, conversion levels obtained in Sets 3 and 4 are shown in Figure 4.8 along with the fitted line equation. The rate reactions are found to be 0.149 and 0.145 mg s μmol$^{-1}$ for Figures 4.7 and 4.8, respectively.

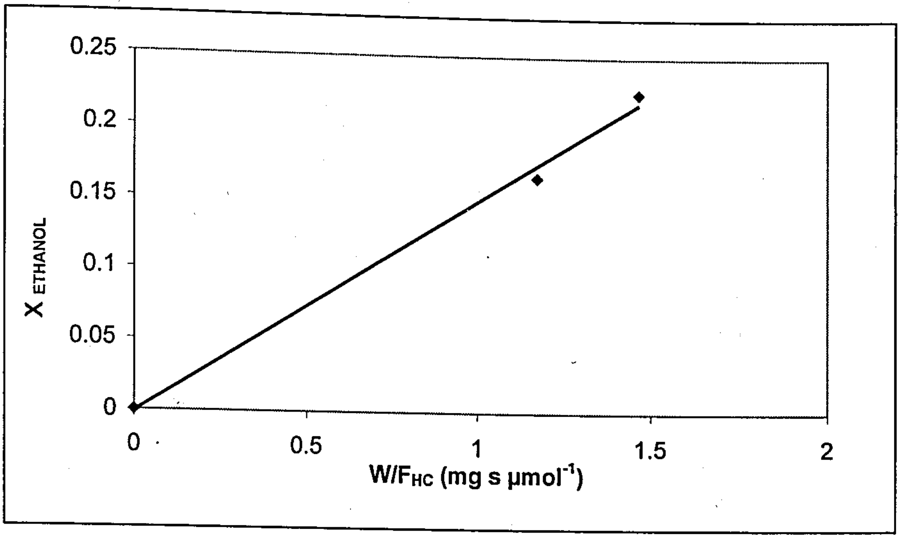

Figure 4.7. Conversion vs. residence time plot of Sets 1 and 2 of kinetic study

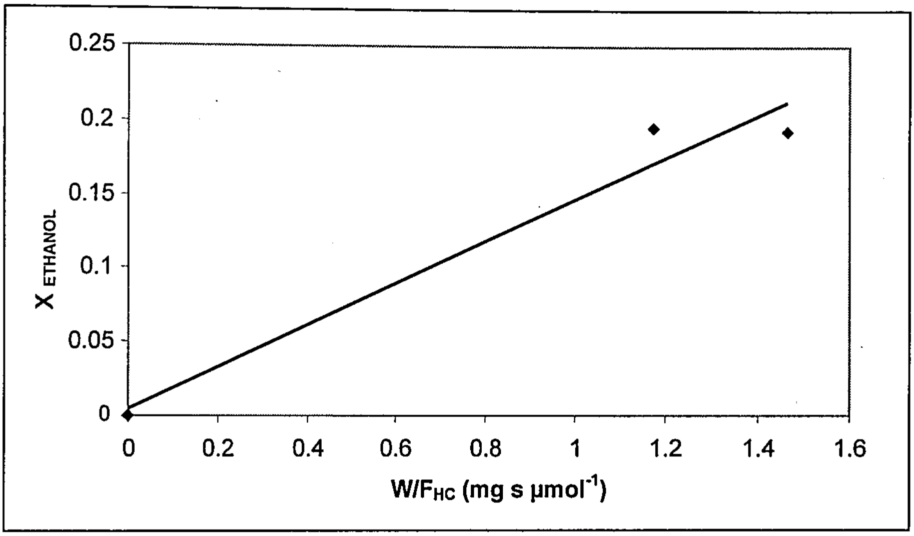

Figure 4.8. Conversion vs. residence time plot of Sets 3 and 4 of kinetic study

The flowrates of the constituents - ethanol, water and nitrogen – were converted to concentrations in mole per cent, and these numbers were equated to partial pressures as the operation pressure was atmospheric. The resulting rate versus partial pressure data of the four experimental sets obtained at 400°C were combined with those taken previously by Örücü (2005). All data points were used to estimate the reaction orders in Equation 4.1 using linear regression analysis. Equation 4.1 was linearized by taking the natural logarithm of both sides prior to the linear regression analysis (Equation 4.2). Orders of reaction are presented in Table 4.2.

$$\ln(-r) = \ln(k_0) - \frac{E_A}{RT} + \alpha \ln(P_{C_2H_5OH}) + \beta \ln(P_{H_2O}) \tag{4.2}$$

Table 4.2. Estimated reaction orders

| | α<br>(with respect to ethanol) | β<br>(with respect to steam) |
|---|---|---|
| Reaction Orders | 1.18 | -0.18 |

The reaction orders indicate that the reaction rate is directly proportional to the partial pressure of ethanol while there is a moderate inhibition effect of steam. This result is in agreement with the literature for steam reforming of *n*-butane over the same bimetallic catalyst (Avcı, 2003; Avcı *et al.*, 2004). The sum of squares of residuals is found to be $3.3 \times 10^{-3}$ mg s μmol$^{-1}$.

The experiment sets given in Table 4.1 were repeated at 425°C and 450°C in order to estimate the activation energy of the reaction. The linear Arrhenius plot of ln(-r) versus $(\frac{1}{T})$ in between 400°C (673 K) and 450°C (723 K) is given in Figure 4.9. The activation energy ($E_A$) calculated from the slope of the straight line in Figure 4.9 $(-\frac{E_A}{R})$ is found to be 39.3 kJ mol$^{-1}$. It is worth noting that the activation energy of *n*-butane steam reforming was found to be around 80 kJ mol$^{-1}$ previously (Avcı, 2003; Avcı *et al.*, 2004). This notable difference may be due to the structural differences between alcohols and alkenes or to the more frequent presence of strong C-H bonds in *n*-butane.

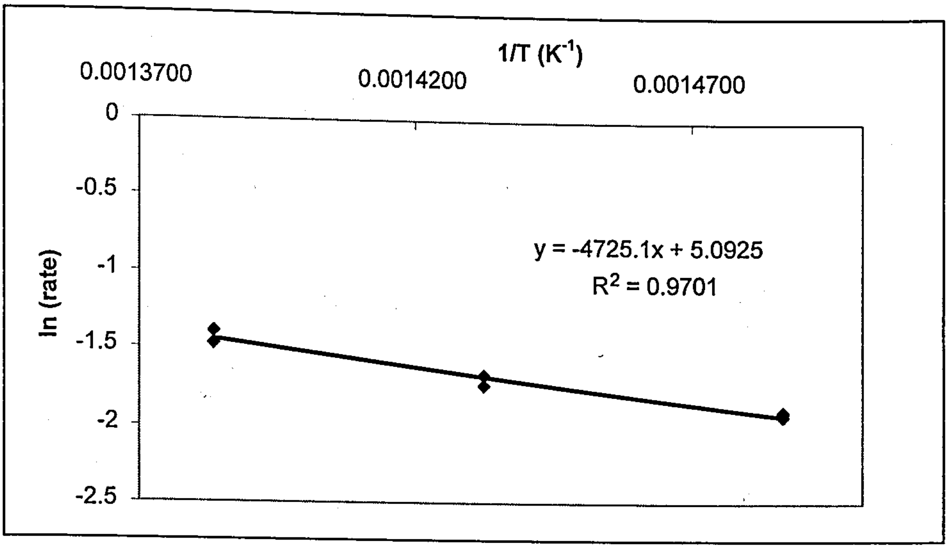

Figure 4.9. Arrhenius plot for steam reforming of ethanol

## 4.4. Indirect Partial Oxidation of the Propane and *n*-Butane Mixture

### 4.4.1. Design of the Experimental Conditions

Experimental conditions were determined in accordance with the previous studies conducted on indirect partial oxidation of LPG (Selen, 2003). The parameters taken into consideration were catalyst weight, temperature, steam/carbon ratio, carbon/oxygen ratio, W/F ratio. The flowrate in the denominator of residence time is selected to be the total flowrate involving the flow of hydrocarbons, steam and dry air.

As the light-off temperatures for total oxidation and steam reforming of propane were previously determined to be 330°C and 350°C respectively (Avcı, 2003; Avcı *et al.*, 2003), Selen (2003) has started IPOX experiments from 350°C. Carbon/oxygen ratios were kept above the stochiometric values, which are 0.6 for propane and 0.616 for *n*-butane. In a 75 per cent propane and 25 per cent *n*-butane mixture, Selen (2003) has experienced coke deposition at steam/carbon ratios less than 3.2; therefore, 5 was selected to be the optimum steam/carbon ratio in the mentioned study.

The experimental conditions in this study were adjusted such that the effect of two parameters, namely steam/carbon ratio and the propane/*n*-butane ratio in LPG, can be determined through direct comparison with the previous work conducted by Selen (2003). Therefore, carbon/oxygen and W/F ratios were taken from Selen (2003), the temperature interval was taken to be between 350°C and 470°C, and the steam/carbon ratio was started from 5 and increased up to 7 when coke formation occurred on the catalyst surface.

The experiments conducted for the indirect partial oxidation of propane and *n*-butane mixture are listed in Table 4.3. In all sets, a 50 per cent propane and 50 per cent *n*-butane mixture was used as the hydrocarbon feed.

Table 4.3. The reaction conditions for IPOX of propane- *n*-butane mixture

| Set # | $C/O_2$ | S/C | $W/F_{Total}$ (mg s $ml^{-1}$) | Total Flowrate (ml $min^{-1}$) | $C_3H_8$ (ml $min^{-1}$) | $C_4H_{10}$ (ml $min^{-1}$) |
|---|---|---|---|---|---|---|
| 1 | 2.12 | 5 | 1.12 | 133.7 | 2.54 | 2.54 |
| 2 | 2.12 | 5 | 1.37 | 109.7 | 2.08 | 2.08 |
| 3 | 2.12 | 6 | 1.37 | 107.1 | 1.79 | 1.79 |
| 4 | 2.12 | 5 | 0.51 | 137.6 | 2.61 | 2.61 |
| 5 | 2.12 | 6 | 0.51 | 126.8 | 2.12 | 2.12 |
| 6 | 1.50 | 5 | 0.51 | 126.8 | 2.14 | 2.14 |
| 7 | 2.70 | 5 | 0.51 | 126.8 | 2.57 | 2.57 |
| 8 | 2.12 | 7 | 1.37 | 109.7 | 1.64 | 1.64 |
| 9 | 2.12 | 7 | 0.51 | 126.8 | 1.90 | 1.90 |
| 10 | 2.70 | 7 | 0.51 | 126.8 | 2.00 | 2.00 |
| 11 | 1.50 | 7 | 0.51 | 126.8 | 1.73 | 1.73 |
| 12 | 2.12 | 7 | 1.12 | 133.7 | 2.00 | 2.00 |

The experiment sets were designed to investigate the effect of parameters like temperature, carbon/oxygen ratio, steam/carbon ratio and W/F ratio on the activity and selectivity of the bimetallic catalyst in IPOX. During the investigation of steam/carbon ratio some problems associated to coke deposition, which sometimes led to activity loss and eventual blockage of the reactor, were encountered.

### 4.4.2. Effect of Steam/Carbon Ratio

Among all reaction tests, 100 per cent hydrocarbon conversion was obtained only in four sets, namely Sets 1, 3, 8 and 12. A comparison made between Sets 3 & 8 and Sets 1 & 12 separately is shown in Figures 4.10 and 4.11 respectively. Selen (2003) has reported a slightly increased hydrogen production in IPOX of pure propane with an increased steam/carbon ratio. This result is parallel to what had been reported for the IPOX of methane on Ni/alumina and Pt-Ni/δ-$Al_2O_3$ catalysts (Ayabe *et al*, 2003, Ma and Trimm, 1996) and for IPOX of propane (Recupero *et al.*, 2005).

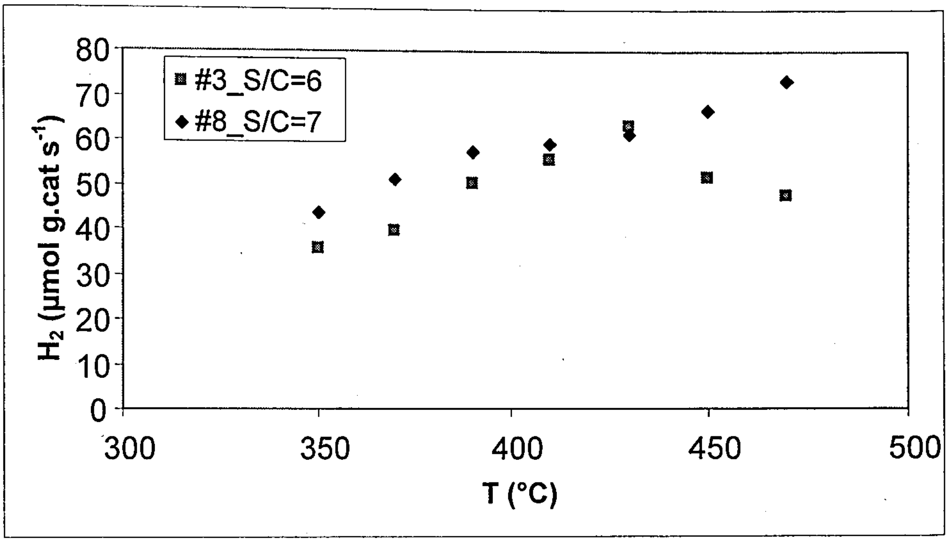

Figure 4.10. The effect of steam/carbon ratio on hydrogen production rate ($C/O_2$=2.12, W/F=1.37)

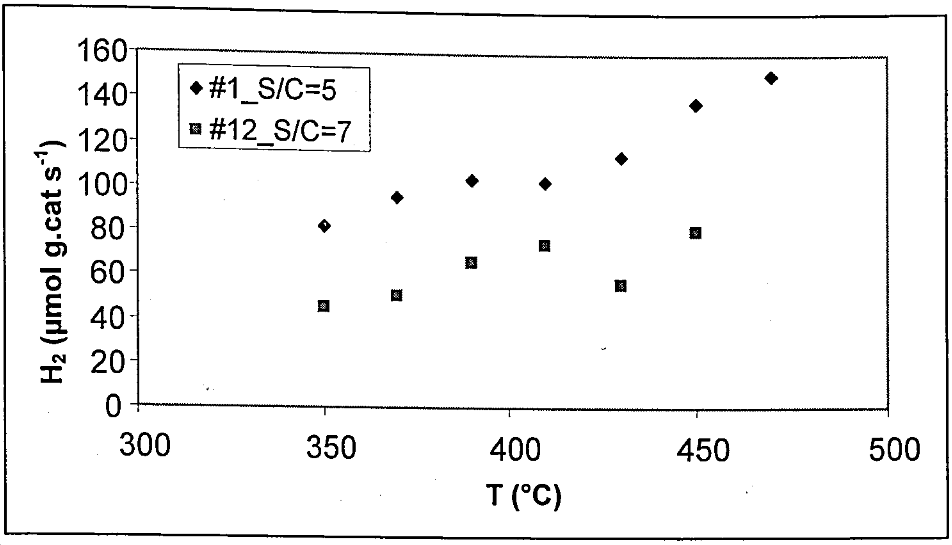

Figure 4.11. The effect of steam/carbon ratio on hydrogen production rate ($C/O_2$=2.12, W/F=1.12)

In Figure 4.10, an increase in hydrogen production is obtained for the higher steam/carbon ratio, which is similar to the results in the literature. However, this situation is reversed for Sets 1 and 12 (Figure 4.11), and the set with the lower steam/carbon ratio gave higher hydrogen production. For both experimental pairs, the sets with lower S/C ratios contained higher amounts of hydrocarbons; therefore, the lower hydrocarbon flowrate in Set 12 compared to Set 1 can not be the reason for lower hydrogen production. An explanation for the deviation from the expected results in Figure 4.11 may be the higher carbon monoxide production in Set 1, which eventually may have led to further hydrogen production through the water-gas shift reaction (Figure 4.12). This trend is also observed in a comparison of Sets 3 and 8, where higher CO production is also accompanied by a greater hydrogen production rate (Figure 4.13).

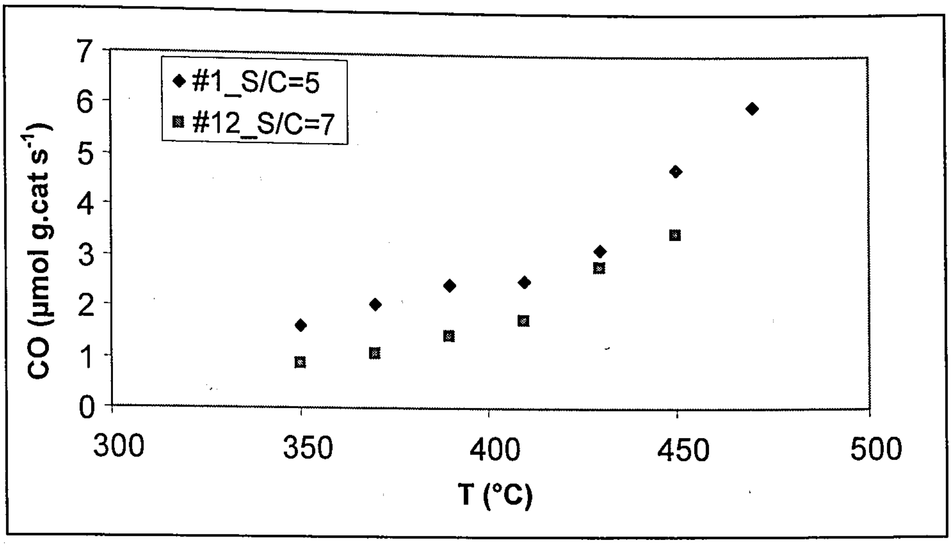

Figure 4.12. The effect of steam/carbon ratio on carbon monoxide production rate ($C/O_2$=2.12, W/F=1.12)

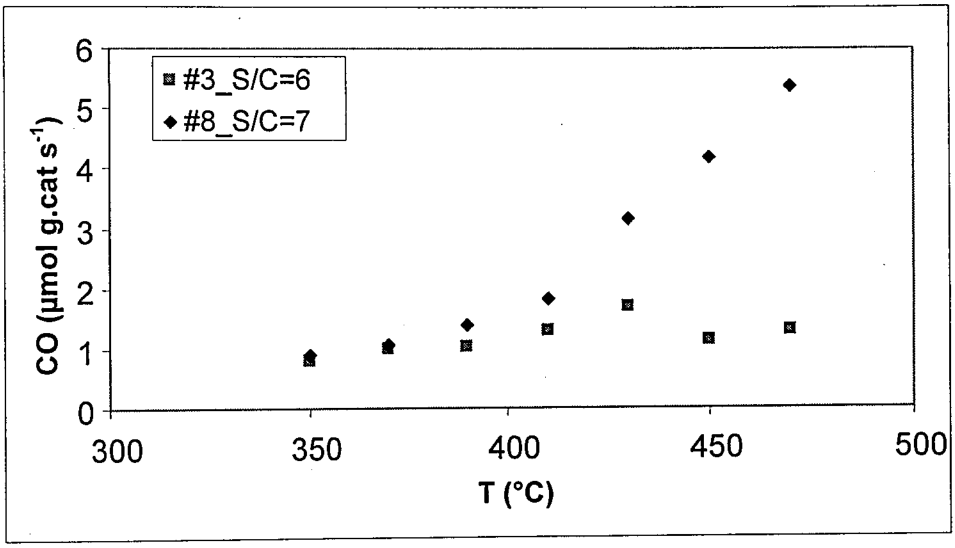

Figure 4.13. The effect of steam/carbon ratio on carbon monoxide production rate ($C/O_2$=2.12, W/F=1.37)

In other pairs of experimental sets with the same W/F and carbon/oxygen ratios, higher steam/carbon ratios have led to higher hydrogen productions (Figures 4.14 and 4.15).

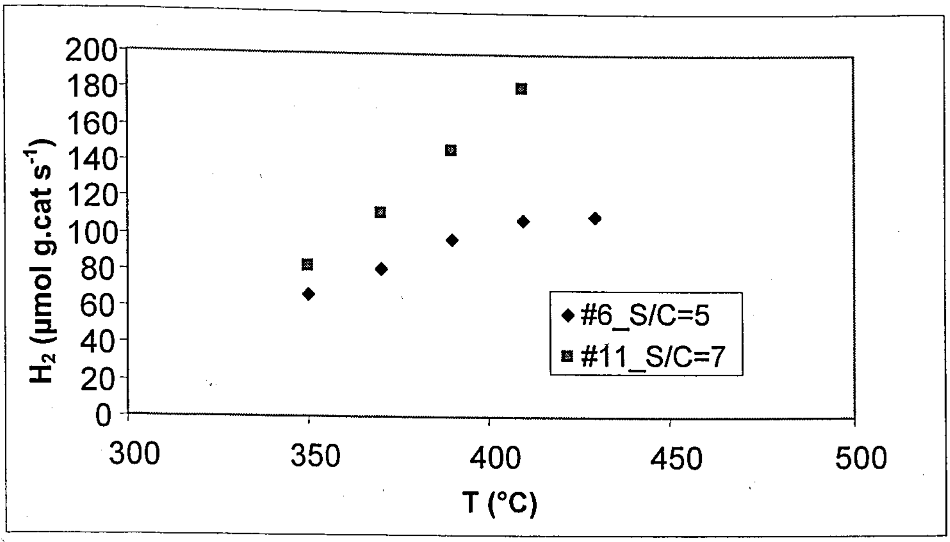

Figure 4.14. The effect of steam/carbon ratio on hydrogen production rate ($C/O_2$=1.50, W/F=0.51)

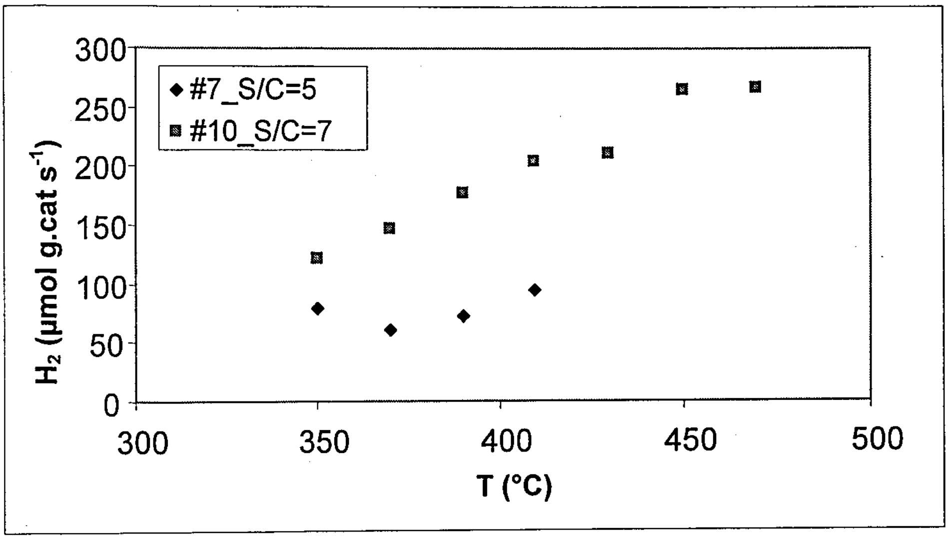

Figure 4.15. The effect of steam/carbon ratio on hydrogen production rate ($C/O_2$=2.70, W/F=0.51)

A very important parameter in hydrogen production processes is the selectivity, especially the $H_2/CO$ ratio in the product stream, which should be as high as possible, since the higher is the $H_2/CO$ production ratio the less will be the necessity for downstream catalytic CO elimination. The $H_2$/CO production ratio increases with an increase in S/C ratio (Figures 4.16 and 4.17).

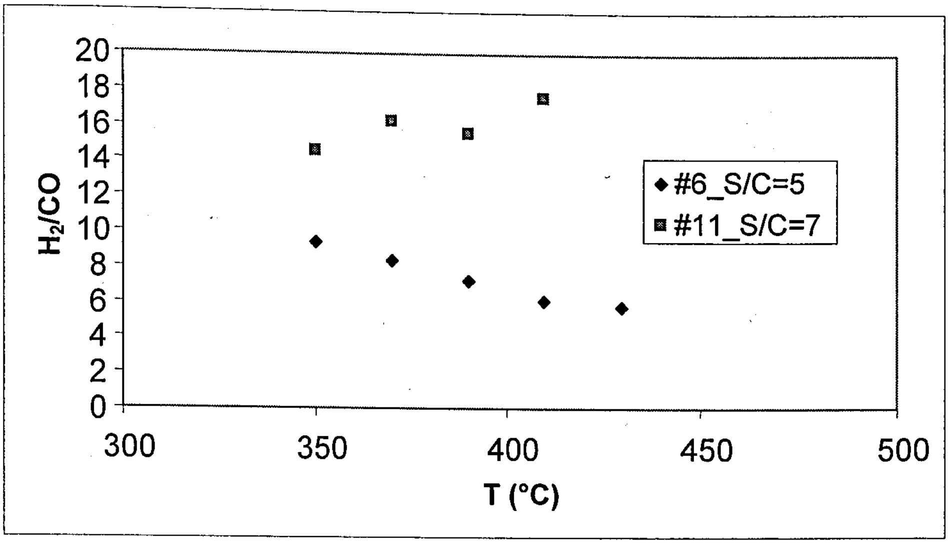

Figure 4.16.The effect of steam/carbon ratio on hydrogen/carbon monoxide ratio ($C/O_2$=1.50, W/F=0.51)

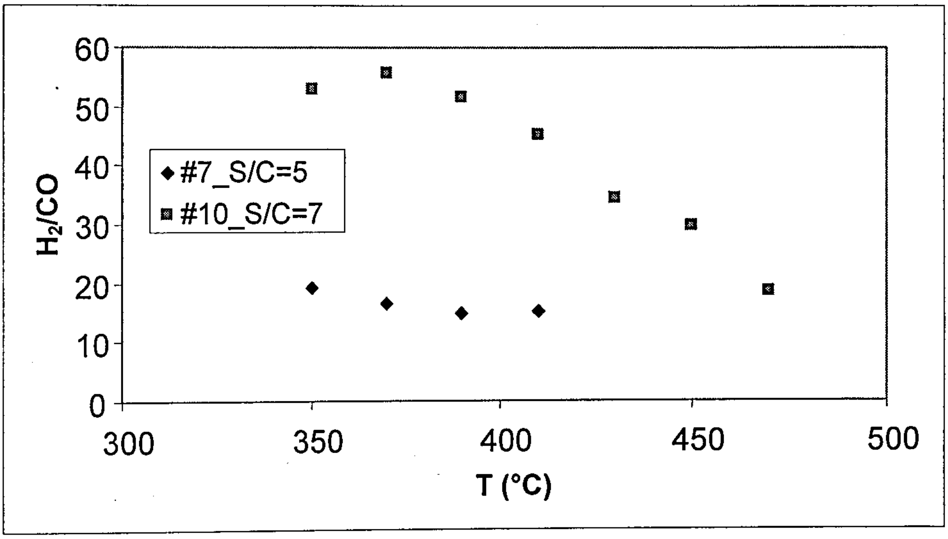

Figure 4.17. The effect of steam/carbon ratio on hydrogen/carbon monoxide ratio ($C/O_2$=2.70, W/F=0.51)

No distinct trend was observed for $CH_4$ production with changing S/C ratios, which indicates the need for further kinetic studies on indirect partial oxidation of LPG.

### 4.4.2. Effect of Residence Time (W/F Ratio)

For fixed steam/carbon and carbon/oxygen ratios, a decrease in the residence time (i.e. an increase in the total flowrate) led to a considerable increase in the hydrogen production, as given in Figures 4.18, 4.19 and 4.20.

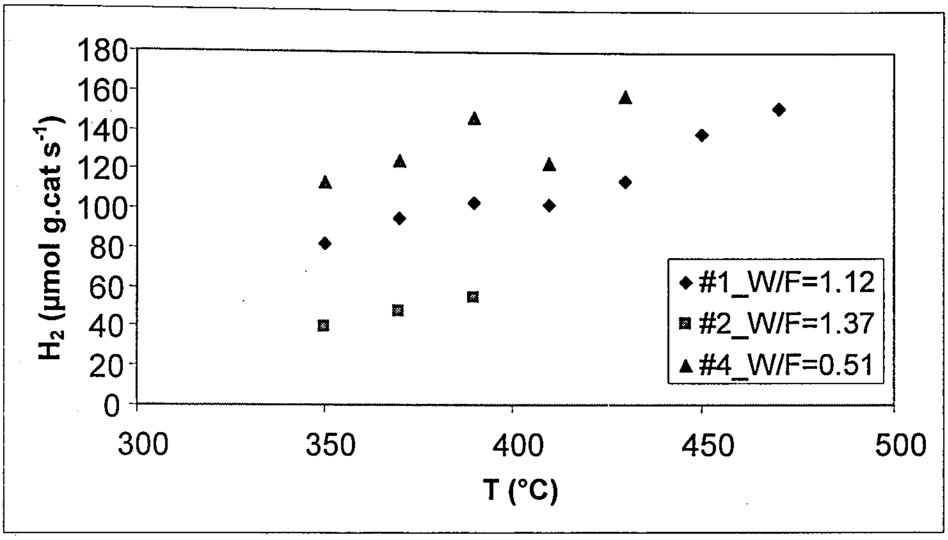

Figure 4.18. The effect of W/F ratio on hydrogen production rate ($C/O_2$=2.12, S/C=5)

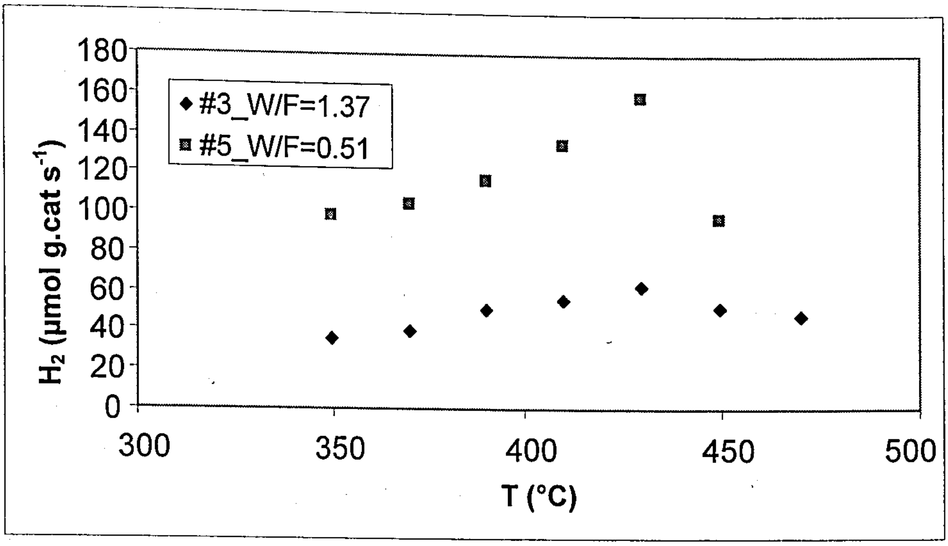

Figure 4.19. The effect of W/F ratio on hydrogen production rate ($C/O_2$=2.12, S/C=6)

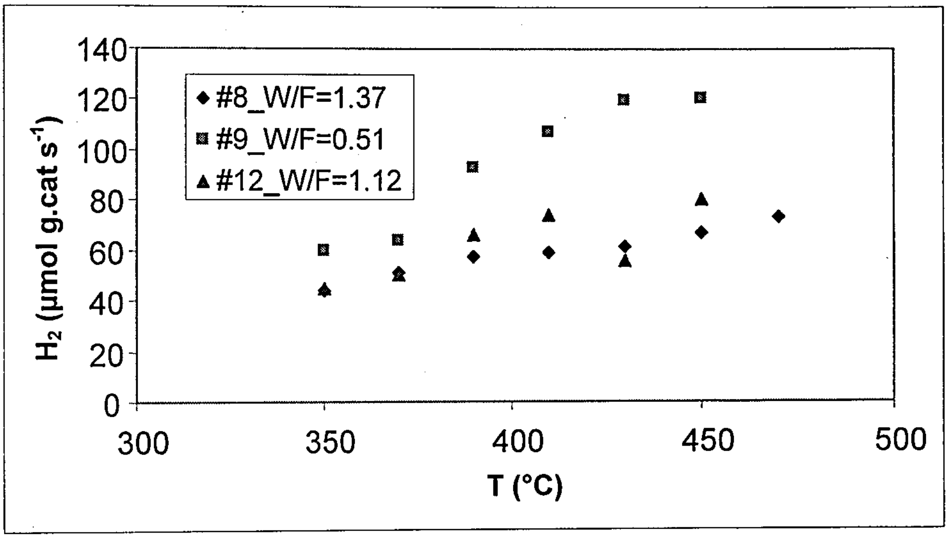

Figure 4.20. The effect of W/F ratio on hydrogen production rate ($C/O_2$=2.12, S/C=7)

The increase in hydrogen production with a decrease in W/F can be explained both by the flow of higher amount of fresh hydrocarbon and the limited residence time of carbon monoxide and hydrogen on the catalyst surface that prevents methanation. The same results have been encountered in previous studies conducted with propane and a propane/*n*-butane mixture as the hydrocarbon feed (Ayabe *et al.*, 2003; Selen, 2003).

The effect of W/F ratio on the hydrogen/carbon monoxide ratio is given below (Figures 4.21, 4.22 and 4.23).

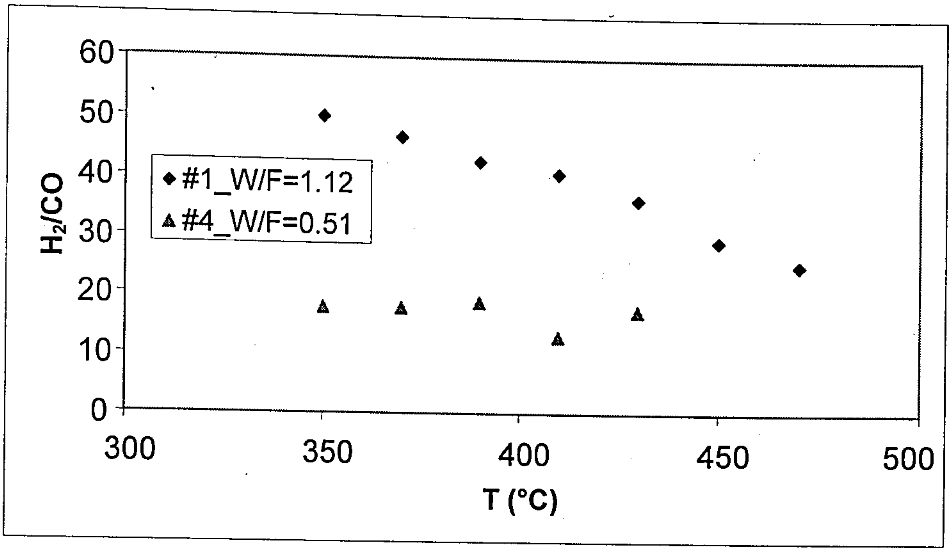

Figure 4.21. The effect of W/F ratio on hydrogen/carbon monoxide ratio (C/$O_2$=2.12, S/C=5)

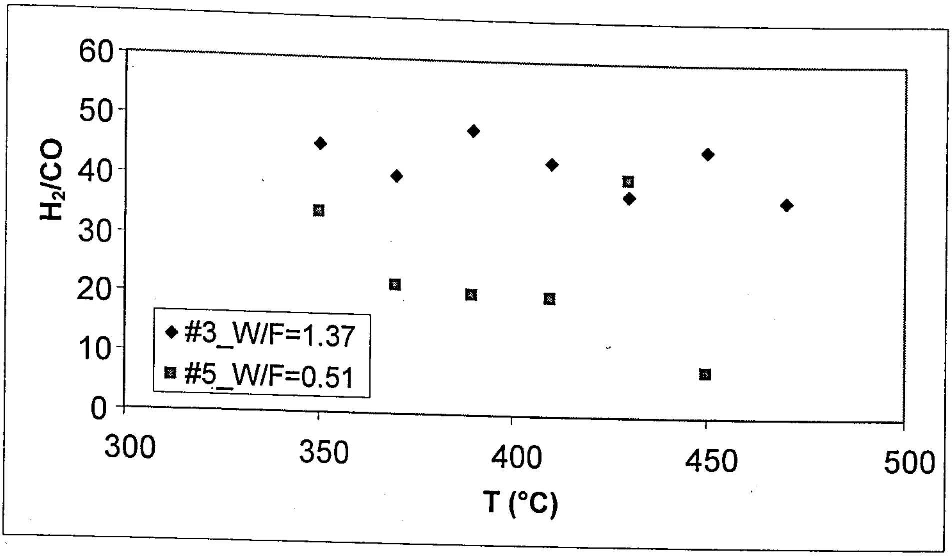

Figure 4.22. The effect of W/F ratio on hydrogen/carbon monoxide ratio ($C/O_2$=2.12, S/C=6)

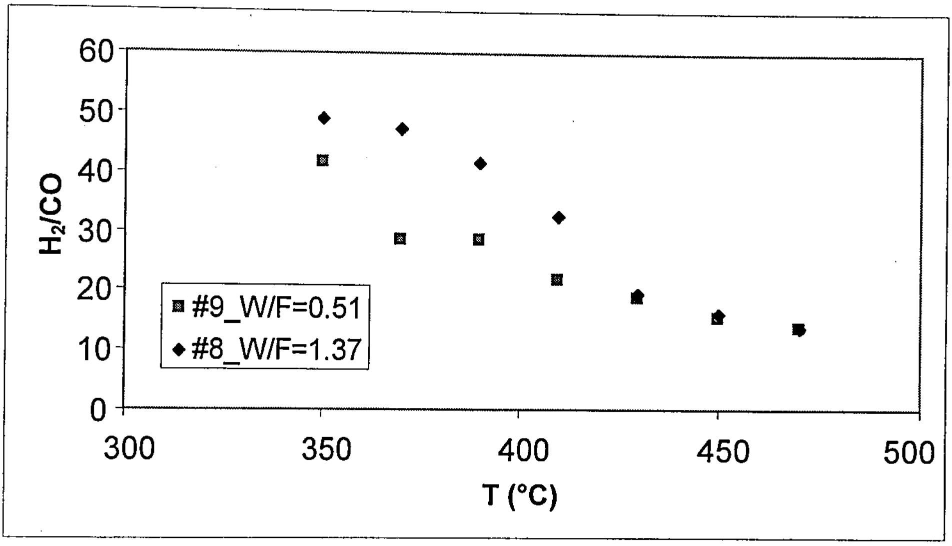

Figure 4.23. The effect of W/F ratio on hydrogen/carbon monoxide ratio ($C/O_2$=2.12, S/C=7)

Higher W/F ratios have generally led to higher hydrogen/carbon monoxide ratios. This can be explained by the presence of platinum in the bimetallic catalyst which has recently been used as a promoter in water-gas shift reaction catalysts (Luengnaruemitchai *et al.*, 2003; Fu *et al.*, 2005; Choung *et al.*, 2005). Higher W/F ratios mean higher residence times and this naturally leads to higher possibility for carbon monoxide to be converted to hydrogen via the water-gas shift reaction on the catalyst. The direct proportionality between the W/F ratio and hydrogen/carbon monoxide was also verified for IPOX of propane by Selen (2003); however, a specific trend could not been inferred for the 75 per cent propane and 25 per cent *n*-butane mixture in the mentioned study.

The direct relation between W/F ratio and methane production rate in Figure 4.24 can be rationalized in a similar manner as explained above for higher hydrogen production rates at lower W/F ratios. Higher total flowrate used in Set 4 has probably prevented the methanation reaction by allowing lower contact time with the catalyst; this is also verified by the higher hydrogen production rate obtained in Set 4 when compared to that of Set 1.

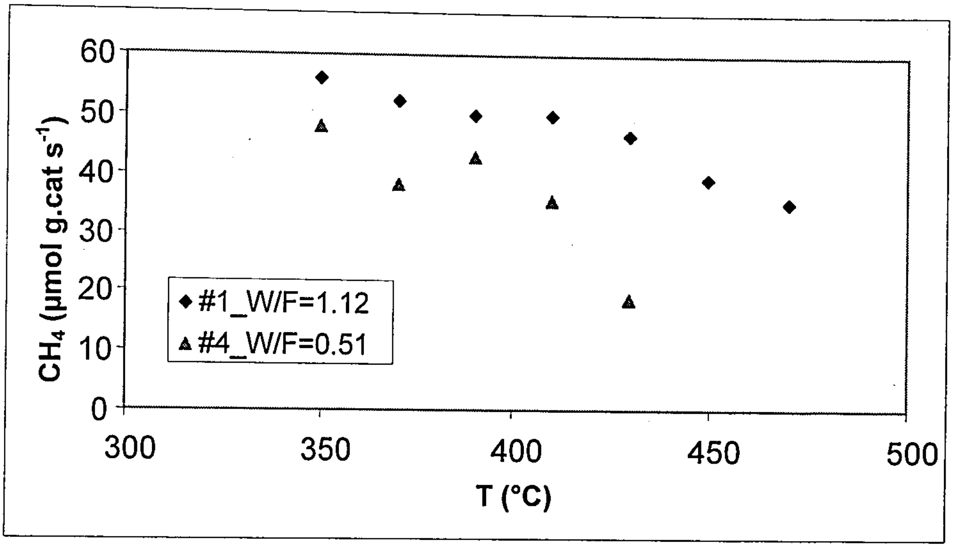

Figure 4.24. The effect of W/F ratio on methane production rate ($C/O_2$=2.12, S/C=5)

This trend is not repeated, however, when the steam/carbon ratio is increased from 5 to 7 (Figure 4.25). This may be explained by either the very close hydrogen production rates of Sets 8 and 12 (Figure 4.20) or the increase in the steam/carbon ratio from 5 to 7 (Figure 4.25). Higher S/C ratio did possibly favor $CO_2$-producing SR (Reaction 2.4) instead of CO-producing SR (Reaction 2.2). Taking the consumption of carbon monoxide during water-gas shift reaction into consideration, the relatively higher amount of carbon dioxide could lead to higher rates of methanation for lower residence times as in the case of Figure 4.25.

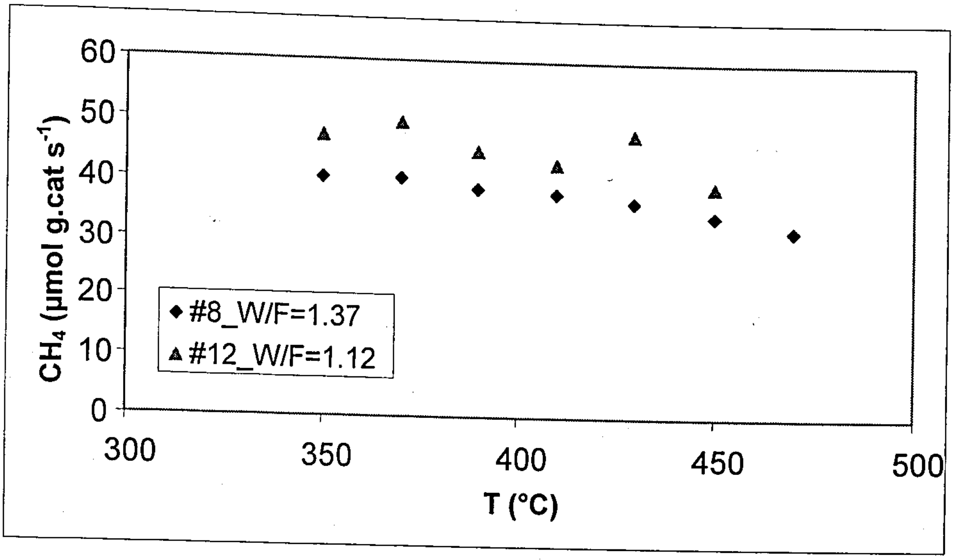

Figure 4.25. The effect of W/F ratio on methane production rate (C/O$_2$=2.12, S/C=7)

### 4.4.3. Effect of Carbon/Oxygen Ratio

An increase in carbon/oxygen ratio has led to a higher hydrogen production rate without formation of coke on the catalyst surface (Figures 4.26 and 4.27). This trend in hydrogen production rate is an expected result as the relative amount of hydrocarbon fuel in the feed stream has been increased when higher carbon/oxygen ratios were applied or respectively lower oxygen is present in the feed that promotes steam reforming at the expense of total oxidation. The direct proportionality of hydrogen production with carbon/oxygen ratio is parallel to the results obtained previously for IPOX of propane (Selen, 2003; and Recupero *et al.*, 2005); but, interestingly, this relationship is in contrast to the IPOX of the 75:25 per cent propane/*n*-butane mixture (Selen, 2003).

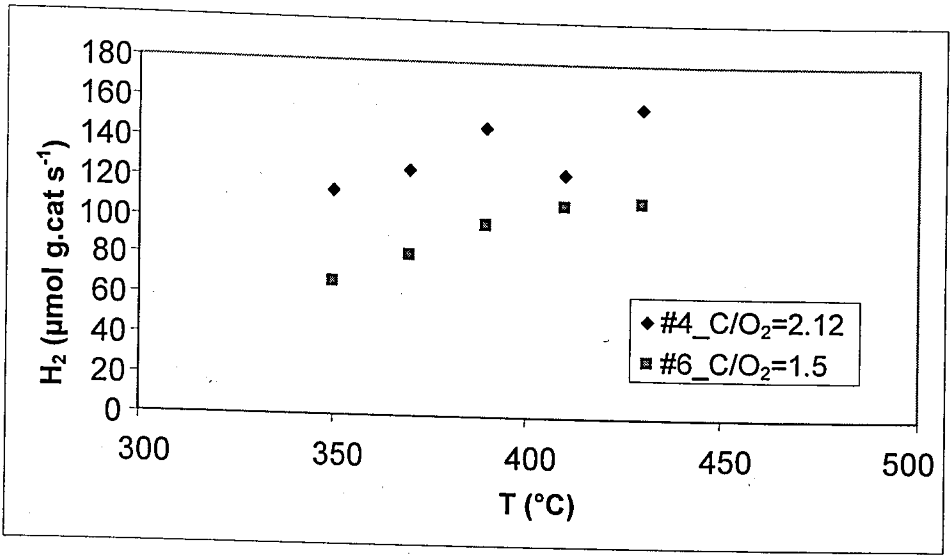

Figure 4.26. The effect of $C/O_2$ ratio on hydrogen production rate (W/F =0.51, S/C=5)

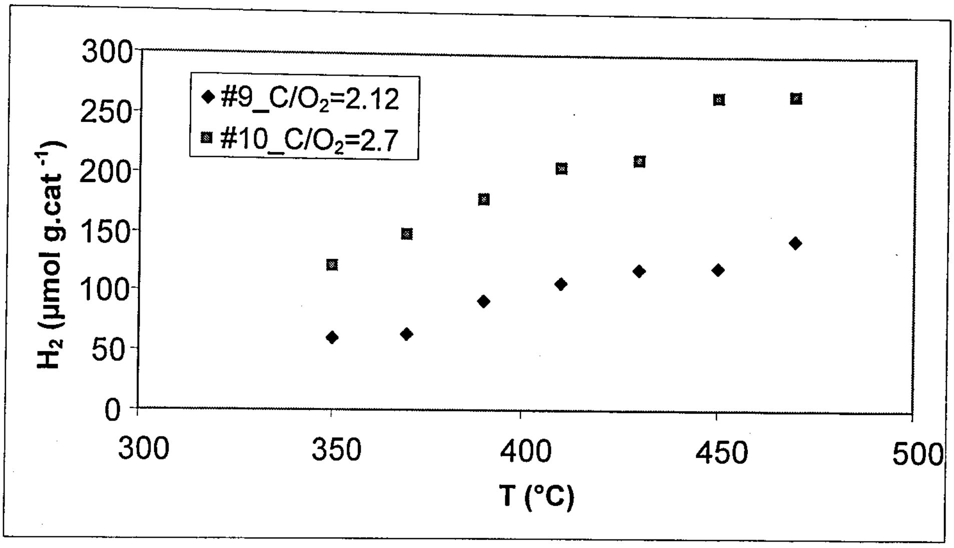

Figure 4.27. The effect of $C/O_2$ ratio on hydrogen production rate (W/F =0.51, S/C=7)

Looking at the methane production rates of the same experiment sets, another expected result would be a decreasing trend in methane production as carbon/oxygen ratios increase, which leads to a higher hydrogen production. This expected outcome was obtained for Set 4 and Set 6 where S/C ratio was equal to five (Figure 4.28). However, the anticipated trend was not observed for Set 9 and Set 10 with an S/C value of 7 (Figure 4.29). The probable explanation is that at the same carbon/oxygen ratios and same residence times, higher steam/carbon ratios favor $CO_2$-producing SR (Reaction 2.4) rather than CO-producing SR (Reaction 2.2), and the greater amount of carbon dioxide promotes methanation (Reaction 2.6).

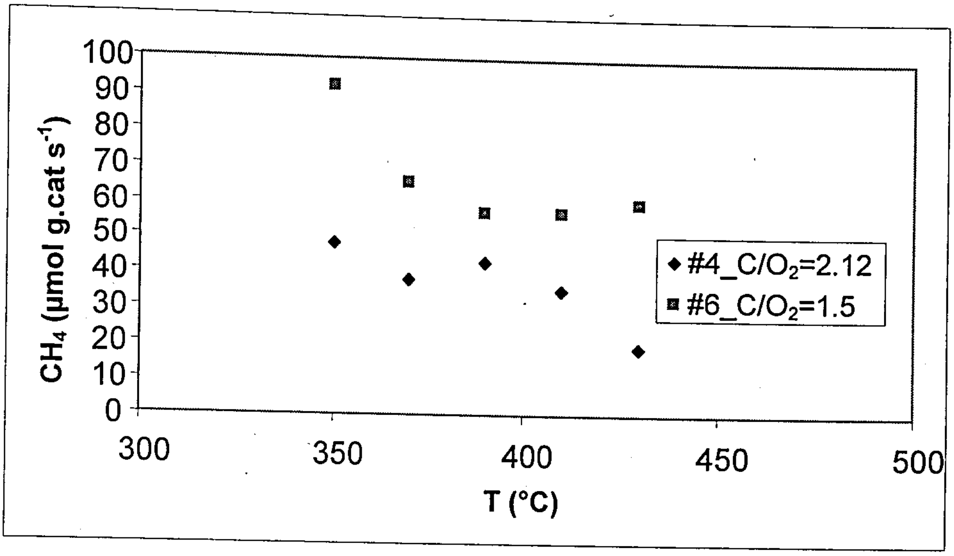

Figure 4.28. The effect of $C/O_2$ ratio on methane production rate (W/F =0.51, S/C=5)

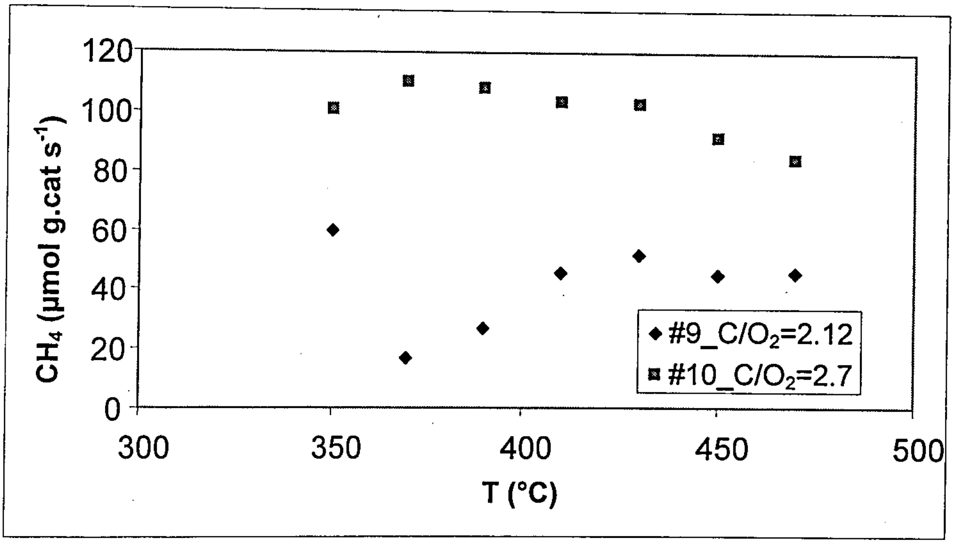

Figure 4.29. The effect of $C/O_2$ ratio on methane production rate (W/F =0.51, S/C=7)

An increase in the carbon/oxygen ratio led to an increase in hydrogen/carbon monoxide production ratio, which can be explained by the higher hydrogen production rates when carbon/oxygen ratio is high (Figures 4.30 and 4.31). This result had been previously proposed and verified in the literature for autothermal reforming of propane (Ayabe *et al.*, 2003; Selen, 2003).

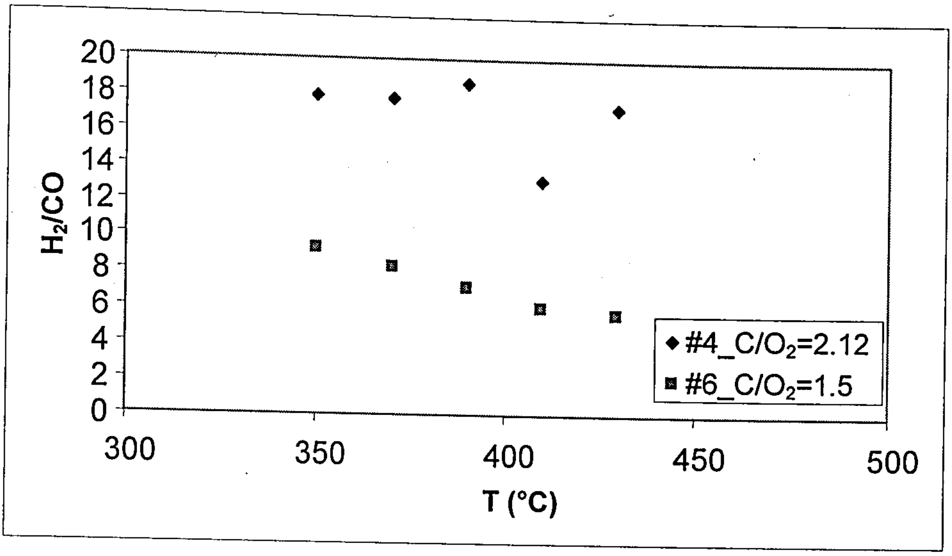

Figure 4.30. The effect of $C/O_2$ ratio on hydrogen/carbon monoxide ratio (W/F =0.51, S/C=5)

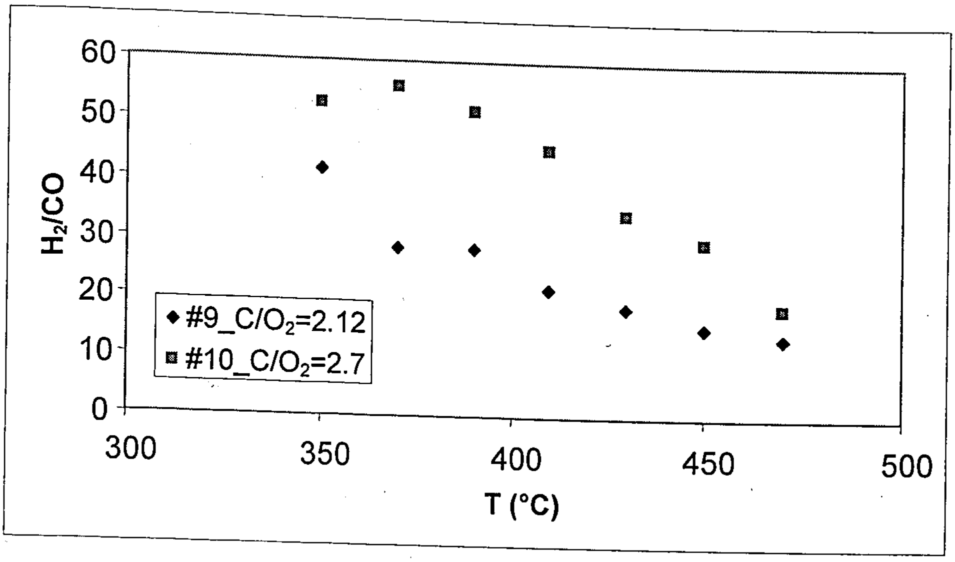

Figure 4.31. The effect of C/O$_2$ ratio on hydrogen/carbon monoxide ratio (W/F =0.51, S/C=7)

### 4.4.3. Summary

The results of the indirect partial oxidation of the 50:50 per cent propane/*n*-butane mixture indicate that hydrogen production rate increases with increasing temperature when no carbon formation occurs on the bimetallic catalyst surface. Hydrogen/carbon monoxide production ratio is the highest at low temperatures and tends to decrease with increasing temperature. In the light of the results discussed in previous sections, the optimum conditions among all the conditions tested are those used in Set 10 corresponding to a steam/carbon ratio of 7, carbon/oxygen ratio of 2.70 and residence W/F ratio of 0.51. The highest hydrogen production activity ($266\,\mu mol\,H_2\,/\,g.cat \times s$) along with a very high hydrogen/carbon monoxide production ratio (56) were obtained for a 50 per cent propane and 50 per cent *n*-butane mixture under these conditions.

A comparison between the performances of fuels in indirect partial oxidation with different *n*-butane contents can be made using the results of the study conducted by Selen (2003) with a 75 per cent propane and 25 per cent *n*-butane mixture. Sets 1, 2, 4, 6 and 7 could be suitable for this purpose, but coke deposited catalysts have congested the mentioned set of experiments except for Set 1. LPG fuel with a propane/*n*-butane ratio of 1:1 seems to be superior to the previously studied ratio, 3:1, considering the hydrogen production rate which is 151 $\mu mol\, H_2 / g.cat \times s$ in the first case and 70 $\mu mol\, H_2 / g.cat \times s$ in the second case; and the hydrogen/carbon monoxide ratios which are 49 and 46 respectively.

# 5. CONCLUSIONS AND RECOMMENDATIONS

## 5.1. Conclusions

This experimental work is conducted in order to (i) determine the power law type kinetics of ethanol steam reforming and (ii) investigate the indirect partial oxidation of 50 per cent propane and 50 per cent *n*-butane mixture over the 0.2wt%Pt-15wt%Ni/δ-$Al_2O_3$ catalyst. The parameters considered were temperature, steam/carbon ratio, carbon/oxygen ratio and residence time.

### 5.1.1. Kinetic Study of Ethanol Steam Reforming

The conclusions drawn for the ethanol steam reforming are:

- The reaction orders with respect to ethanol and steam were determined to be 1.18 and -0.18 respectively indicating a promotion effect of ethanol which is close to unity and a small inhibition effect of steam in ethanol steam reforming reaction.
- The activation energy of ethanol steam reforming was found to be 39.3 kJ $mol^{-1}$ in a temperature range of 400-450°C, about a half of the activation energy of *n*-butane steam reforming over the same catalyst.

### 5.1.2. Indirect Partial Oxidation of LPG

The conclusions drawn for the IPOX of a propane/*n*-butane mixture are:

- Higher steam/carbon ratios resulted in greater hydrogen production rates with only one exception.
- A decrease in the residence time (i.e. an increase in the total flowrate) led to a considerable increase in the hydrogen production.
- High W/F ratios promoted the production of methane due to the higher probability of methanation reaction on the catalyst surface at a steam/carbon ratio of 5. However, at a

steam/carbon ratio of 7, higher methane production rate was observed for lower residence times mostly because of the promotion of $CO_2$-producing SR.

- When there is no coke formation n the catalyst surface, higher carbon/oxygen ratios gave rise in hydrogen production rate as the relative amount of hydrocarbon fuel in the feed stream has been increased when higher carbon/oxygen ratios were applied.
- Methane production rate tended to decrease with an increase in carbon/oxygen ratio at a steam/carbon ratio of 5 because of the increase in hydrogen production. This trend is reversed at high steam/carbon ratios due to the domination of $CO_2$-producing SR.
- Hydrogen/carbon monoxide ratio i.e. selectivity to hydrogen, was found to increase with increasing steam/carbon ratio, carbon/oxygen ratio and $W/F_{Total}$.
- Optimum conditions for IPOX of propane/*n*-butane were found as steam/carbon ratio of 7, carbon/oxygen ratio of 2.7 and W/F ratio of 0.51 for the parameter ranges tested.
- A comparison between the performances of fuels in indirect partial oxidation with different *n*-butane contents revealed that increasing the n-butane percentage in the fuel enhances the activity and the selectivity of the process considerably with a trade-off of more possibility of carbon deposition on the catalyst surface.

## 5.2. Recommendations

Under the light of the results of the present work, the following studies are recommended:

- Langmuir-Hinshelwood Hougen-Watson type kinetic studies should be performed on ethanol steam reforming reaction.
- A series of indirect partial oxidation experiments should be performed for *n*-butane for the same conditions (i.e. sets with the same $C/O_2$ and W/F ratios) and be compared with those obtained from the tests for which propane/*n*-butane mixture used as the feed aiming to understand the effect of the changes in C/H ratio in the hydrocarbon feed on the IPOX performance of the bimetallic catalyst used.
- Studies about the prevention of catalyst deactivation due to the filamentous carbon growth in the reactor should be conducted for the bimetallic Pt-Ni/$\delta$-$Al_2O_3$ catalyst in order to increase the applicability of the process in fuel cell processors.

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