

YSZ-CERIA FOR CHEMICAL LOOPING SYNGAS PRODUCTION

by

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ABSTRACT

The increase of carbon footprint over the years is a serious cause of concern for mankind in recent times. As a consequence, carbon capture and sequestration has been given unprecedented focus. Chemical looping combustion (CLC) is one of the novel methods of carbon capture. A rotary reactor developed recently for CLC has been discussed extensively. The applicability of the chemical looping process in syngas production has been studied in this experiment. Ceria is used as the oxygen carrier material and YSZ (Yttria-Stabilized Zirconia) as the support material.

Gas productions at different temperatures are studied to have a generic understanding of the reactions at different temperatures. Chemical looping reaction is observed to be a good method for syngas production, involving lesser steps than most conventional methods. Ceria is found to be a good oxygen carrier material. It is further noted that the quantity of syngas produced is higher as reactions are carried out at higher temperatures. Syngas produced using the chemical looping process allows for direct capture and sequestration of CO₂, making the process in turn carbon neutral, sustainable and environment friendly.

LIST OF ABBREVIATIONS AND SYMBOLS

AR	Air Reactor
ASU	Air Separation Unit
CAD	Computer Aided Design
CCS	Carbon Capture and Sequestration
CFD	Computer Aided Design
CLC	Chemical Looping Combustion
DAQ	Data Acquisition
LCF	Lanthanum Calcium Iron Oxide
FR	Fuel Reactor
GCMS	Gas Chromatography and Mass Spectrometer
GHG	Green House Gas
GUI	Graphical User Interface
ITM	Ion Transport Membrane
MFC	Mass Flow Controller
MS	Mass Spectrometer
NI	National Instruments
OC	Oxygen Carrier

PPM	Parts Per Million
RGD	Reacting Gas Dynamics
SEM	Scanning Electron Microscope
CO	Carbon Monoxide
CO ₂	Carbon Dioxide
CH ₄	Methane
Ar	Argon
d _p	Particle Size
d _{sphere}	Diameter of spherical particles
E _a	Activation energy
k	Reaction Constant
YSZ	Yttria Stabilized Zirconia
m _{oc}	Mass of oxygen carrier
m _{supportmatrl}	Mass of support material
P	Pressure
T	Temperature
R _e	Reynolds number
R	Universal gas constant
t	Time

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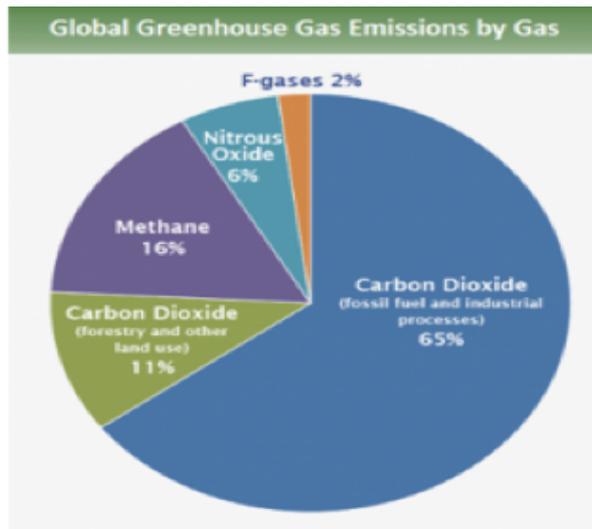
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CHAPTER 1: INTRODUCTION

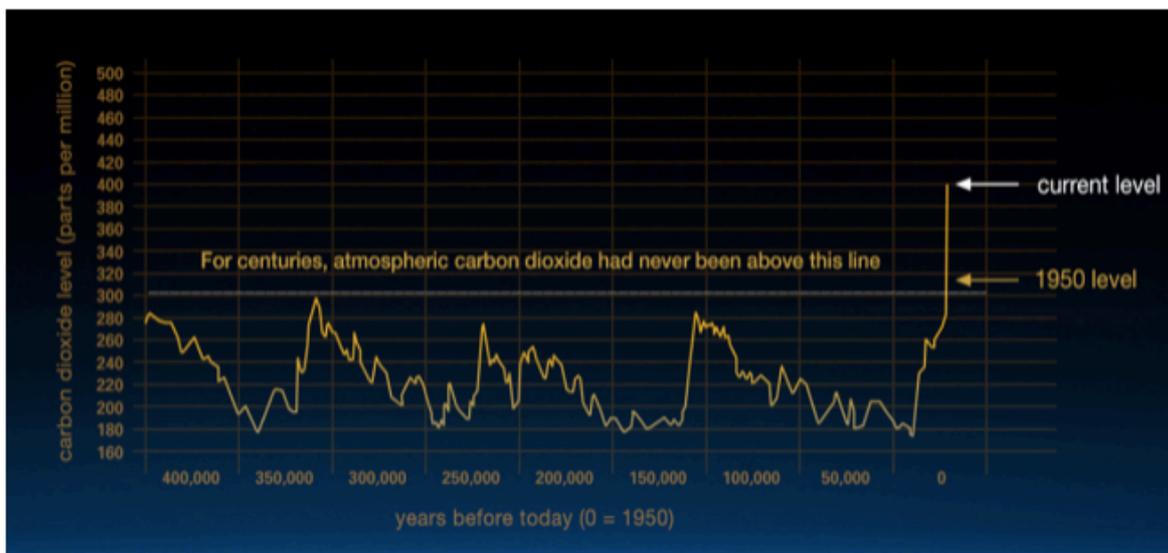
Fossil fuels have provided for more than 80% of total U.S. energy consumption for more than 100 years. In 2015, fossil fuels had a share of 81.5% in the total U.S energy consumption according to the US Energy Information Administration (EIA)- Annual Energy Outlook 2016. Although 2015 also saw the highest share of renewables at 10%, it is needless to state that our overdependence on fossil fuels is still to continue for years.

Easy availability, high calorific value and low cost might have made people turn to fossil fuels as the energy of choice, however, it has over years resulted in emission of harmful gases- in particular carbon dioxide at levels unforeseen before. With global warming being an increasing cause of concern, our attention has focused on greenhouse gases, which are the principle cause of it. The United States Environmental Protection Agency (EPA) estimated that in 2014 carbon dioxide had a share of 81% among all greenhouse gases that result in global warming. It has now been scientifically proven that human beings contribute to global warming. Among the different economic sectors, industry contributes above 20% in the greenhouse gas emissions. [1] The Carbon Dioxide levels are the highest in 650000 years with the present value at 405 ppm [2]



Source: Intergovernmental Panel on Climate Change (IPCC 2014)

Figure 1: Global greenhouse gas emissions by gas (2014)



Source: NASA

Figure 2: Change in CO₂ levels over the years

Studies have suggested that industrialization and human activities have increased the emission of carbon dioxide, which in turn over years has resulted in global surface temperatures to be higher by 1.1°C since the late 19th century. [2]

This has resulted in rise in sea levels, warming of oceans, shrinking of ice sheets and glacial retreat and also rise in frequency of extreme weather patterns like cyclones and tornadoes. [3]As this poses a serious threat to our planet and the human existence, more focus has been placed recently on renewables and turning to cleaner and greener forms of energy. Different methods have also been developed to capture carbon dioxide and prevent its emission to the environment in the first place. The warming that now is inevitable cannot be stopped completely, but it can be stopped before it becomes catastrophic. In and around areas of the Antarctic, sections of ice provide evidence that there is a 4-6metres of ocean level rise. [2] The Pentagon of the United States has declared this to be a national security issue and not just an environmental issue. The recent Paris Climate Agreement, where 195 countries (signatories) came together unanimously to mitigate the release of greenhouse gases (Holding the increase in the global average temperature to well below 2 °C above pre-industrial levels) sets a much needed architecture in place to hold countries accountable for not doing their fair share.

1.1 Carbon capture and sequestration

Carbon capture and sequestration refers to the process of removing carbon from a point source and depositing it in a reservoir; hence preventing its release to the atmosphere. There are essentially three methods of carbon capture and sequestration-

Post Combustion Capture

CO₂ separated from the mixture of flue gases created after combustion. However, since CO₂ is diluted by other gases, the efficiency typically isn't high. This process incurs energy penalty for CO₂ separation.

Pre Combustion Capture

Fuel is reacted with air to create a synthesis gas consisting of carbon monoxide and hydrogen. The carbon monoxide is then oxidized to get CO₂. Also incurs energy penalty for CO₂ separation

Oxy-fuel combustion

Fuel is reacted with pure oxygen to create CO₂ and water as combustion products. Water is then condensed to get a pure stream of CO₂.

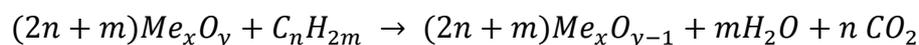
The advantages of this process over the others are:

- Eliminates the energy penalty for CO₂ separation
- High overall efficiency
- Eliminates harmful NO_x emission

1.2 Chemical Looping Combustion

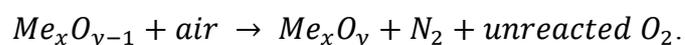
Chemical Looping Combustion is a novel method in which oxygen is physically transported to help in a REDOX reaction. Metal oxides, termed as oxygen carriers (OC) are oxidized and reduced to help in oxygen separation by absorption and desorption.

Mechanism- There are two reactors, the Air reactor and the Fuel reactor. The cycle starts in the Fuel reactor where the OC reacts with the gaseous fuel. [4]



The reaction products are mainly carbon dioxide and water, from which CO₂ can be easily captured and sequestered by condensing the water.

Afterwards, the reduced OC is then put in the Air reactor and after reaction gets regenerated for the next cycle.



CO, H₂

Combustion Products (CO₂, H₂O)

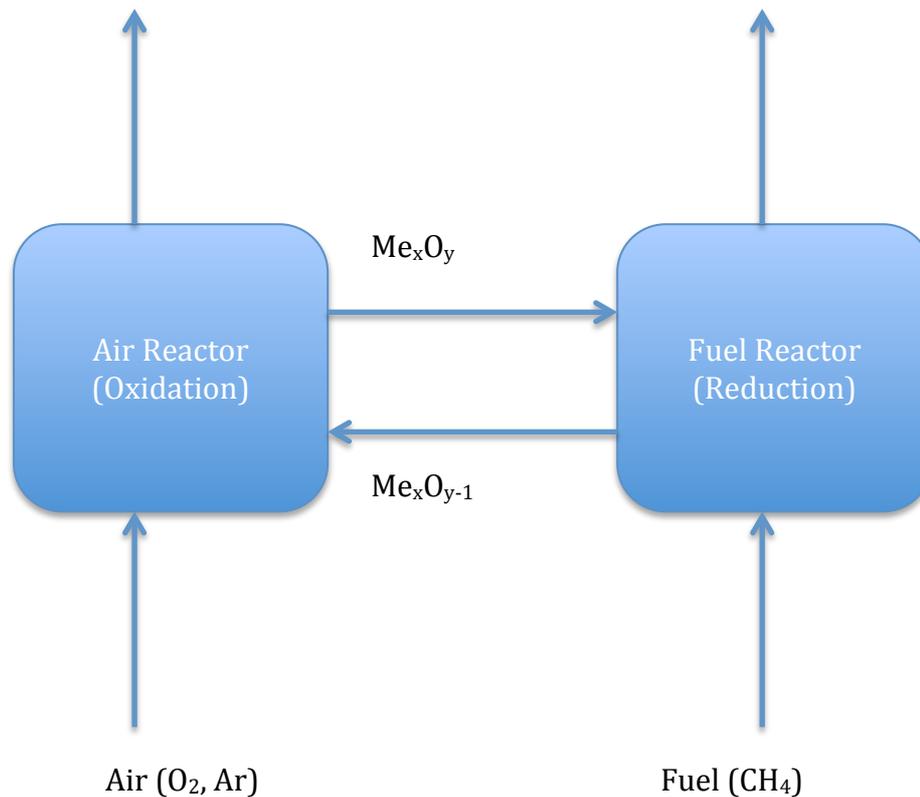


Figure 3: Schematic diagram of the Chemical Looping Combustion (CLC) process

1.3 Syngas Production

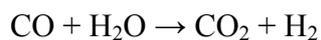
Along with the sequestration of carbon dioxide, SYNGAS, also known as synthesis gas, which is a mixture of CO and H₂, is also produced during this experiment that also acts as a source of energy and can be utilized. The typical uses of syngas are that it is used as a fuel source; used as an intermediate in creating synthetic petroleum and generating natural gas; used for preparing methanol and ammonia. Being a renewable source of energy, syngas is used for electricity generation with almost zero carbon emissions.

Syngas Production Methods

There are essentially four major methods for syngas production: Partial Oxidation (POX), Steam Methane Reforming (SMR), Dry Reforming and Autothermal Reforming.

Partial Oxidation (POX)

Sub-stoichiometric mixture of feedstock and pure oxygen are reacted together. [5] This produces syngas with high H₂ concentrations. The feedstock is fed into POX reactor. Carbon of feedstock reacts with oxygen to form CO. There is a lack of oxygen in the reaction, therefore no formation of CO₂. This reaction is exothermic in nature. Afterwards, CO goes to the water shift reactor where CO reacts with steam forming CO₂ and H₂. H₂/CO ratio is 1.6-1.7



There are two sub-categories of this method

Thermal POX

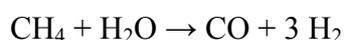
In thermal POX, temperatures higher than 2200°F is required. In this process, high sulphur feedstocks are used.

Catalytic POX

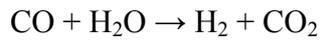
In Catalytic POX, temperature range of 1475-1650°F is required. In this process, low sulphur feedstocks are used.

Steam Methane Reforming (SMR)

Heated mixture of natural gas and steam flows through pipes filled with nickel based catalyst. Natural gas is used as the feedstock to produce syngas with high H₂ concentrations. Reactions occur at 1,470 - 1,740 °F. This reaction is endothermic. External heat is required to be supplied. Reforming takes place in two reactors in series. [5]



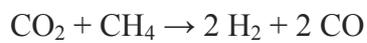
Afterwards, syngas flows to the water shift reactor.



H₂/CO ratio 3:1

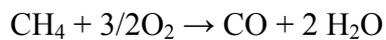
Dry Reforming

Dry reforming is also known as carbon dioxide reforming. Carbon dioxide and hydrocarbons like methane react together to form synthesis gas. This method is given more precedence in recent years over steam reforming due to the issue of global warming. The reaction mechanism is-



Autothermal Reforming

This process combines the thermal POX and low-sulphur natural gas reforming processes in a single reactor. [5] Natural gas is partially oxidized with O₂ in the reactor to produce syngas. The H₂/CO ratio in this reaction is typically 2:1



	Partial Oxidation (POX)	Steam Methane Reforming (SMR)	Dry Reforming	Autothermal Reforming
Reaction Steps	$C + \frac{1}{2} O_2 \rightarrow CO$ $CO + H_2O \rightarrow CO_2 + H_2$	$CH_4 + H_2O \rightarrow CO + 3 H_2$ $CO + H_2O \rightarrow H_2 + CO_2$	$CO_2 + CH_4 \rightarrow 2 H_2 + 2 CO$	$CH_4 + 3/2 O_2 \rightarrow CO + 2 H_2O$
Temp. Range	Thermal POX: >2200°F Catalytic POX: 1475-1650°F	1,470 - 1,740 °F		
H ₂ /CO Ratio	1.6-1.7	3:1		2:1

Table 1: Comparison of the different syngas production methods

Chemical Looping Syngas Production

Along with these well-established methods, the process of chemical looping combustion will be studied in this experiment as an alternative for preparing syngas.

The Chemical looping process allows for direct capture and sequestration of CO₂ as stated before, which therefore makes the process carbon neutral. This process will be studied in more detail over the course of the experiments.

Furthermore, this process can be applied to a wide range of carbonaceous fuels, making it a versatile process and the hydrogen produced via this method is shown to be 99.97% pure, which makes it suitable for different applications like the Fischer-Tropsch synthesis. [6]

1.4 Types of Reactor Designs

1. Inter-connected fluidized bed reactor
2. Moving bed reactor

3. Packed bed reactor
4. Horizontal rotating reactor
5. Packed bed reactor

Fluidized bed Reactor

In the fluidized bed reactor set-up, oxidation and reduction reactors are separate and the OC particles are circulated between the two in the form of a continuous cycle. The demerits of this type of reactors are large pressure drops, operation challenges at high pressure and temperature, agglomeration and attrition, and lower efficiency. [4]

Fixed Packed Bed Reactor

In this reactor set-up, air stream and fuel streams are switched in tandem to start the oxidation and reduction phases. This design although compact and easy to operate, the large temperature fluctuations is the major downside.

Rotating Packed Bed Reactor

The reactor set-up consists of a packed bed containing OC particles which rotates as air and fuel streams are let in. [4] This design allows for improved gas-solid contact and reduces the cost of circulation. The major demerit of this design is the gas leakage over course of the rotational motion.

CHAPTER 2: OXYGEN CARRIER SELECTION

The selection of suitable oxygen carrier material is one of the most crucial aspects in conducting the Chemical Looping Reaction. The major characteristics that are looked into before selecting an oxygen carrier material are:

- Fuel conversion rate
- Oxygen transport capacity
- Reactivity
- Stability
- Good attrition resistance
- Low carbon deposition

Fuel conversion rate

At the operating temperature and pressure selected, high H₂O and CO₂ content is expected when the material is a good oxygen carrier.

Oxygen transport capacity

The ability of the oxygen carrier material to transport oxygen to and from the metal oxide is extremely important. A material with a higher oxygen transport capacity would enhance the reaction rate, and is thus desired.

Reactivity

Oxygen carrier materials which increase the redox reactions are desirable as higher reaction result in smaller overall reactor size.

Particle Size

Particle size plays a crucial role in the reaction rate. Smaller spherical sized particles help in the better circulation of the OC material.

Stability

As the OC material will be used in the looping reaction, a material with strong structural stability which would not wear off over time is desired.

Attrition resistance

The OC material should be resistant to attrition, which is the wearing off of the material with repeated use.

Carbon deposition

Carbon deposition during the oxidation phase is something that causes problems, and an OC which avoids this is preferred for the experiments.

2.1 Research Objective

The objective of this research is to test the validity of production of syngas using chemical looping combustion process with Ceria as the oxygen carrier and YSZ as the support material. Redox cycles are performed at different temperatures. The production of different gases is observed to draw a parallel between the reaction temperature and the reaction rate. The experiments finally would help to answer the following questions-

- Is chemical looping is suitable mechanism for syngas production over a range of temperatures?
- Can ceria be counted as a good oxygen carrier material?
- Is there a pattern noticeable in the gas productions over redox cycles at different temperatures?

CHAPTER 3: METHODOLOGY

3.1 Rotary Bed Reactor

Design

Although this experiment does not directly make use of the rotary bed reactor, it is worth mentioning about the rotary reactor design developed recently in the Reacting Gas Dynamics Lab at Massachusetts Institute of Technology (MIT), which would serve as the reactor of choice for future CLC experiments at the University of Alabama.

In this reactor, there is a central rotating wheel supported by two stationary gas chambers on top and bottom. Pressurized air and fuel gases are fed from the bottom and taken out from the top after redox reaction. Insulating the reactor reduces thermal energy losses. The rotary bed consists of peroxide OC support materials packed in the form of discs. The support layer has a porous top layer coated with an OC material. The feed gas chamber consists of four sections- fuel, air and two purges. Air is used during the purge cycles to remove residual air and fuel from mixing. [7]

Working Mechanism

During the operation, the channel first enters the fuel sector where the reduction reaction is initiated. Afterwards, the combustion gases leave the fuel zone and purging is initiated. This then is followed by the channels entering the air sector and initiating the oxidation reaction, where the OC is regenerated. [8]

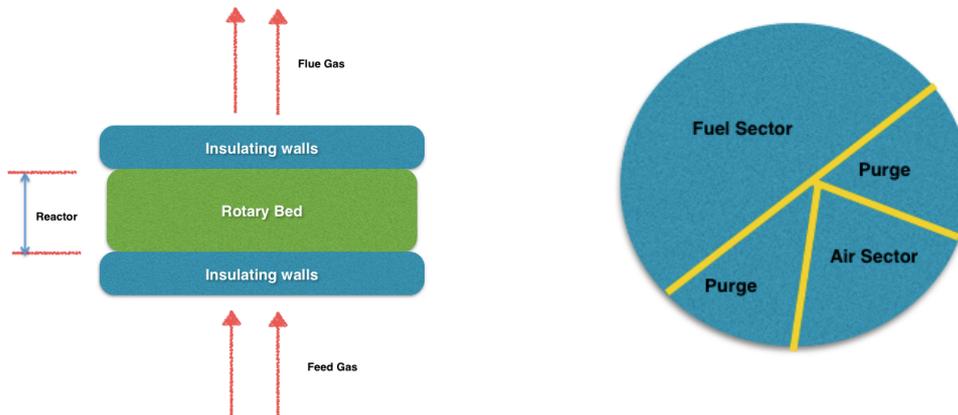


Figure 4: Schematic diagram of rotary CLC system (a) front view, (b) bottom view

Advantages and disadvantages of the rotary reactor design-

Advantages

- Separation of air and fuel streams
- Compactness
- Ability to scale up in the future

Drawbacks

- Temperature fluctuation
- Carbon deposition

It has been proven that both the fuel conversion efficiency and the carbon separation efficiency is close to unity for this type of reactor. [7] One past experiment with rotary reactor with copper oxide as the oxygen carrier concluded that fuel conversion occurs continuously from the inlet to the end of the reactor, while in the air sector, OCs are rapidly regenerated, consuming a large amount of oxygen from the air. A total of 99.9% of the fuel is converted within 75% of the channel. [9]

Laboratory requirements for our experiment

- Mass Flow Controller
- MAX300-LG Mass Spectrometer
- Reactor
- Sentro ST-1700C-445 High Temperature Box Furnace
- ATS 3210 Furnace
- Gas cylinders

The laboratory equipment listed above will be studied in more detail over the chapters.

Why Ceria?

In the recent past, some experiments on CLC with Ceria as the OC were carried out and some specific traits were observed which are listed below, because of which for the purpose of our experiment, Ceria was chosen [8]

- Fast surface kinetics of Ceria leads to higher H₂ production during its use as an OC
- High oxygen ion diffusivity
- Large oxygen carrying capacity
- Structural stability
- Large nonstoichiometric capacity allows it to effectively adsorb and desorb oxygen at different operating conditions

3.2 Support Material Preparation

There were two support materials which were there in our lab for the experiments. The first is LCF powder (Lanthanum Calcium Iron Oxide) and the other is YSZ powder (Yttria Stabilized Zirconia). Preparation of support material using both the compounds are described below.

Preparing LCF powder (LaO.9Ca0.1FeO₃)

Requirements

1. Lanthanum 3 nitrate hezahydrate $La(NO_3)_3 \cdot 6 H_2O$
2. Calcium nitrate tetrahydrate $Ca(NO_3)_2 \cdot 4 H_2O$
3. Iron 3 nitrate nonahydrate $Fe(NO_3)_3 \cdot 9 H_2O$
4. Citric acid $C_6H_8O_7$

Mass of each component required for making the LCF mixture-

	La(NO ₃) ₃ ·6 H ₂ O	Ca(NO ₃) ₂ ·4 H ₂ O	Fe(NO ₃) ₃ ·9 H ₂ O	C ₆ H ₈ O ₇
Molecular Mass (g)	433.01	236.15	404	192.12
Mole	0.0117	0.0013	0.013	0.0143
Mass (g)	5.066217	0.306995	5.252	2.747316

Table 2: Chemical compounds and their properties for preparing LCF mixture

Total mass of LCF powder = 5.066217+0.306995+5.252+2.747316 = 13.37253g

After preparation of the LCF powder, about 15ml of ethylene glycol was added per 3g of final LCF powder mass. This was done to keep the structural integrity of the powder to make sure the components do not stick to each other. All materials were weighed and taken as per the proportion required. Afterwards, all materials were mixed together in distilled water and taken in a beaker. The beaker was put on the stirrer machine and the stirring process was allowed for 1 day.

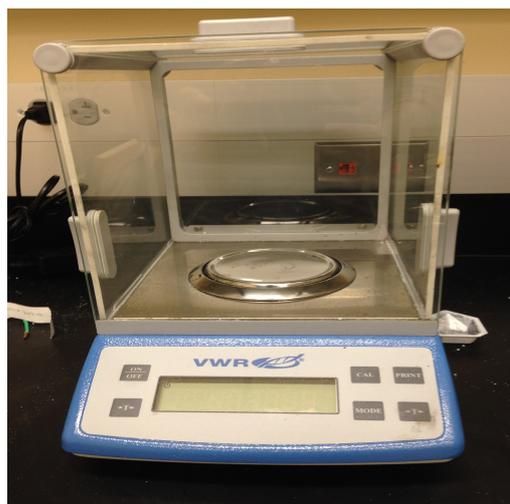


Figure 5: Weighing balance for taking appropriate quantities of different chemical compounds

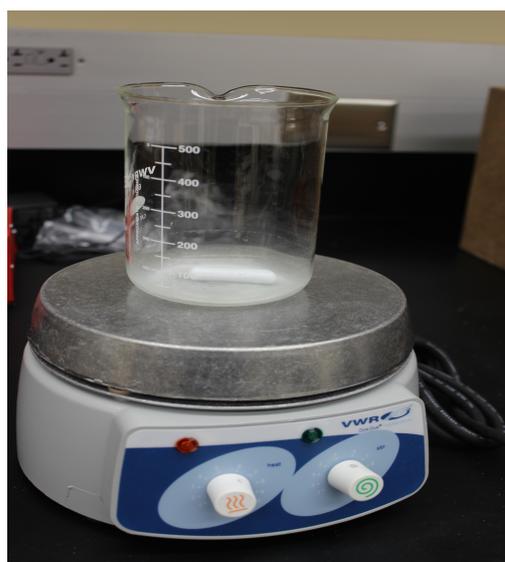


Figure 6: Stirring machine combined with heater for mixing chemical compounds

After the stirring process was complete, the powdered LCF peroxide was sintered in the SENTRO box furnace. The reaction mechanism followed is depicted below-

The LCF peroxide was first heated from 0 degrees to 600°C with increments of 2°C /min. Then it was kept at that temperature for 4 hours and finally brought down to 0 degrees by decrementing in steps of 3°C /min. Although LCF was not used as the support material in this

experiment due to time constraints, it was always the second choice available if YSZ did not perform well as a support material.

YSZ (Y2O3 Stabilized ZrO2) Powder

As opposed to LCF powder where the powder has to be prepared from the scratch by mixing of constituent mixtures in appropriate quantities, YSZ powder comes fully prepared, ready for direct use.

3.2.1 Tape Casting

Whether LCF or YSZ is chosen as support material, the next process of preparing disc shaped ceramic structures out of it involves the process of Tape Casting, as was chosen for in this experiment. The choice of disc shape was primarily due to the fact that it would better fit inside the channel and allow for more surface contact area for the REDOX reactions. During the Tape Casting process, Butvar polyvinyl butyral resin was used as the binder for processing of ceramic tape cast material. This resin imparts good strength and flexibility to the ceramic tape. It also has the quality of burning out cleanly during the sintering process.

The generic methodology of tape casting is as follows [10]

1. Mixture of YSZ and graphite (equal in proportion by volume) is dried at 90-100°C for 24hrs
2. Menhaden fish oil weighed and dissolved
3. Ethyl alcohol is weighed and added
4. YSZ and graphite powder mixture weighed and added
5. The materials are allowed to properly disperse as a mixture
6. Benzyl Butyl Phthalate (S160) and polypropylene glycol are weighed and added
7. B-98 binder powder weighed and added
8. Mixture allowed to homogenize

9. Mixture poured and de-aired in vacuum chamber

The following sintering cycle was executed afterwards-

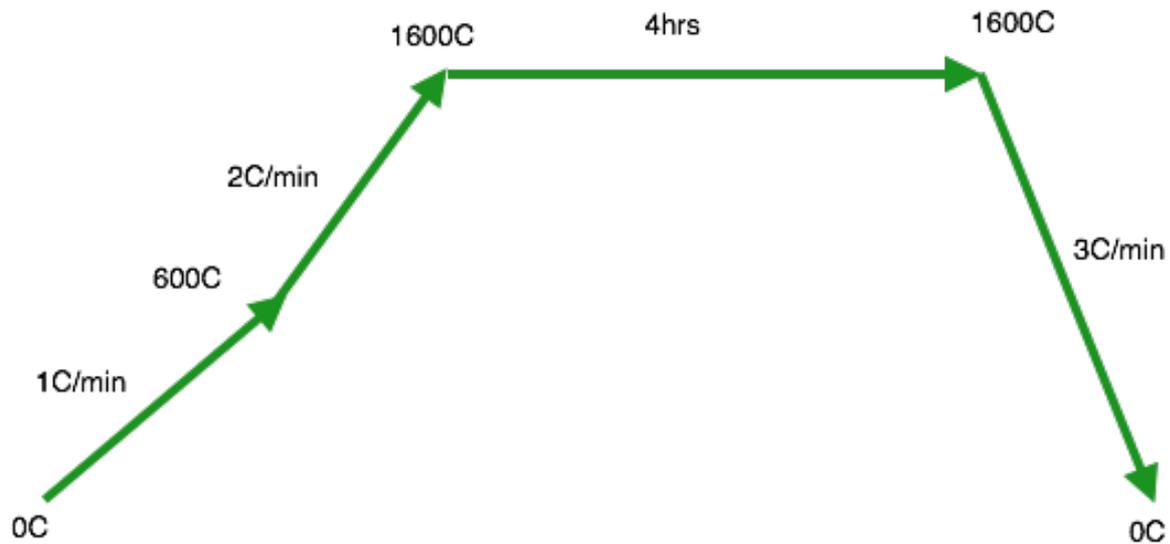


Figure 7: The sintering cycle in the Sentro Box Furnace

3.2.2 Impregnation- Coating Oxygen Carrier Metal

In this experiment, for coating the oxygen carrier metal on the porous support layer, the process of Impregnation was adopted. This method is generally suitable for most types of oxygen carriers and results in high reactivity and complete conversion of the oxygen carriers.

Process

1. Cerium nitrate hexahydrate in the proportion of 1:1.5M prepared.
2. 10ml of the solution taken for every 6.51g of support material mixture prepared earlier.
3. Afterwards, the discs were immersed in the solution for 16hrs at 60°C
4. Calcination was performed at 550°C

Disc shaped Cerium Oxide oxygen carriers were taken out of beaker (where it was impregnated) and weighed

Mass of the disc initially = 0.473g

Mass of disc after impregnation = 0.593g

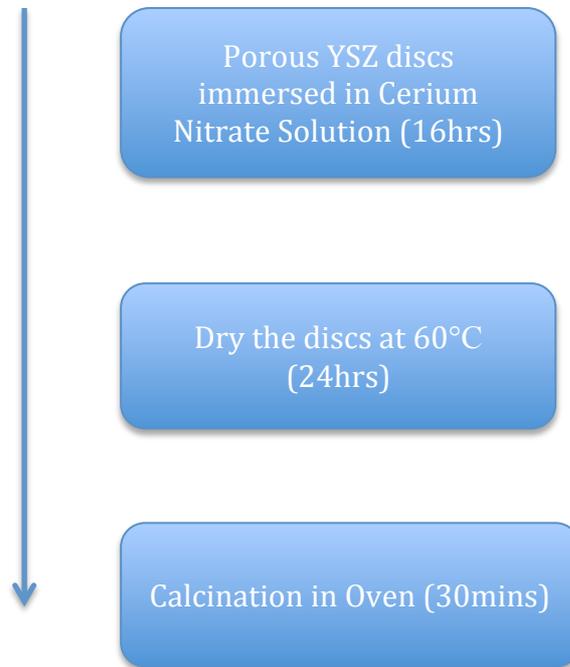


Figure 8: Schematic diagram of the Impregnation process

CHAPTER 4: EXPERIMENTAL SETUP

The flow of the various gases was controlled by a previously developed MATLAB user interface. The thermocouples placed inside the reactor and the Mass Flow Controller report flow rate in the form of analog voltage signals. These signals are then converted to digital ones by the National Instruments Data Acquisition Device (DAQ). After controlling the flow mechanics, the feedback gets transmitted to the MFCs. The voltage level of 0-5V in the MFCs was linearly scaled to correspond to a flow rate of zero to maximum sccm. Similarly, the temperature was also scaled corresponding to voltage level between 0-10V. [11] The oxidation, reduction and purging phases were controlled by the MATLAB GUI. With the initiation of one phase, the others are turned off. The real-time temperature and flow rate data can be analyzed as the experiment runs. The upper right corner panels display temperature readings and total time elapsed as the experiment proceeds.

4.1 Sentro ST-1700C-445 High Temperature Box Furnace

Furnace Power	3 kW
Voltage (single phase)	240V
Max working temperature in air	1700°C
Max temperature in argon	1600°C
Max heating rate	15°C /min
Recommended heating rate	10°C /min
Heating elements connection	Series
Number of heating elements	4
Heating chamber size	4" X 4" X 5"

Table 3: Specifications of the Sentro ST-1700C-445 high temperature box furnace

Before running the furnace for the first time, the furnace was heated in air to 1500°C for 4hrs with heating and cooling rates of 8°C/min. This process burns out any trapped water vapor inside.



Figure 9: Sentro high temperature box furnace

Structure of the furnace

The furnace has a double shell construction, which operates at high 1800°C temperature inside and low outside surface temperature. The furnace uses vacuum formed high temperature ceramic fiber board materials in the heating chamber.

4.2 ATS 3210 Split Tube Furnace/Oven

Series	3210-3.75-14-12
Wattage	3600W
Amps	5.3A
Volts	230V

Table 4: Specifications of the ATS 3210 Split Tube Furnace

Structure

The furnace has a low K-factor vacuum cast ceramic fiber insulation, which results in high energy retention. The structure of the furnace is rigid with stainless steel shell and allows custom zone arrangement and variety of configurations (isothermal, gradient and adiabatic)



Figure 10: ATS 3210 Split Tube Furnace

Working Mechanism

The split tube furnace consists of a quartz reactor tube inside and provides for an isothermal temperature up to 1100°C. After one complete cycle of the Redox reaction, a small quantity of gaseous mixture is extracted through a capillary tube and analyzed. The local surface temperature inside the furnace is measured using thermocouples.

In addition, the split tube furnace has three individually controlled heating zones that can set the temperature as required in the reactor tube. The gas enters the system through the inlet tube and after reaction, the majority of it exits through the exit port, while a small

amount is captured before exit for further study and analysis as described above.

Furthermore, there is a needle valve at the exit which can control the pressure and hence reduce the leakage of flue gases.



Figure 11: Manual control of the ATS Split Tube Furnace

4.3 MAX300-LG Mass Spectrometer

The Mass Spectrometer helps in analyzing the intensity of the different species as a function of time. The ratio of intensity of the measured species to that of an inert calibration gas gives the concentration value. [4] Scan Mode and Single Ion Monitoring modes are the two modes that can be used to study the masses of interest. A water syringe pump is used for calibration purpose before running the experiment. Kinetic studies in this experiment have been done by means of a mass spectrometer. Mass Spectrometer has the advantage of detecting every species since it has a fast sampling frequency of close to 1000Hz. The voltage setting controls the magnetic field and allows ions having a specific mass to charge ratio to pass at a time. [4]

4.4 Brooks GF40 MultiFlo Mass Flow Controller

Mass Flow Controllers are used for the purpose of gas delivery in the experiment. Four of the Brooks GF40 MultiFlo™ digital MFCs are used in this project. The MFCs can be reprogrammed for different gases as and when required.

The different MFCs along with the corresponding gases used in the CLC experiment is given below-

Mass Flow Controller Number	Gas Composition
MFC 1	Ar (Argon)
MFC 2	CH ₄ (Methane)
MFC 4	Ar/O ₂ (Mixture of Argon and Oxygen)
MFC 5	CO/H ₂ (Mixture of Carbon Monoxide and Hydrogen)

Table 5: Different Mass Flow Controllers used in the experiment

A pre-defined MATLAB code was used to run the different cycles. The buttons located at the top are used for initiating the oxidation, reduction and purge phases. The maximum flow rate and the set point values can be set in sccm. With each phase, the corresponding MFC is initiated. During the oxidation cycle, MFC 4-O₂ and MFCs 1&5- Inert

gases are initiated. During the reduction phase, MFC 2- CH₄, MFCs 1&5- Inert gases are initiated. During the purging cycle, both MFC 4 and MFC 2 is disabled to prevent mixing of gases together.

In the MFCs, a voltage level between 0-5Volts is linearly scaled to correspond to a flow rate between 0 to maximum. The actual flow rate is also displayed once the set point values are set.



Figure 12: Arrangement of the different MFCs used in the experiment

4.5 Reactor Design

The reactor in essence is a quartz tube placed inside the split tube furnace. The furnace has three heating zones within it that can be separately and individually controlled. It has a temperature range till 1100°C. Gases are introduced from the bottom of the reactor through the inlet tube and flows around the disc samples and finally exits through the exit port at the top of the reactor. The reactor is a quartz tube with ½ inch outer diameter.

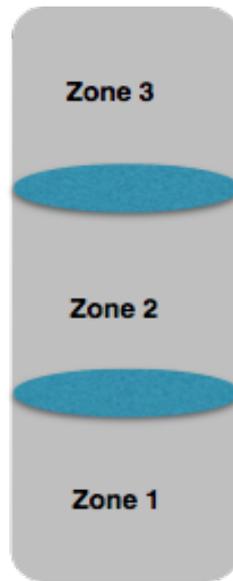


Figure 13: Different heating zones within the split tube furnace

Leakage of gases is checked for and connections are cross-examined to make sure there is minimal leakage as it can adversely affect the accuracy of the gas concentrations. A quartz capillary probe is inserted from the exhaust port and kept close to the bottom of the inlet tube to extract and read the values of the gas concentrations. The fittings are made generally of stainless steel for long-term durability.

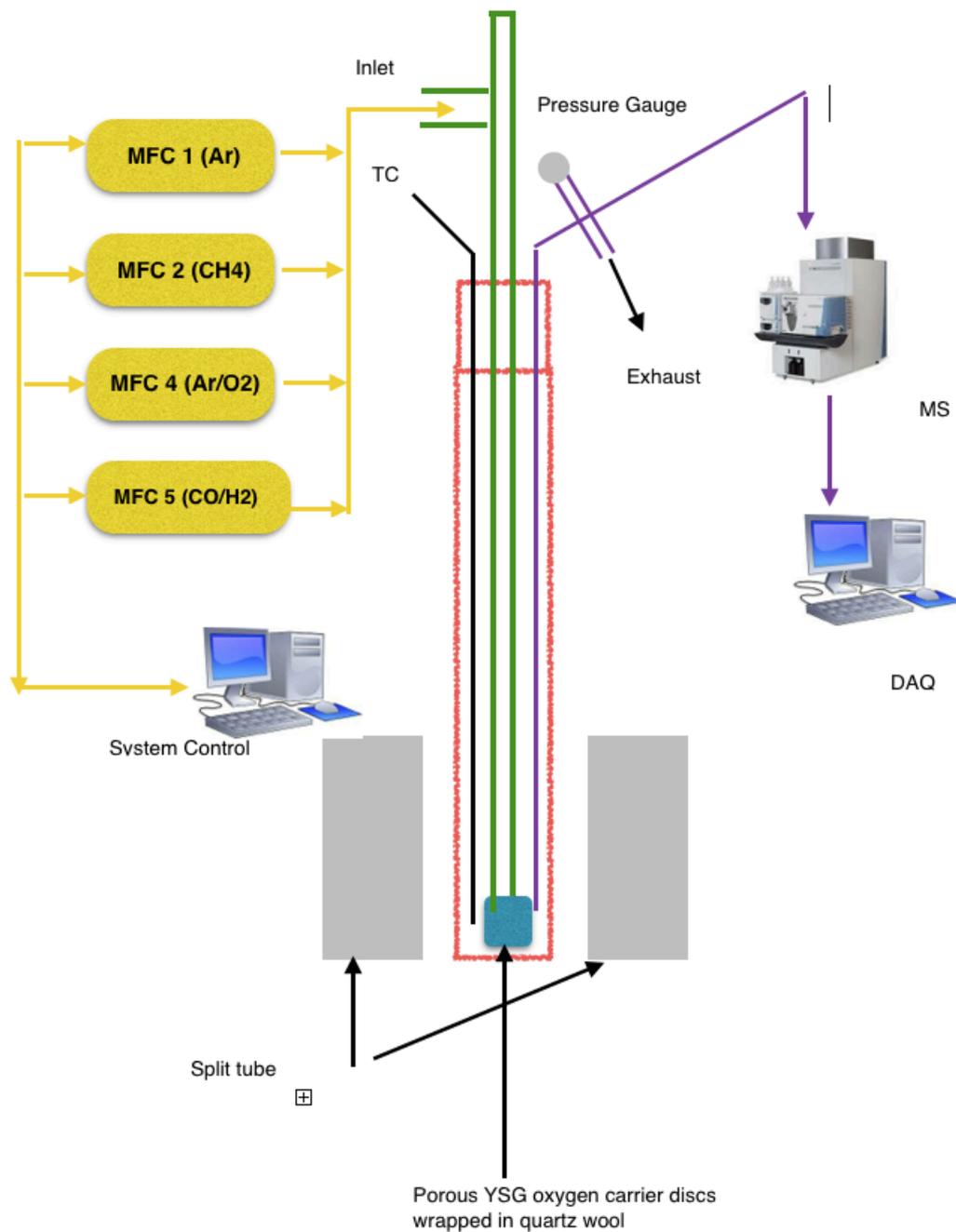


Figure 14: Overall experimental system layout diagram

A 0.25mm internal diameter capillary tube manufactured by Restek is used for reading the concentrations of the different gases inside the reactor close to the disc surface.

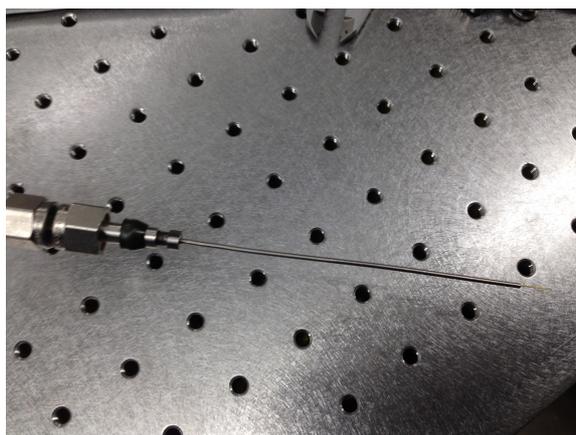


Figure 15: Capillary tube at the end of probe used for measuring concentration of different gases



Figure 16: (a) National Instruments DAQ; (b) Control Box

The overall CLC experimental platform is shown below. The furnace is wrapped with glass wool to prevent heat escape. The hood at the top acts as the exhaust. The capillary tube entering the MS from the reactor is also wrapped to prevent heat escape.



Figure 17: (a) and (b) Photos of the CLC experimental platform

CHAPTER 5: EXPERIMENTAL PROCEDURE

Porous ZSG discs (5 in number) were prepared using tape casting and impregnation as described earlier. The diameter of the discs was kept 8 mm with a thickness of 0.8-0.9 mm. Next, the discs were wrapped properly in a quartz wool (making sure they are not damaged) and inserted in the quartz inner reactor tube. After setting up the reactor properly, the system was purged for sometime with inert gas Ar to remove any traces of other gases. The furnace heating in all three chambers was then switched on. It was programmed using the SpecView software where the required temperature value is manually input. The furnace was wrapped with glass wool to reduce any amount of heat escape. Furthermore, heating tape was wrapped around the sampling line and set at a temperature of 100°C to remove moisture. A linear ramping profile was programmed and the ramping rate was set to 3°C /min. Direct mixing of oxygen and fuel was avoided by using inert gas to fill the gas lines before starting the fuel flow. Once the system stabilized at the set temperature, 5 oxidation and reduction cycles were run at the following temperatures: 700°C, 800°C, 900°C and 1000°C. A gas flow rate of 350 sccm was used.

The SpecView software is used to set the temperatures at all three zones of the furnace online.



Figure 18: SpecView software used for setting the temperatures at the different zones within the furnace

A screenshot of the pre-defined MATLAB code used to trigger the different MFCs during the oxidation and reduction phases discussed before, has been given below.

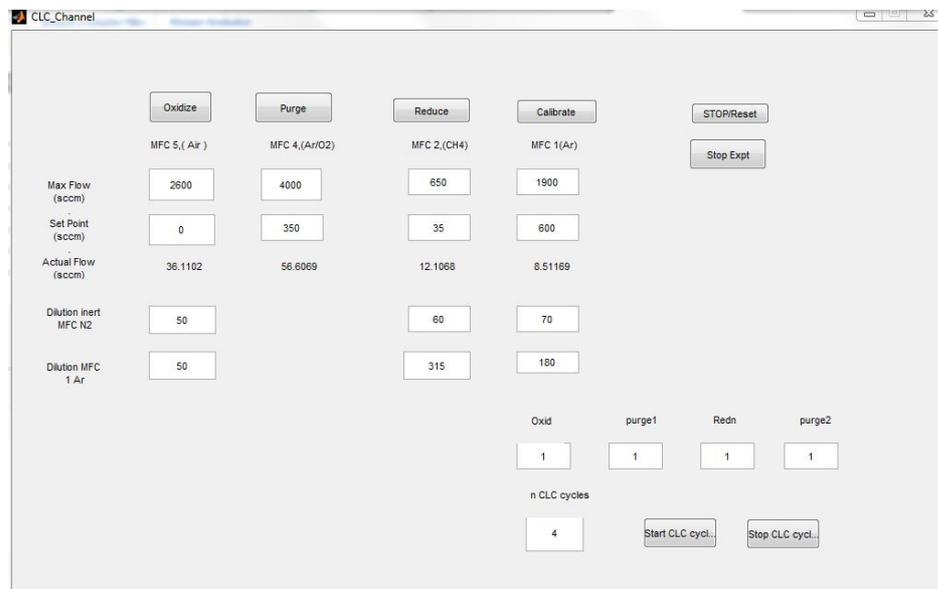


Figure 19: MATLAB graphical user interface control panel

A typical time frame of the Redox reaction followed in the experimentation is given below. The oxidation phase was allowed for 1min followed by the purging with synthetic air for another 1min, which then was followed by the reduction phase for another 1min.

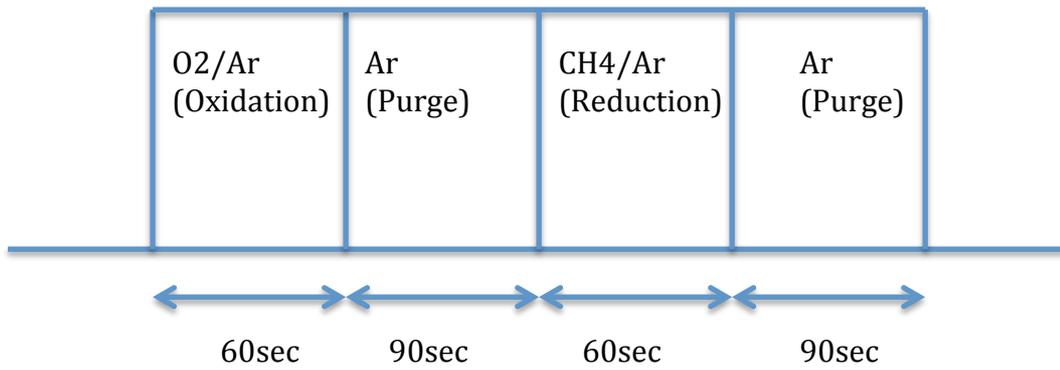


Figure 20: Typical Redox cycle followed during the experiments

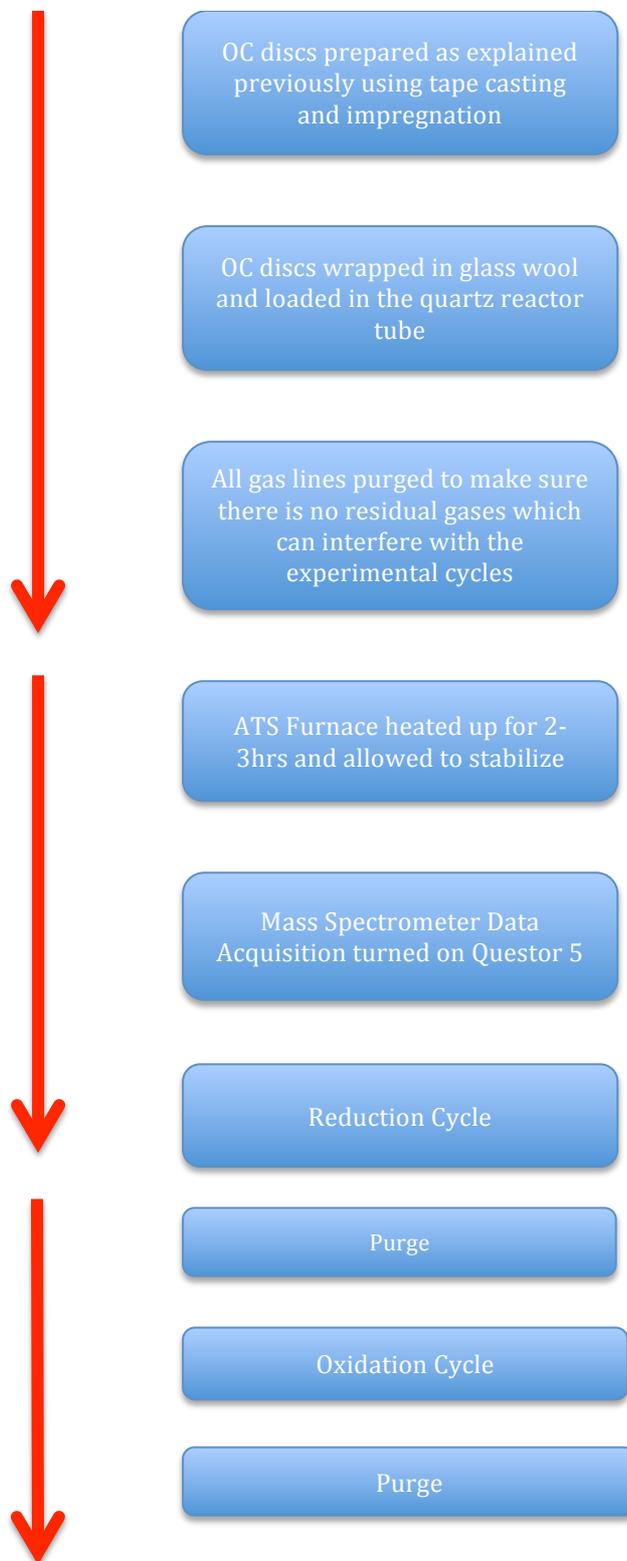


Figure 21: Flowchart of the sequence of experimental procedure

CHAPTER 6: RESULTS

After each of the 5 cycles were completed at the different temperatures, Questor 5 software provided by the Extrell Mass Spectrometer was used to study the experiment during the oxidation and reduction cycles. This software gives the molar flow rate of all the individual species of gases over time. These molar flow rate values were then extracted in Excel and graphs were plotted to study the variation of different gas production and consumption over time. The graphs were analyzed to study the pattern of oxygen and methane consumption over time.

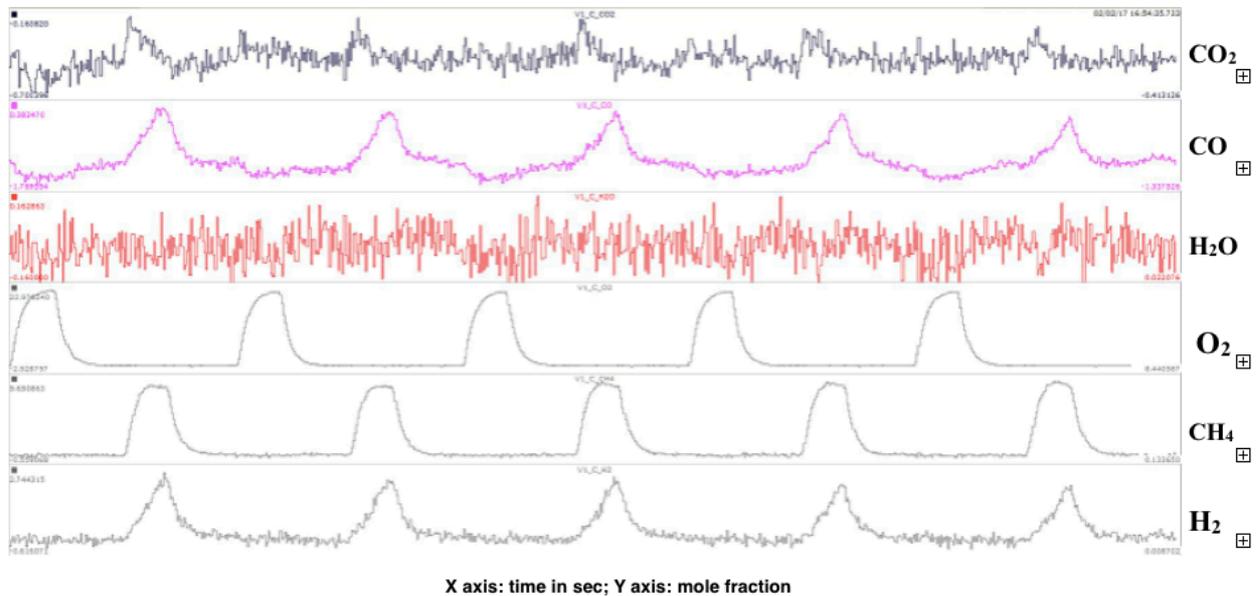


Figure 22: Screenshot of graphs showing the automated REDOX cycles running and the changes in different gas concentrations over time

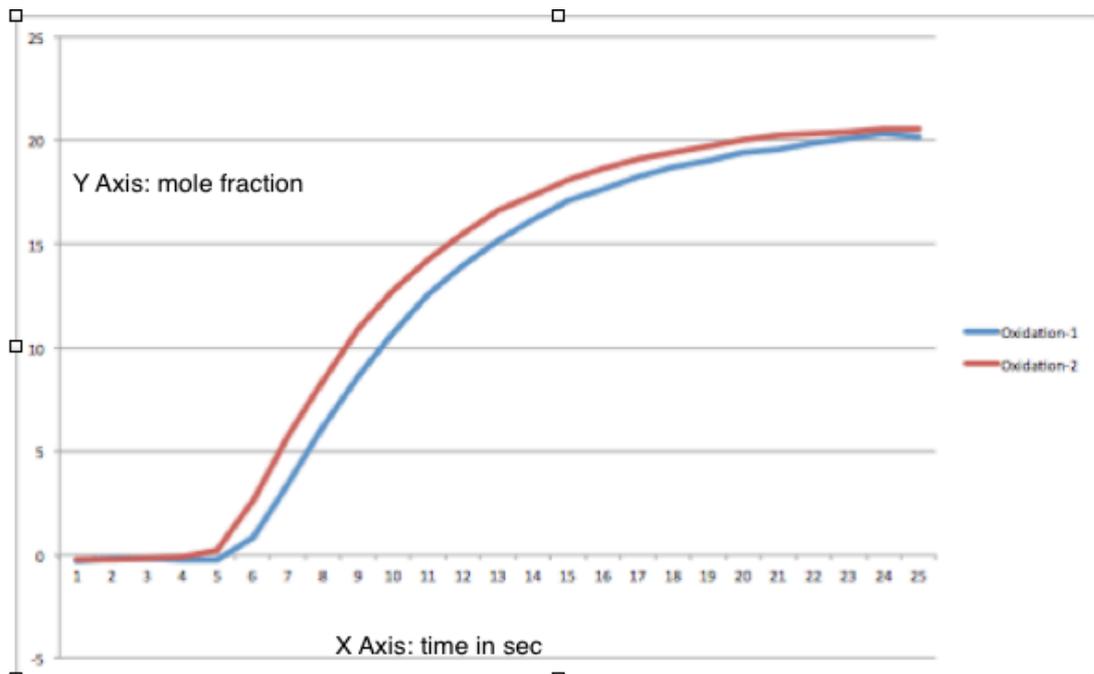
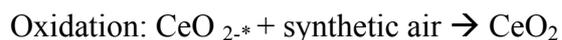


Figure 23: Comparison of two successive oxidation cycles at 700°C

Production of Syngas-



The oxidation and reduction cycles were studied in detail at the two extreme temperatures used in the experiment—700°C and 1000°C. During the reactions, CO, H₂, H₂O and traces of CO₂ were released during the reduction phase when the metal oxide reacts with fuel gas. The pattern of gas production at two temperatures, 700°C and 1000°C were observed closely to draw some rough conclusions.

At 700°C

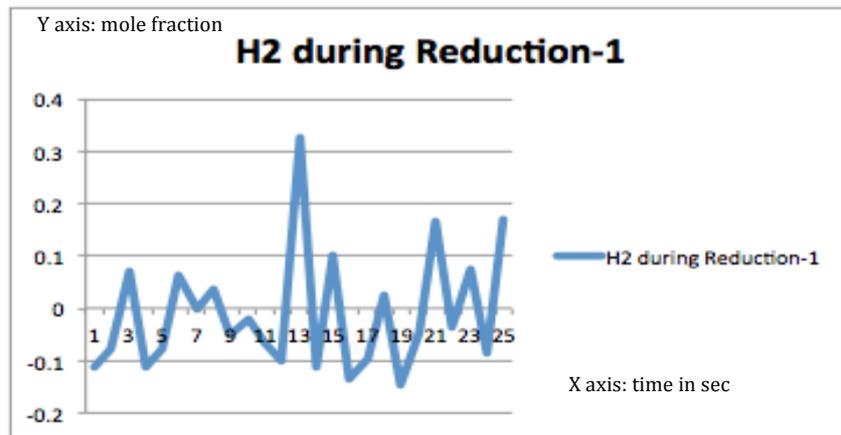


Figure 24: Production of H₂ during two successive reduction cycles at 700°C

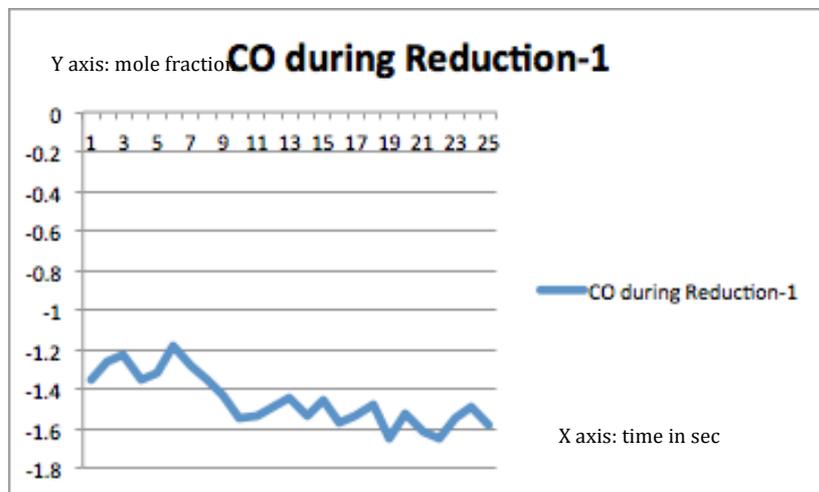


Figure 25: Production of CO during two successive reduction cycles at 700°C

At 1000°C

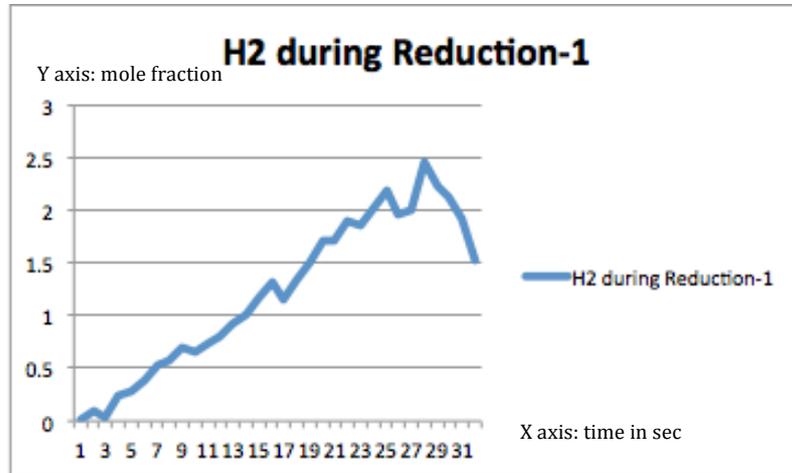


Figure 26: Production of H₂ during two successive reduction cycles at 1000°C

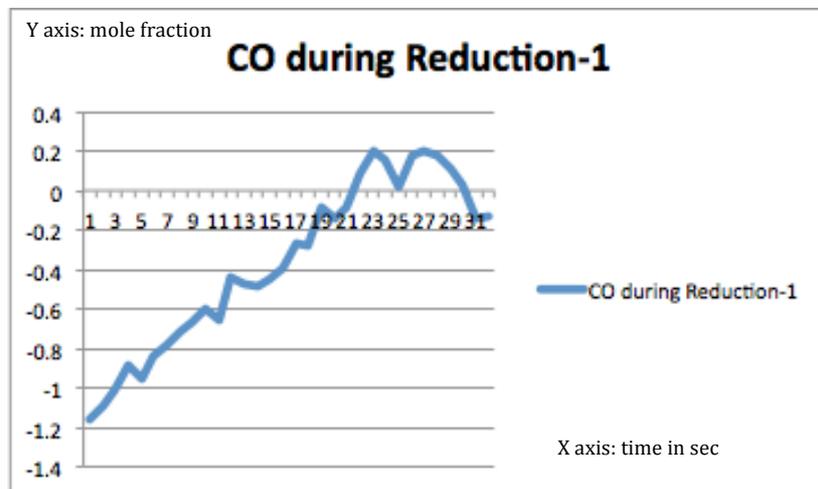


Figure 27: Production of CO during two successive reduction cycles at 1000°C

Safety Measures after running the experiments

To adhere to the safety measures, the following equipment were switched off immediately after completion of running the experiments-

1. Furnace
2. Tape heater
3. Cylinders
4. MFC Valves
5. Filament
6. IM heater
7. Mass Spectrometer Data Collection

The sintering process should be carried out at specified proper temperatures, disregarding which can damage the discs.



Figure 28: Structural damage to YSZ discs caused due to overheating during sintering process

CHAPTER 7: CONCLUSIONS

The redox cycles carried out at the different temperatures unanimously concluded the production of syngas, one of the main objectives of the experiment. When compared to other methods of syngas production, the chemical looping mechanism has not only been proven to have lesser number of steps, but is also cost-effective. The comparison of oxygen consumption at the two successive cycles at 700°C clearly shows that the oxygen consumption during the 2nd oxidation cycle was higher. The consumption of oxygen also increased slightly over successive oxidation cycles.

Comparison of the two graphs showing H₂ production during the CLC process at 700°C and 1000°C respectively clearly showed that the production was higher at 1000°C. Furthermore, comparing the CO production graphs at 700°C and 1000°C also showed higher production of CO at 1000°C. This therefore concluded that the experimental rate and hence, the syngas production rate was significantly higher as the experiment was carried out at a higher temperature. The pattern of O₂ consumption was also studied over the different temperatures at which the experiment was conducted; and it was noted that as the temperature increased, the O₂ consumption increased. This not only showed that our chosen OC, Ceria, was a good choice, but also showed that Ceria as an OC reacted better at 1000°C than at lower temperatures. Among the different oxygen carrier materials that have been tried in the past, Nickel has been proven to be very promising, but has high cost and toxicity and exhibits limited capacity in the pure state.

Copper is cheaper and not toxic, however the reactivity is slower and has a low melting point. Iron is also cheap and non-toxic, however with CH₄ in specific, the reactivity is slower. [8] Ceria has earlier been proven to have fast surface kinetics and high ionic diffusivity, and has been seen to be an effective OC over the course of the experiments carried out.

DISCUSSIONS

Although the redox cycles at different temperatures were carried out as planned, there was some noticeable carbon deposition during the oxidation phase, which was uncalled for. Past studies using channels in the rotary bed reactor also showed carbon formation on the walls. Studies showed that carbon deposition formed as a layer outside the OC such that further reaction was inhibited. In addition, carbon formation in fuel sector could be oxidized in the air sector and therefore, lower the carbon capture efficiency. [7]

Carbon deposition is a serious issue and future work on CLC would require measures to mitigate it. Earlier studies have shown that ceria-, and perovskite-based OCs exhibit over an order-of-magnitude faster kinetics compared to the state-of-the-art, enabling improved H₂ production/CO₂ reduction efficiency isothermally at 600-700°C [8]

Even our experiments showed that Ceria was a good OC, however there was a slight change in weight of the OC discs before and after the experiments which could mean either YSZ is getting consumed or ceria is not being fully regenerated, which is another issue that has to be looked into in future studies.

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