DIRECT CHEMICAL LOOPING FOR HYDROGEN PRODUCTION USING COAL WITH IRON OXIDES – BASED OXYGEN CARRIER

A DISSERTATION

Submitted in the partial fulfilment of the
requirements for the award
of

INTEGRATED DUAL DEGREE

(Bachelor of Technology and Master of Technology)
in

CHEMICAL ENGINEERING

(With Specialization in Hydrocarbon Engineering)

By

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MAY, 2016

CANDIDATE’S DECLARATION

I hereby declare that the work presented in this dissertation report entitled **“**Direct Chemical Looping for Hydrogen Production using Coal with Iron Oxide - Based Oxygen Carrier**”** in partial fulfilment of the requirements for the award of the degree of Integrated Dual Degree (B.Tech in Chemical engineering and M.Tech with specialization in Hydrocarbon engineering), is an authentic record of my own work carried out during the period from May 2015 to May 2016, under the supervision of **Dr. Bikash Mohanty**, Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee, India.

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CERTIFICATE

This is to certify that **Mr. Rahul Gurjar** has completed this Dissertation report under my supervision and the above statement made by the candidate is correct to the best of my knowledge.

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ABSTRACT

The present work entitled as “Direct Chemical Looping for Hydrogen production using coal with iron oxide-based oxygen carrier” is related to the modeling of the Coal direct chemical looping (CDCL) and Syngas chemical looping (SCL) processes as described Gnanapragasam et. al (2009). The models take in to consideration twenty-two reactions (coal-Devolatilization, char gasification, oxygen carrier reductions and oxidations, char combustion) taking place inside various reactors involved in the processes. The results are verified with the published results. Further, the verified model is used to study the suitability of Indian coal for coal direct chemical looping process.

The simulation results shows that the Hydrogen production is maximum at the lower oxygen input flowrate to main reactors (Fuel reactor in CDCL and Gasifier in SCL). Also, the Hydrogen production is higher in CDCL than the SCL process, unlike, the Carbon dioxide emission which is constant and same for both the processes. This observation concludes that the both the processes are capable of about 100% carbon capture. The effect of Coal carrier gas was found to be negligible at the set operating conditions. In case of temperature effect analysis, the hydrogen production increases with Temperature increment till the temperature of 580^0C after which the effect of temperature found to be negligible.

TABLE OF CONTENTS

Candidate's Declaration **ii**

Acknowledgement **iii**

Abstract **iv**

List of Figures **vii-ix**

List of Tables **x**

Chapter-1 Introduction **1-7**

- Hydrogen as Clean fuel 1
- Chemical Looping process 3
- Coal Direct Chemical Process-Process overview 4
- World coal industry: Reserves 5
- Objectives 6

Chapter-2 Literature Review **8-14**

Chapter-3 Problem Description **15-18**

Chapter-4 Process Description and Modeling **19-31**

- 4.1Process Description 19
  - Syngas Chemical Looping system 19
  - Coal Direct Chemical Looping System 20
- 4.2 Reaction Thermodynamics 22
- 4.3 Modeling and Simulation 26

Chapter-5 Results and Discussion **32-54**

5.1 Results segment 1: Validation of the two processes proposed by [14] 33

5.1.1 Comparison of Simulation results of CDCL process 33

5.1.2 Comparison of Simulation results of SCL process 35

5.1.3 Comparison of simulation results of CDCL and SCL process 37

5.2 Results segment 2: Simulation results for Indian Coal 40

5.2.1 Gas and Solid composition at the outlet of each of the reactors in both the processes 41

- Comparison of final product output and resource requirement 49
- Effect of Temperature of the main reactors of both the processes 53

Chapter-6 Conclusions and Recommendations **55-57**

References **58-61**

LIST OF FIGURES

Fig. no.	Description	Page no.
1.1	Main Hydrogen Pathways: the long term perspective	2
1.2	Chemical looping process outline	3
1.3	Schematic diagram of Coal-Direct Chemical Looping process.	5
1.4	World proven Coal reserves history(R/P in previous years)	6
3.1	Schematic diagram of syngas chemical looping (SCL) combustion system.	16
3.2	Schematic diagram of coal direct chemical looping (CDCL) combustion system.	16
3.3	ASPEN PLUS Process Flow Diagram MODEL for SCL system	30
3.4	ASPEN PLUS Process Flow Diagram MODEL for CDCL system	31
5.1	(CDCL) Output variation and resource requirements with O_2 inlet mass flowrate for the present ASPEN plus model	34
5.2	(CDCL) Output variation and resource requirements with O_2 inlet mass flowrate as published in [14].	34
5.3	(SCL) Output variation and resource requirements with O_2 inlet mass flowrate in the present Model	36
5.4	SCL) Output variation and resource requirements with O_2 inlet mass flowrate as published in [14].	36
5.5	Comparison of CDCL and SCL process on the basis of Product output with O_2 inlet mass flowrate in the present Models.	38
5.6	Comparison of CDCL and SCL process on the basis of Product output with O_2 inlet mass flowrate published in [14]	38
5.7	Comparison of CDCL and SCL process on the basis of resource requirement with O_2 inlet mass flowrate in the present Models	39
5.8	Comparison of CDCL and SCL process on the basis of Hydrogen production to Carbon dioxide (specific ratio) with O_2 inlet mass flowrate in the present Models	39

5.9	Gas composition at the outlet of the Fuel reactor-Partial Combustor in CDCL when input is 5kg/s Coal with Coal carrier gas as CO_2 (10kg/s)	45
5.10	Gas composition at the outlet of the Fuel reactor- Top section (Gasification and Oxygen Carrier reduction) when Process input is Coal 5kg/s with Coal carrier gas as CO_2 (10kg/s)	45
5.11	Product composition at the outlet of the Fuel reactor- Bottom section (FeO reduction) when Process input is 5kg/s Coal with Coal carrier gas as CO_2 (10kg/s)	46
5.12	Product composition at the outlet of Hydrogen reactor when Process input is 5kg/s Coal with Coal carrier gas as CO_2 (10kg/s)	46
5.13	SCL process: Gas composition at the outlet of the Gasifier when input is 5kg/s Coal with Coal carrier gas as CO_2 (10kg/s)	47
5.14	SCL process: Product composition at the outlet of the Reduction reactor-1 when input is 5kg/s Coal with Coal carrier gas as CO_2 (10kg/s)	47
5.15	SCL process: Product composition at the outlet of the Oxidation reactor-1 when input is 5kg/s Coal with Coal carrier gas as CO_2 (10kg/s)	48
5.16	SCL process: Product composition at the outlet of the Oxidation reactor-2 when input is 5kg/s Coal with Coal carrier gas as CO_2 (10kg/s)	48
5.17	Overall process output product composition of the Coal Direct Chemical Looping Process when input is 5kg/s Coal and 10kg/s Coal carrier gas (CO_2)	49
5.18	Overall process output product composition of the Coal Direct Chemical Looping Process when input is 5kg/s Coal with 10kg/s Coal carrier gas (N_2)	49
5.19	Overall process - output product composition of the Syngas Chemical Looping Process when input is 5kg/s Coal and 10kg/s Coal carrier gas (CO_2)	50
5.20	Overall process - output product composition of the Syngas Chemical Looping Process when input is 5kg/s Coal and 10kg/s Coal carrier gas (N_2)	50
5.21	Utilities requirement for the Coal Direct Chemical Looping Process when input is 5kg/s Coal and 10kg/s Coal carrier gas (CO_2)	51
5.22	Utilities requirement for the Coal Direct Chemical Looping Process when input is 5kg/s Coal and 10kg/s Coal carrier gas (N_2)	51
5.23	Utilities requirement for the Syngas Chemical Looping Process when input is 5kg/s Coal and 10kg/s Coal carrier gas (CO_2)	52

5.24	Utilities requirement for the Syngas Chemical Looping Process when input is 5kg/s Coal and 10kg/s Coal carrier gas (N_2)	52
5.25	SCL Process: Effect of Gasifier Temperature variation on overall process Hydrogen Production when input is 5kg/s Coal with Coal carrier gas as CO_2(10Kg/s)	53
5.26	SCL Process: Effect of Gasifier Temperature variation on overall process Hydrogen Production when input is 5kg/s Coal with Coal carrier gas as N_2(10Kg/s)	54

LIST OF TABLES

Table No.	**Description**	**Page No.**
3.1	Feed Details	17
3.2	Proximate analysis of the Segment-1 study solid fuel, Pittsburgh#8 Coal	17
3.3	Ultimate analysis of the Segment-1 study solid fuel, Pittsburgh#8 Coal	17
3.4	Sulphur analysis of the Segment-1 study solid fuel, Pittsburgh#8 Coal	17
3.5	Proximate analysis of the Segment-1 study solid fuel, Indian Coal lb valley#C1	18
3.6	Ultimate analysis of the Segment-1 study solid fuel, Indian Coal lb valley#C1	18
3.7	Sulphur analysis of the Segment-1 study solid fuel, Indian Coal lb valley#C1	18
4.1	List of reactions proposed by [14] for model validation	22
4.2	List of other significant reactions other than proposed by [29]	23
4.3	Thermodynamics parameters for feasibility check of each of the reactions mentioned in Table 4.1	23
4.4	Thermodynamics parameters for feasibility of each of the reactions mentioned in Table 4.2	25
4.5	Model type and operating conditions of the Blocks used in the ASPEN Plus Simulation	29

In the current era, Energy and Global warming are the two inter-wound global issues of significant magnitude. With atmospheric CO_2 level recently reaching to 400 ppm [1] level mark, it has become vital to develop clean and cost effective energy conversion processes. Renewable energies like hydro, solar, biomass and wind are unlikely to meet the energy demand in reckonable future. While, Nuclear energy is unlikely to play a vital role in meeting future energy demand due to its constraints on spent fuel management and susceptibility to tragic hazards.

Even with the recent developments in the areas of renewable energy, nuclear power and other sources, fossil based fuels meet around 85% of world's energy demand. Thus makes the fossil fuels as the most impending source of energy in near future [2]-[3]. In the past decade, researchers and scientists facing considerable challenge posed by the Carbon Emissions from fossil fuels as estimated by IPCC [4]. Conspicuously, the clean technologies such as chemical looping combustion, oxy-fuel combustion, fuel cells and similar technologies are becoming attractive alternative in reckonable future. Most of the conventional and proven oil as well as gas sources have already been exploited. However, the energy demand is increasing continuously, particularly in developing countries like India and China [2]. Therefore, the availability of ample coal reserves in country like India to meet energy demand for 200+ years is to be utilized properly. One of the economic drivers for coal utilization is its cost which is cheaper than other fossil fuels, as well as, its pricing which is locally controlled.

Hydrogen as Clean fuel

Hydrogen can be produced from a variety of resources. These include fossil resources, such as coal and natural gas, as well as renewable resources, for example biomass and water, using renewable energy sources (*e.g.* sunlight, wind, tides or hydro-power). A variety of process technologies can be employed, in addition to, chemical, biological, electrolytic, photolytic and thermo-chemical. Process technologies are in different stages of development progress, and each offers distinctive opportunities, benefits and challenges. The choice and timing of the various options for hydrogen production will be influenced by various factors such as, development stage of the technologies, regional availability of feedstock, market applications, as well as, demand, policy issues, and costs.

In Fig.1.1, a future hydrogen pathway is illustrated. In the short and medium span, hydrogen production options are mainly based on the electrolysis of water and on the reforming of natural gas and coal. It is anticipated, production of hydrogen with larger integrated plants to be installed in the longer span. These plants will possibly be based on fossil fuels or biomass with integrated CO_2 capture and storage.

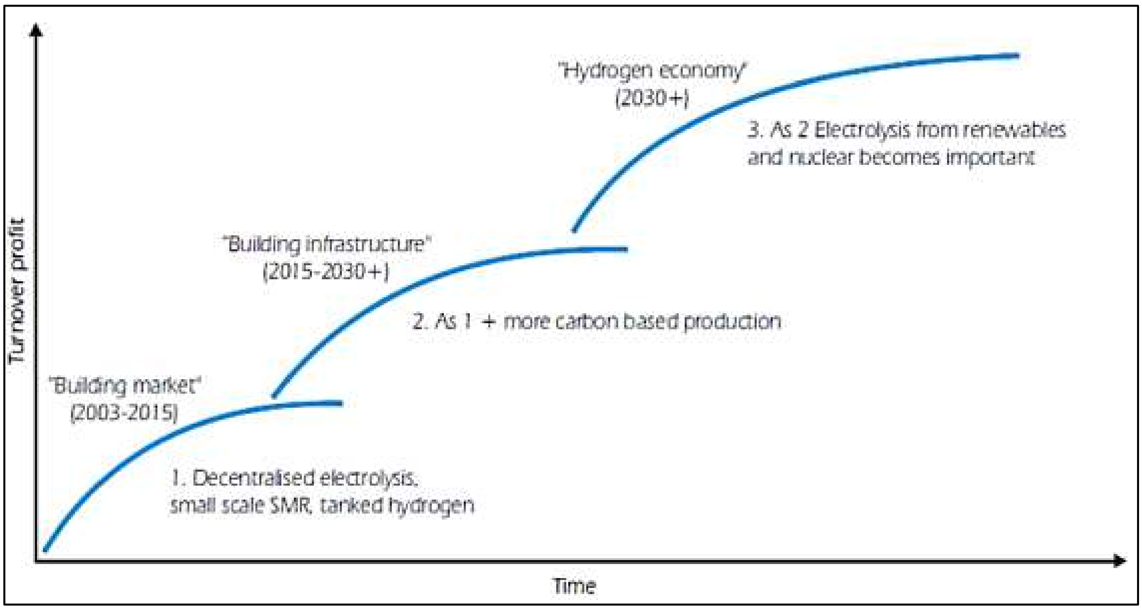


Fig.1.1: Main Hydrogen Pathways: the long term perspective [28]

The production of Hydrogen basically categorized into two broad Processing technologies:

1. **Fuel Processing**: These technologies reform the hydrogen containing materials, such as natural gas, gasoline, methanol, or ammonia into a hydrogen-rich stream. The most common hydrogen production method commercially used is the Steam reforming natural gas/fuel processing of methane. Hydrocarbon fuels generally contain some amount of sulfur which could poison the catalyst used in fuel processing. This problem is perhaps the biggest challenge to reforming**.**
2. **Non-Reforming Technologies**: Hydrogen is also produced by many methods other than reforming. These include processes under hydrogen from biomass and coal, splitting of water.

Chemical looping processes are the advanced processes for Hydrogen production with CO_2 capture.

Chemical Looping Process

Conventional technologies that generate electricity from fossil fuel via gasification or combustion process produce flue gas, separation of carbon dioxide from which is costly and technically cumbrous. The most important benefit of chemical looping technology is that it provides sequestration-ready carbon dioxide stream, and thus significantly increases its cost effectiveness.

In 1951, a process was proposed by Lewis and Gilliland [5] based on chemical looping to generate pure carbon-dioxide using oxidation of carbonaceous material.

Recent applications of Chemical looping processes, based mainly on the requirement for developing optimized reactions minimizing the exergy loss involved the chemical and, or, energy conversion system. Numerous modern chemical looping processes have been developed like Chemical looping combustion process, Syngas Chemical looping process, Coal Direct chemical looping process that uses Coal or coal-derived syngas as a feedstock.

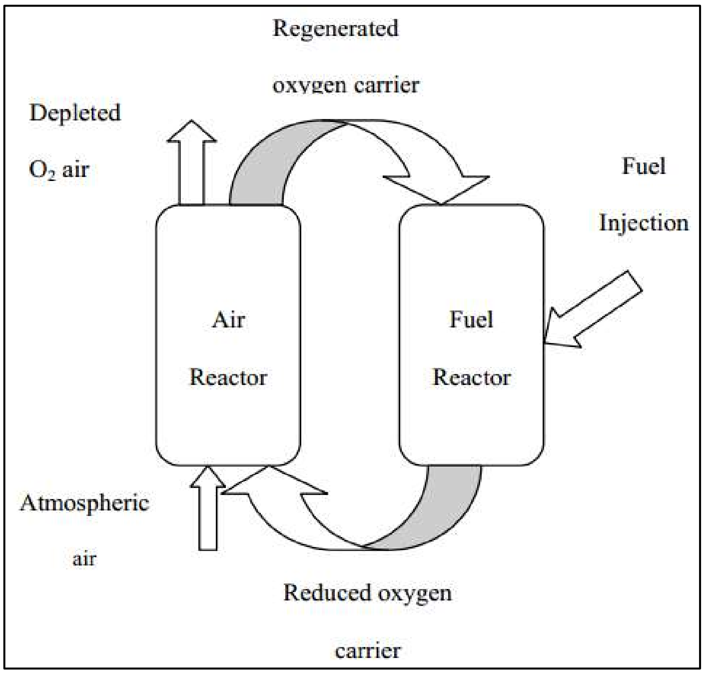


Fig. 1.2 Chemical looping process outline [5]

In chemical looping combustion process, carbonaceous fuel, for example coal, formerly reacts with an oxygen carrier, probably a metal oxide, in a fuel reactor and subsequently gets reduced to metal. The products of the result of above reaction are carbon dioxide and steam, where, carbon dioxide is readily separable by condensing steam. The reduced metal in the fuel reactor is regenerated to initial state of metal oxide in the air reactor by oxidation with air. The metal oxide is then reused as oxygen carrier by recycling back to the fuel reactor.

Coal-Direct Chemical Looping (CDCL) Process

Process Overview:

There are many configurations of CDCL process and one such is shown in Fig.1.3. The CDCL process comprises of three reactors, i.e., the Reducer or the Fuel reactor, the Oxidizer, and the Combustor. In the reducer reactor, carbonaceous fuels are converted to CO_2 while oxygen carrier (metal oxide such as,Fe_2O_3) is reduced to a mixture of its reduced states (Fe and FeO in case of Fe_2O_3). In the oxidizer reactor, the reduced oxygen carrier (Fe/FeO particles) is oxidized to its highest oxidation state (here, Fe_3O_4) using Steam, producing a Hydrogen-rich gas stream; the combustor reactor re-oxidizes the Fe_3O_4 particles to Fe_2O_3 while conveying the Fe_3O_4 particles from the H_2 reactor (oxidation reactor) to the reducer inlet using air.

Due to the size of Coal ash, significantly smaller than Fe_2O_3 particles, its separation from the oxygen carrier particles is easier. This is done using a cyclone before the reducer. To maintain reactivity of oxygen carrier in the reducer, fresh particles are also used as makeup and fed to the reactor.

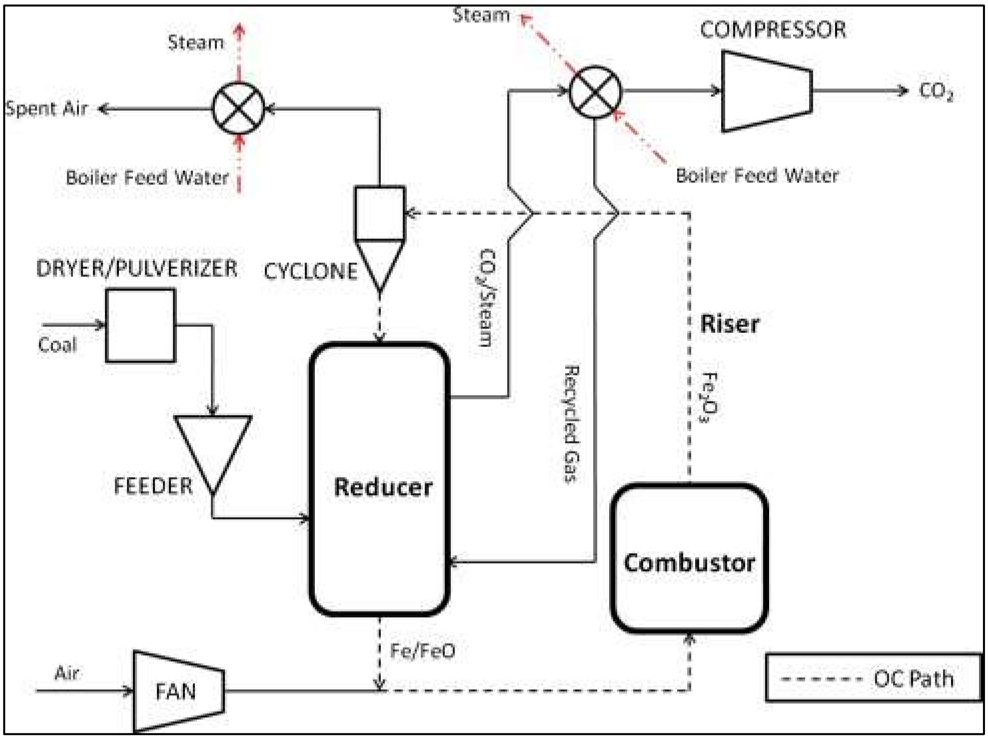


Fig.1.3 Schematic diagram of Coal-Direct Chemical Looping process. [6]

World Coal Industry: Reserves

According to United States Energy Information Administration (EIA) estimated total world coal reserves equals to 948 billion tons by 2009. According to BP statistical review of 2015[2], amount of coal reserve proven by 2014 will meet the demand sufficiently for 109 year which is highest for any fossil fuels. World’s largest coal reserves are in U.S.A., Russia, China, Australia, India and Germany.

At the end of 2014, their respective shares estimated in global coal reserves are:

USA – 26.6%
Russia – 17.6%
China – 12.8%
Australia- 8.6%
India – 6.8%
Germany – 4.5%

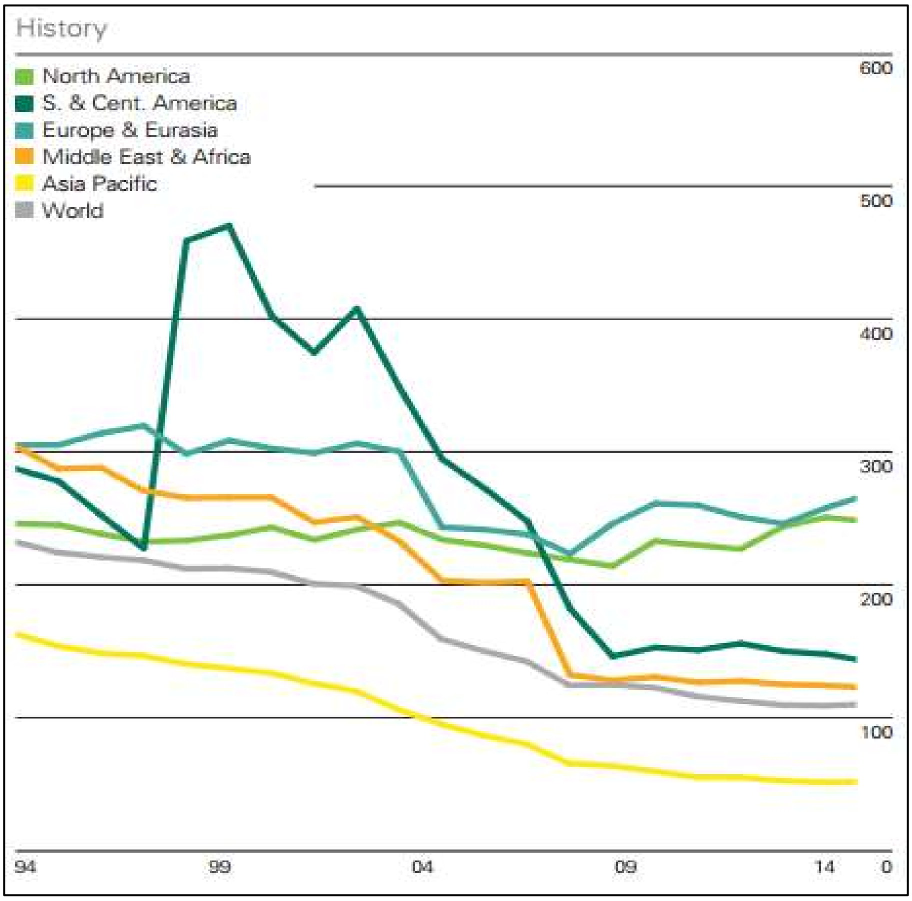


Fig.1.4: World proven Coal reserves history(R/P in previous years) [2]

Note: Ratio R/P –Reserves remaining at the end of the year divided by the production in that year.

Objectives

Recent developments from a decade in Chemical looping combustion seeking for an alternative process for efficient and clean technology for Hydrogen production along-with Carbon capture is the major driver of the present study.

In the past decade, various studies on gas based feedstock for Chemical looping combustion has been the major focus. While, solid based feedstock for Chemical looping combustion had got little attention in the beginning of last decade. The Solid fuel based Chemical looping combustion process, Coal Direct Chemical looping, which mainly uses Coal as its fuel is freshly taken into research & investigation due to cheap fuel source.

In the Study report by BP Statistical Review of World Energy- June 2015 [2], India has Coal Reserves around 7% of the World total, left after year 2014.

In view of the above, it was decided to work on the Modeling and Simulation of Coal Direct Chemical Looping system for Hydrogen production in respect of Indian Coal using Iron oxides-based Oxygen carrier.

- The present study work is divided in two segments :
  1. Thermodynamic analysis through minimization of Gibbs free energy using ASPEN PLUS v8.4 modeling and simulation for Validation of the two process systems, as proposed by [14], has been done. Namely:
     - ➢ Syngas Chemical looping process, and
     - ➢ Coal-Direct Chemical looping process
  2. Development and Simulation of ASPEN MODEL in respect of Indian Coal considering all the possible reactions for,
     - Coal-Direct Chemical looping process, and
     - Syngas Chemical looping process
     - ➢ To study the effect of the feed Coal composition, Coal carrier gas, and Air (oxygen) inlet flowrate (in Fuel reactor) on:
       - Hydrogen production,
       - CO_2 emission,
       - Oxygen carrier requirements,
       - Steam requirements.
     - ➢ To study the effects, on Hydrogen production, of :
       - Fuel Reactor Temperature in CDCL process,
       - Gasifier (reactor) Temperature in SCL process.

In chronological order, a brief review of earlier done work, available in literature, is presented here:

1. **Meyer Steinberg et. al. (1989) [7]:** They presented a study on hydrogen production using conventional and advanced processes which included assessment of the technology and economics. They assessed six conventional processes: steam reforming of natural gas, partial oxidation of residual oil, gasification of coal by the Texaco process, gasification of coal by the Koppers-Totzek process, steam-iron process and water electrolysis. The advanced processes that were assessed: high temperature electrolysis of steam, coal gasification and electrochemical shift, integrated coal gasification, high temperature electrolysis, thermal cracking of natural gas and the coal-HYDROCARB thermal conversion. In brief, the thermochemical water splitting, high energy nuclear radiation, plasma and solar photovoltaic-water electrolysis and by-product hydrogen from the chemical industry were also discussed. They concluded that among the conventional processes, methane steam reforming is the most economic process in near-term. Processes based on conventional partial oxidation and coal gasification are two to three times more expensive than steam reforming of natural gas.

2. **Shiying Lin et al. (2001) [8]**: They carried out investigation of Hydrogen generation in a flow-type reactor during the reaction of a Coal/CaO mixture with high pressure steam. Coal, CaO and CO reactions with steam, and CO_2 absorption by $Ca(OH)_2$ or CaO occurred simultaneously in the experiment. They found that H_2 was the primary resultant gas, comprising about 85% of the reaction products. Pyrolysis of the coal/CaO mixture carried out in N_2 was also examined. The pyrolysis gases were compared with gases produced by general coal pyrolysis. While general coal pyrolysis produced about 14.7% H_2, 50.5% CH_4, 12.0% CO and 12.0% CO_2, the gases produced from coal/CaO mixture pyrolysis were 84.8% H_2, 9.6% CH_4, 1.6% CO_2 and 1.1% CO.

3. **K. Svoboda et al (2007) [9]:** They carried out investigation for hydrogen production with higher purity by Chemical looping at lower temperatures. The

investigation is done using Iron based oxygen carrier on Thermodynamic constraints & possibilities. The oxidation of iron by steam was found to be thermodynamically favored at temperatures 400–800 K, and even at relatively low H_2O/H_2 molar ratios (0.2–0.4). Reduction of magnetite at lower temperatures (400–700 K) requires a relatively high H_2/H_2O ratio, increasing with decreasing temperature.

4. **C.C. Cormos et al. (2008) [10]**: They carried out investigation of the technical aspects of innovative hydrogen production concepts based on coal gasification with CO_2 capture. More specifically, focused on the technical evaluation and the assessment of performance of a number of plant configurations based on standard entrained-flow gasification processes (dry feed and slurry feed types) producing hydrogen at pipeline pressure, which incorporate improvements for increasing hydrogen purity and pressure.

5. **Paolo Chiesa et al. (2008) [11]:** They carried out analysis of a novel process based on chemical looping (CL) techniques for hydrogen production from natural gas allowing for simultaneous capture of carbon dioxide. The process consists of a three-reactors CL system, where iron oxide particles are circulated to: (i) oxidize natural gas (thus providing, after cooling and water condensation, a CO_2 stream ready for sequestration), (ii) reduce steam, to produce hydrogen as the final product of the process, (iii) consume oxygen from an air stream, to sustain the thermal balance of the system.

6. **J.P.E. Cleeton et al. (2009) [12]**: They carried out study of a Chemical looping combustion (CLC) system, using haematite (Fe_2O_3) as an oxygen carrier, has been simulated in conjunction with a steam–coal gasification process. They found that for low to moderate flows of oxidizing steam, it was possible to operate within a regime which could be fully heat-integrated.

7. **C.C. Cormos (2009) [13]:** They assessed the transformation of coal through gasification into energy as power and hydrogen. The assessment includes coal feed with & without the addition of renewable-energy sources/solid waste. The study includes simultaneous carbon capture and storage. They investigated to produce a flexible ratio of power & hydrogen with 90% carbon capture rate.

8. **N.V. Gnanapragasam et al. (2009) [14]**: They assessed operating conditions for Coal-direct chemical looping and Syngas chemical looping, directed towards hydrogen production from coal with the objective to increase the overall H_2/CO_2 ratio for a given amount of coal, based on the various conditions.

9. **C.C. Cormos (2010) [15]:** Evaluation of a Chemical looping system, using iron oxides based oxygen carrier. The process investigated is adjoined with gasification process of coal along-with biomass with Carbon Capture and Storage.

10. **Wenguo Xiang et. al. (2010) [16]:** They analyzed a novel process based on chemical looping combustion (CLC) and gas turbine combined cycle for production of hydrogen and electricity from coal. They evaluated process for intrinsic capture of carbon dioxide. The core process consisted three-reactors CLC system, where iron oxide is circulated to: (i) oxidize syngas in the fuel reactor (FR) providing, (ii) reduce steam to produce hydrogen in the steam reactor (SR), (iii) consume oxygen in the air reactor (AR). The air from AR releases heat to sustain the thermal balance of the system, as well as, to generate electricity. Attempted to produce a CO_2 stream ready for sequestration. They proposed a fluidized bed composed of two fuel reactors for higher conversion of fuel gases. Using the Aspen Plus software, they simulated the gasification CLC combined cycle process plant for cogeneration of hydrogen and electricity with $Fe_2O_3/FeAl_2O_4$ as oxygen carriers. The plant consisted three-reactors SR at 815 ^{0}C, FR at 900 ^{0}C and AR at 1000 ^{0}C. The results of the simulation show that the electricity & hydrogen efficiencies are 14.46% & 36.93%, respectively. This included compression of hydrogen & CO_2 to 60 bar & 121 bar, respectively. The CO_2 capture efficiency was found to be 89.62%.

11. **Juan Adanez et. al. (2011) [17]:** They reviewed the Chemical-Looping Combustion (CLC) & Chemical-Looping Reforming (CLR) processes and reported the advances up to 2010. They stated that CLC in recent years has arisen as a very promising combustion technology. This process is very efficient for power plants and industrial applications providing inherent CO_2 capture. CLR uses the chemical looping cycles for Hydrogen production and comes with additional advantages when considered for CO_2 capture. The review compiled with the main landmarks

reached in recent years. This comprised of the development of these technologies in respect of the use of gaseous or solid fuels, development of the oxygen carriers, and modelling and experimentation at several scales. There are as many as more than 700 different materials as oxygen carriers have been compiled upto 2010 based on Ni, Cu, Fe, Mn, Co, and other mixed oxides as well as low cost materials. Modelling work has also been reviewed in regards to the design & optimization, as well as the scale-up of the CLC process. They concluded considering the great advances reached till the date that the CLC and CLR are very promising technologies in the context of the options for integrated CO_2 capture.

12. **Shiyi Chen et al (2012) [18]:** They carried out modeling and simulation of an integrated combined cycle based on the Fe and Ni loopings using Aspen plus software. Steam-iron process (Fe looping) and NiO based chemical looping combustion (Ni looping) are integrated for hydrogen production with inherent separation of CO_2.

13. **Christopher Higman et al (2013) [19]:** They reviewed the advances in the Production of Chemicals and Fuels through Gasification of Coal, Hydrogenation, & Gas Treating. The review study included the Research and Development in Gasification, advances in Gas Treating, production of Chemicals from Syngas, production of Chemicals from Pyrolysis, Evaluation of Gasification by- products and investigation studies for Direct Hydrogenation to Liquids.

14. **Yongxing Zhang et. al. (2014) [20]:** The conducted experimental investigation for the fundamental reactor design to understand the energy consumption for the reduction kinetics mechanism of Fe_2O_3 (hematite). They used the haematite with 0.5 vol % CH_4 for the purpose of the study and estimated the kinetic parameters based on the thermogravimetric analysis. Two oxygen carriers (i.e., Fe25Al and Fe45Al) were initially prepared to be used in the TGA experiment. They observed that the process of Fe_2O_3 reduction follows through two-steps. In the first step, Fe_2O_3 is converts at a fast reaction rate into Fe_3O_4 (magnetite). The second step follows is a slow step which corresponds to the reduction of Fe_3O_4 to $FeAl_2O_4$. They applied the Hancock and Sharp's method to determine the most suitable kinetic model for the process of reduction. It was concluded that within wt % of

25−45 of the Fe_2O_3 there was found to be no change in the reduction kinetic mechanism alogn-with which similar activation energy was obtained.

15. **Esmail R. Monazam et. al. (2014) [21]:** They conducted experiments for the analysis of the oxidation of magnetite (Fe_3O_4). Thermogravimetric analysis (TGA) was done for the experiments conducted at temperatures 750 to 900 °C over 10 oxidation cycles. Oxidation experiments were carried out for residence time of 30 min. in a continuous stream of air. The oxidation of magnetite (Fe_3O_4) leading to the formation of hematite (Fe_2O_3), was then reduced. The reduction was driven by continuous stream of CO (5% and 10%) with balance N_2. The gain in weight of oxygen leads to the determination of oxidation reaction rate. Analysis indicated that the oxidation followes a two-stage process. The initial oxidation, found to be very fast, took place within 2 min and follows the low activation energy-nucleation and growth processes. In the next step, the reaction found to be developed within the surface, the oxygen transports through the product layer. And thus the second step becomes the rate-controlling step.

16. **Liangyong Chen et. al. (2014) [22]:** They carried out study for the selection of the best oxygen carrier. For this purpose they proposed the abundant red mud-bauxite waste as a cost effective oxygen carrier with the use of a method of direct granulation. This red mud is produced as bauxite waste from Bayer’s alumina production process. Screening test was carried out at various calcination temperatures. They investigated the regeneration and reduction behaviour of red mud OCs in a simulated CLC process. During this investigation they considered the influence of water vapor and reaction temperature. As a reference for the performance evaluation of the red mud OCs, a synthetic iron-based OC was used. For the interpretation of the behaviour of the solid particles, the fresh, as well as used OC particles were characterized with the help of XRD, SEM, &BET analyses.

17. **Calin-Cristian Cormos et. al. (2014) [23]:** They conducted a study for the evaluation of the conceptual designs Gasification of Coal and proposed one for large scale plant. Their purpose to meet the design with pre-combustion as well as post-combustion capture based on various chemical looping options. The results concluded with generation of around 420–600 MW net electricity with at least 90%

carbon capture rate. Co –generation of hydrogen with electricity leads to formation of a flexible hydrogen output. The results described the net electrical efficiency ranges from 35 to 41%. For most of the cases, the carbon capture rate was found to be just greater than 99%.

18. **Stephen G. Gopaul et al. (2014) [24]**: They carried out comparison of the simulations of two chemical looping gasification (CLG) types using the ASPEN Plus simulation software for the production of H_2 using poultry litter (PL) biomass. The first CLG type used in situ CO_2 capture utilizing a CaO sorbent, coupled with steam utilization for tar reforming, allowing for the production of a CO_2-rich stream for sequestration. Near-total sorbent recovery and recycle was achieved via the CO_2 desorption process. The second type utilized iron-based oxygen carriers in reduction-oxidation cycles to achieve 99.8% Fe_3O_4 carrier recovery and higher syngas yields.

19. **Qingjie Guo et al (2015) [25]:** They investigated performance of Ca based oxygen carrier. Using a mechanical mixing-impregnation method, a $CaSO_4$–CaO/bentonite) compound was prepared. The purpose was to meet the performance of the oxygen carrier with excellent catalytic reactivity and stabilizing ability. The investigation included the reaction performance and cycle-ability along-with the release of sulfur. The evaluation was performed in a batch fluidized-bed reactor with steam serving as the gasification–fluidization medium. The results demonstrated that this oxygen carrier has excellent catalytic reactivity. The carbon conversion rate, and syngas content reached 96.84%, and 66.98%, respectively at temperature 900°C,. At the same temperature, the cold gas efficiency was found to be reaching 88.28%. The advantage of addition of CaO is it leads to inhibition of the $CaSO_4$ side reactions. Due this advantage the stability of the oxygen carrier improved.

20. **S. Chakravarty et. al. (2015) [26]:** They conducted study for evaluation of the chemical and mineralogical compositions of Indian coal. Three different seams were chosen for the collection of samples. All of the three seams were from a particular borehole of Samaleswari Block, Ib river coalfield, Odisha, India. The prediction and correlation of the chemical and mineral composition of coal ash to

ash fusion temperatures were conducted using different experimental and theoretical studies. The experimental studies included the determination of the proximate analysis, ultimate analysis & gross calorific value. Apart from this, quantification of major oxides is obtained from the chemical analysis of coal ash. For identification of the mineral phases present in coal and ash samples, the techniques employed were X-ray diffraction & electron probe micro analysis. For understanding the ash fusion , in addition to, the prediction of the phase transformations occurring during the coal combustion process, FactSage Thermodynamics Model was used.

The present study is segmented in two parts, in the first segment development of Process Models is carried out using ASPEN PLUS v8.4 for the validation of Simulation results published by [14] for the two processes: Coal Direct Chemical looping and Syngas chemical looping. The validation is comprised of comparison of results generated from the Models developed in the present study with that of published in [14] which includes Hydrogen production, and Resource requirements data. Further, the first segment i.e. model validation utilizes the set of the reactions proposed by [14].

In the second segment, the Models developed in the first segment is redesigned for Simulation in respect of the Indian Coal. This segment includes comparison of the two processes on the basis of effect of Coal carrier gas and Main reactors' Temperature. Furthermore, the second segment includes study of the Gas and Solid composition at the outlets of each of the reactors of both the processes. Additional set of reactions other than those proposed by [14] has been considered in this segment study.

Schematic diagrams of Syngas chemical looping (SCL) combustion system and Coal direct chemical looping (CDCL) combustion system for Hydrogen production are shown in Fig. 3.1 and Fig. 3.2, respectively.

The Operating as well as Input Feed conditions and parameters of the Models for the above mentioned Systems as described by [14] has been considered for the ASPEN Plus simulation. These are tabulated in Table 3.1. The properties of Solid fuel i.e. Coal used in the study of segment-1 are tabulated in Table 3.2, 3.3 & 3.4. While the Coal used in the study of segment-2 i.e. Indian Coal is shown in Table 3.5, 3.6 & 3.7.

The Input feed parameters and conditions for the two Systems are shown in Table 3.1. For model validation, the solid fuel used is the Pittsburgh #8 coal whose properties are shown in Table 3.2, Table 3.3 and Table 3.4. While the solid fuel used in segment-2 study is Indian Coal (seam C1, lb valley, Orissa). Its properties are shown in Table 3.5,3.6, and 3.7.

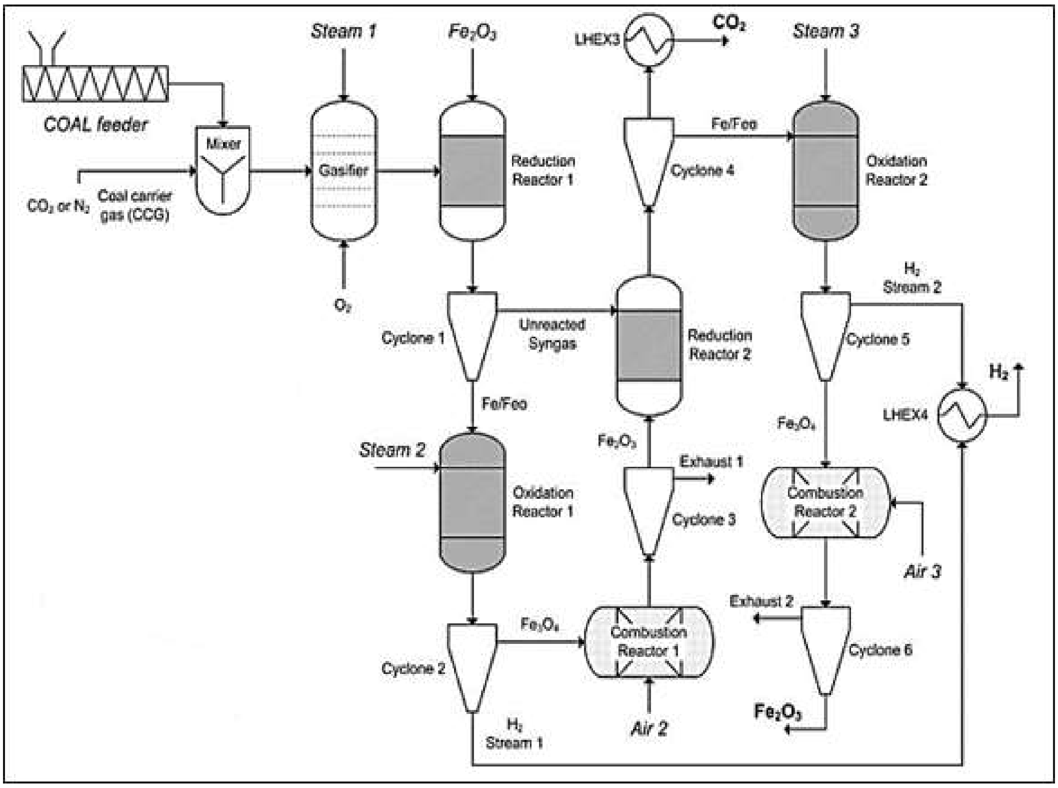


Fig.3.1: Schematic diagram of syngas chemical looping (SCL) combustion system. [14]

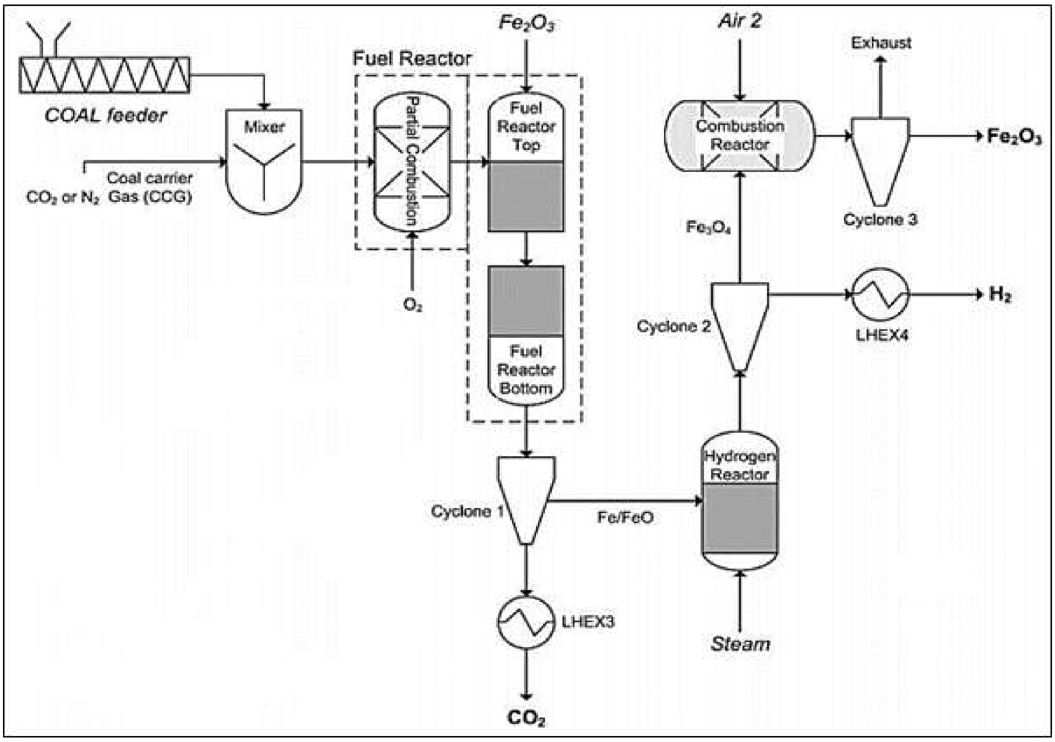


Fig.3.2: Schematic diagram of coal direct chemical looping (CDCL) combustion system. [14]

Table 3.1- Feed Details [14]

Parameter/Condition	**Feed Component**	
	Coal	**Coal carrier gas**
Type	Pittsburgh #8, or Indian Coal-seam C1,lb valley, Orissa	CO_2 or N_2
Flow rate (kg/s)	5	10
Temperature (^0C)	30	--
Pressure (bar)	~1	30

Table 3.2- Proximate analysis of the Segment-1 study solid fuel, Pittsburgh#8 Coal [27]

Constituent	**Wt. %**
Moisture	1.65
Fixed carbon (dry basis)	52.93
Volatile matter(dry basis)	37.82
Ash(dry basis)	9.25

Table 3.3- Ultimate analysis of the Segment-1 study solid fuel, Pittsburgh#8 Coal [27]

Element	**Wt. % (dry basis)**
ASH	9.25
CARBON	75.5
HYDROGEN	4.83
NITROGEN	1.49
CHLORINE	0.11
SULFUR	2.19
OXYGEN	6.63

Table 3.4- Sulphur analysis of the Segment-1 study solid fuel, Pittsburgh#8 Coal [27]

Constituent	**Wt. %**
PYRITIC S	1.37
SULFATE S	0.01
ORGANIC S	0.81

Table 3.5-Proximate analysis of the Segment-1 study solid fuel, Indian Coal lb valley#C1 [26]

Constituent	**Wt. %**
Moisture	3.87
Fixed carbon (dry basis)	39.83
Volatile matter(dry basis)	24.7
Ash(dry basis)	31.6

Table 3.6-Ultimate analysis of the Segment-1 study solid fuel, Indian Coal lb valley#C1 [26]

Element	**Wt. % (dry basis)**
ASH	31.6
CARBON	44.91
HYDROGEN	1.99
NITROGEN	1.14
CHLORINE	0
SULFUR	0.36
OXYGEN	20

Table 3.7- Sulphur analysis of the Segment-1 study solid fuel, Indian Coal lb valley#C1 [26]

Constituent	**Wt. %**
PYRITIC S	0.02
SULFATE S	0.01
ORGANIC S	0.33

In this chapter, a basic process description of both the processes has been described. Along-with the process description all the significant reactions have been included in the Tables 4.1 and 4.2. Apart from this, the assumptions and steps for modeling the processes described by [14] are also included.

4.1 Process Description

Syngas chemical looping (SCL) system

This system involves the chemical looping combustion concept. The process uses the syngas, produced through gasification of coal, for further processing. The processes, following the gasification, along-with the corresponding chemical reactions are discussed below:

- Reduction Reactor:

The syngas from the Gasifier, produced through gasification, contains mostly CO, H_2, CO_2 and CH_4. This gaseous mixture reduces the oxygen carrier (Fe_2O_3) to its reduced states (Fe and FeO). Iron oxide (Fe_2O_3) does not involve catalytically dependent reactions which is the major advantage of it to be used as an oxygen carrier. The gaseous products from this reactor are CO_2 and steam. Condensation of steam leads to a formation gas stream containing sequestration-ready CO_2. The reactions involved are given below:

$$Fe_2O_3 + CO \rightarrow 2FeO + CO_2 \quad (1)$$

$$FeO + CO \rightarrow Fe + CO_2 \quad (2)$$

$$Fe_2O_3 + H_2 \rightarrow 2FeO + H_2O \quad (3)$$

$$FeO + H_2 \rightarrow Fe + H_2O \quad (4)$$

The above reactions (1)–(4) occur at a pressure of 30 atm and temperatures ranging from 750 to 900 ^{0}C.

- Oxidation reactor:

This reactor is used as an Hydrogen generation reactor to produce 99% pure hydrogen. The reactor operates at 30 atm and 500–700 ^{0}C and the Steam is used to oxidize the Fe/FeO produced in the reduction reactor. The by-product magnetite (Fe_3O_4) of the reactor is important from the view of regeneration of the oxygen carrier. The reactions follow:

$$Fe + H_2O \rightarrow FeO + H_2 \quad (5)$$

$$3FeO + H_2O \rightarrow Fe_3O_4 + H_2 \quad (6)$$

Both reactions are slightly exothermic and therefore, some of the heat may be used for making of steam by preheating of feed water.

- Combustor reactor:

The magnetite, formed in the oxidation reactor, converts to a more stable form of Iron (Ferric) oxide by reacting with oxygen (from air) in the combustion reactor. A significant amount of heat is produced during the oxidation of Fe_3O_4 to Fe_2O_3. The reaction is:

$$4Fe_3O_4 + O_2 \rightarrow 6\,Fe_2O_3 \quad (7)$$

- System details:

In the development of the current model, the three reactors are divided into two stages since there is some unreacted syngas in the single pass through the reduction reactor. In the second stage of the process, only the required amount of Fe_2O_3 is used for complete conversion of the unreacted syngas coming from the first stage reduction reactor. The remaining Fe_2O_3 is carried along-with Fe/FeO particles to the cyclone separator and further to the oxidation reactor of the second stage.

Coal direct chemical looping (CDCL) system

The CDCL system also involves the chemical looping combustion concept. But the advantage of CDCL is that it does not involves the gasification instead involves coal reaction directly with oxygen and iron oxide in a fuel reactor. The principal difference in the CDCL system and the SCL system is replacement of Gasifier and reduction reactor to a single Fuel reactor. The fuel reactor consists of three different sections dedicated for different purposes: Partial-combustion at entrance, Char gasification alogwith oxygen carrier reduction at the top-section, and Wustite (FeO) reduction at the bottom-section. The chemical reactions involved are discussed below:

- Partial combustion:

The devolatilisation of Coal and then partial combustion occur at this section. The reactions are as follows:

$$\text{Coal} \rightarrow CH_4 + C + CO_2 + H_2O \quad (8)$$

$$C + O_2 \rightarrow CO_2 \quad (9)$$

- Fuel reactor top:

At this section, gasification of the char produced after devolitilization, pyrolysis and partial combustion occurs along-with iron oxide (oxygen carrier) reduction. The reactions involved are as follows:

$$2C + O_2 \rightarrow 2CO \quad (10)$$

$$C + CO_2 \rightarrow 2CO \quad (11)$$

$$C + H_2O \rightarrow CO + H_2 \quad (12)$$

$$CH_4 + 4Fe_2O_3 \rightarrow CO_2 + 2H_2O + 8FeO \quad (13)$$

- Fuel reactor bottom:

At the bottom section of the fuel reactor reduction of Wustite (FeO) takes place. This follows the reactions (2) and (4).

The CO_2 stream in the CDCL system does not contain methane unlike the SCL system. The possible reason could be the presence of the reaction (13) in the CDCL process which converts all the methane to CO_2 and H_2O using the reduction of oxygen carrier Fe_2O_3.

- System details:

The other two reactors hydrogen (oxidation) and combustion in the CDCL system performs the same function as in the SCL system. Also the reactions involved are same as in case of SCL system given by Eqs. (5)–(7).

4.2 Reaction Thermodynamics

The feasibility of reactions depends on Gibbs free energy value. If Gibbs free energy is negative then only it feasible and spontaneous in forward direction. Zero Gibbs free energy leads to equilibrium reaction. In thermodynamic study of reactions, Temperature range for which Gibbs free energy is negative is investigated.

Figure 4.1 shows the reactions study that are proposed by [14]. While, Figure 4.2 shows the reactions considered in the Present study other than published in [14]. The thermodynamic parameters are described in the Table 4.3 and 4.4.

Table 4.1: List of reactions proposed by [14] for model validation.

Reaction No.	Reaction
4.1	Coal De-volitilization: Coal → $C + CH_4 + CO_2 + H_2O$
4.2	$C + O_2 \rightarrow CO_2$
4.3	$2C + O_2 \rightarrow 2CO$
4.4	$C + CO_2 \rightarrow 2CO$
4.5	$C + H_2O \rightarrow CO + H_2$
4.6	$CH_4 + 4Fe_2O_3 \rightarrow CO_2 + 2H_2O + 8FeO$
4.7	$Fe_2O_3 + CO \rightarrow 2FeO + CO_2$
4.8	$FeO + CO \rightarrow Fe + CO_2$
4.9	$Fe_2O_3 + H_2 \rightarrow 2FeO + H_2O$
4.10	$FeO + H_2 \rightarrow Fe + H_2O$
4.11	$Fe + H_2O \rightarrow FeO + H_2$

4.12	$3FeO + H_2O \rightarrow Fe_3O_4 + H_2$
4.13	$4Fe_3O_4 + O_2 \rightarrow 6Fe_2O_3$

Table 4.2: List of other significant reactions other than proposed by [29].

Reaction No.	**Reaction**
4.14	$C + 2H_2 \rightarrow CH_4$
4.15	$CO + H_2O \leftrightarrow CO_2 + H_2$
4.16	$CH_4 + H_2O \leftrightarrow CO + 3H_2$
4.17	$CO + 0.5O_2 \rightarrow CO_2$
4.18	$2Fe_2O_3 + C \rightarrow 4FeO + CO_2$
4.19	$2Fe + 1.5O_2 \rightarrow Fe_2O_3$
4.20	$2FeO + 0.5O_2 \rightarrow Fe_2O_3$
4.21	$2FeO + H_2O \rightarrow Fe_2O_3 + H_2$
4.22	$2H_2 + O_2 \rightarrow 2H_2O$

Table 4.3: Thermodynamics parameters for feasibility check of each of the reactions mentioned in Table 4.1 [30]

Reaction no.	**ΔH^o (kJ/mol)**	**ΔS^o (kJ/mol K)**	**Temperature (^oC)**	**ΔG^o (kJ/mol)**	**Keq**
4.2	-393.5	+0.003	25	-394.4	$1.33 * 10^{69}$
			> 25	Negative	
4.3	-110.5	+0.089	25	-137.2	$1.1 * 10^{24}$
			> 25	Negative	
4.4	+172.5	+0.176	25	+120	$9.09 * 10^{-22}$

			25-707	Positive	
			> 707	Negative	
4.5	+131.3	+0.134	25	+91.4	$9.45*10^{-17}$
			25-707	Positive	
			>707	Negative	
4.6	-	-	>25	Negative	-
4.7	-	-	25-2600	Negative	-
4.8	-	-	25-2000	Negative	-
4.9	-	-	25-1900	Negative	-
4.10	-	-	25-2200	Negative	-
4.11	-	-	For current operating condition	Negative	-
4.12	-	-	25-1500	Negative	-
4.13	-471.6	-0.266	25	-392.2	$5.62 *10^{68}$
			< 1,498	Negative	
			>1,498	Positive	

Table 4.4: Thermodynamics parameters for feasibility of each of the reactions mentioned in Table 4.2 [30]

Reaction no.	**ΔH^{o} (kJ/mol)**	**ΔS^{o} (kJ/mol K)**	**Temperature (^{o}C)**	**ΔG^{o} (kJ/mol)**	**Keq**
4.14	-74.8	-0.081	25	-50.7	$7.76*10^{8}$
			25-650	Negative	
			> 650	Positive	
4.15	+2.9	+0.077	25	-20.0	3,270
			> 25	Negative	
4.16	+250.1	+0.334	25	+150.7	$3.83*10^{-27}$
			25-475	Positive	
			> 475	Negative	
4.17	-283.0	-0.087	25	-257.2	$1.21*10^{45}$
			25-2980	Negative	

			> 2980	Positive	
4.18	-	-	25-1400	Negative	-
4.19	-824.2	-0.275	25	-742.3	$>10^{100}$
			25-2,726	Negative	
			>2,726	Positive	
4.20	-	-	25-2600	Negative	-
4.21	-	-	25-2350	Negative	-
4.22	-571.7	-0.327	25	-474.3	$1.37* 10^{+83}$
			25-1,477	Negative	
			>1,477	Positive	

4.3 Modeling and Simulation

ASPEN Plus v8.4 software has been used to Model and Simulate the Process proposed by [14].

The assumptions taken before the development of Models are:

1) Ash component of the Coal is assumed to be inert throughout the process and considered as a solid.
2) The Nitrogen, Chlorine and Sulphur contents have been considered as inert i.e. non-reactive in the process due to their less content (0-2 %) in the Coal.

Steps followed while modeling in ASPEN Plus:

1) Selection of Global unit

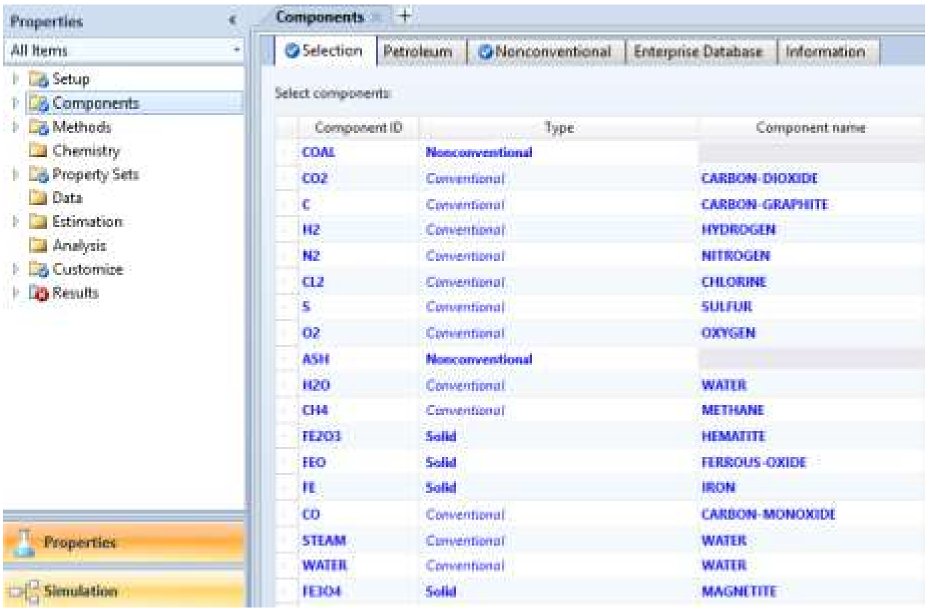
Title:

Global unit set: METSOLID

Valid phases:

Free water: No

2) Selection of Components involved in the process

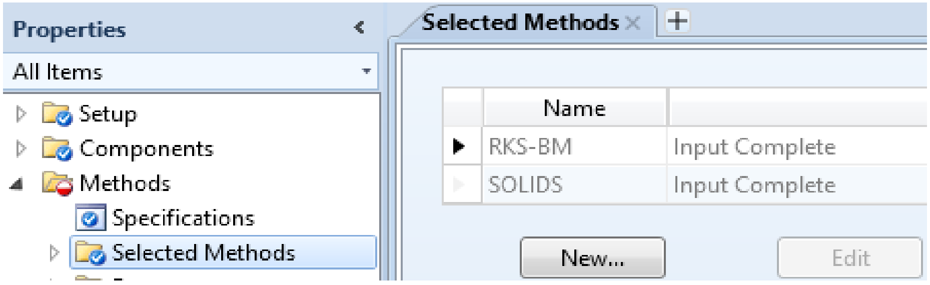


Select components:

Component ID	Type	Component name
COAL	Nonconventional	
CO2	Conventional	CARBON-DIOXIDE
C	Conventional	CARBON-GRAPHITE
H2	Conventional	HYDROGEN
N2	Conventional	NITROGEN
CL2	Conventional	CHLORINE
S	Conventional	SULFUR
O2	Conventional	OXYGEN
ASH	Nonconventional	
H2O	Conventional	WATER
CH4	Conventional	METHANE
FE2O3	Solid	HEMATITE
FEO	Solid	FERROUS-OXIDE
FE	Solid	IRON
CO	Conventional	CARBON-MONOXIDE
STEAM	Conventional	WATER
WATER	Conventional	WATER
FE3O4	Solid	MAGNETITE

3) Selection of Methods to be used for calculation of properties of each of the components.

Methods depend on the Components taking part and the type of the process.

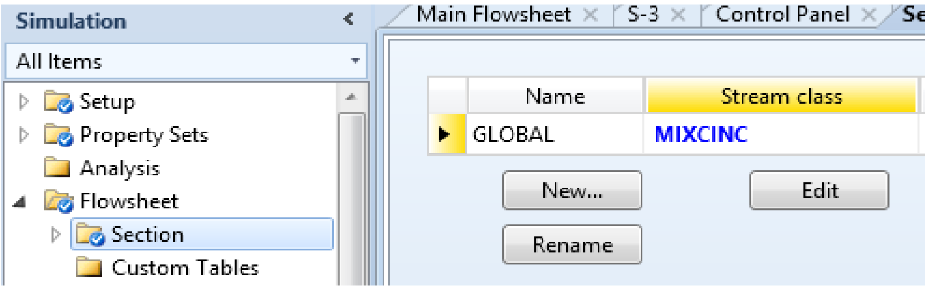


Selected Methods

	Name	
▶	RKS-BM	Input Complete
	SOLIDS	Input Complete

4) Creating the Flowsheet.

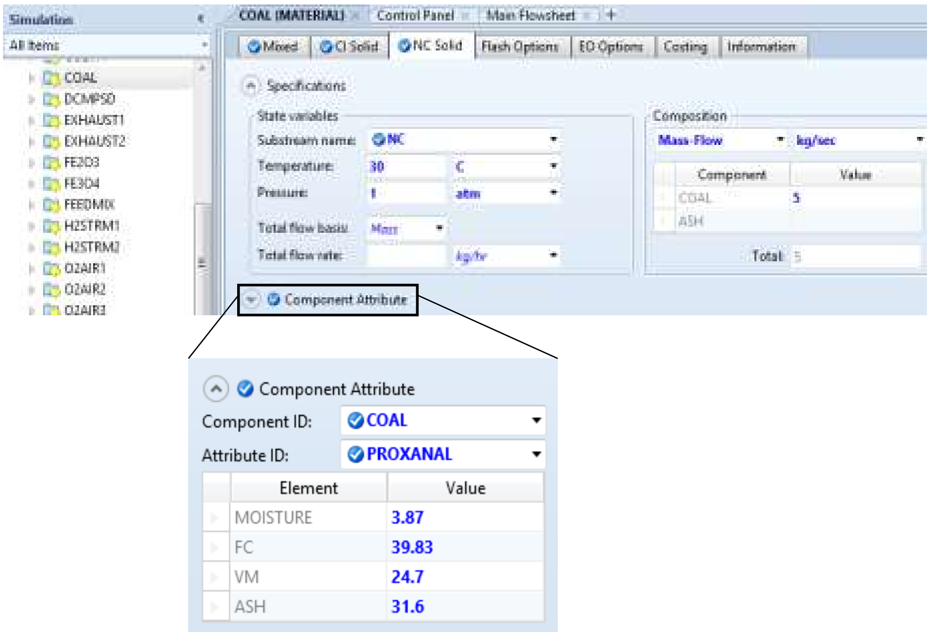
5) Selection of Global stream type as MIXCINC. This type of stream includes all type of components in stream i.e. Mixed (conventional Gases and Liquids), Conventional solids and Non-conventional solids.



	Name	Stream class
▶	GLOBAL	MIXCINC

6) Setting of Operating conditions of the Process input streams.

7) Providing Attributes for the Non-conventional solid-Coal.



Substream name: NC
Temperature: 30 C
Pressure: 1 atm
Total flow basis: Mass
Total flow rate: kg/hr

Mass-Flow kg/sec

Component	Value
COAL	5
ASH	

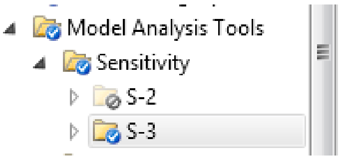
Total: 5

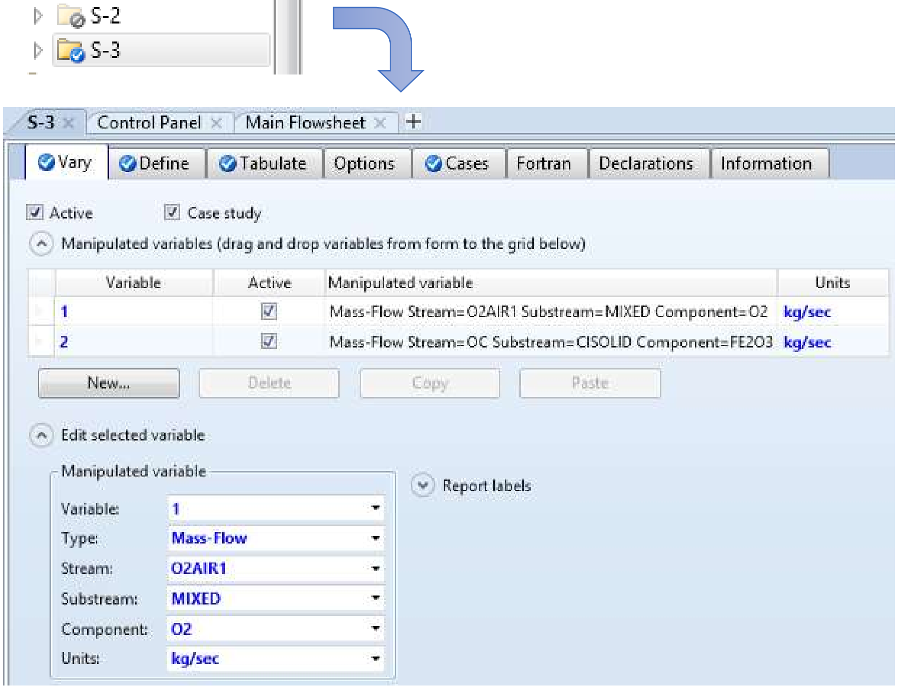
Component Attribute
Component ID: COAL
Attribute ID: PROXANAL

Element	Value
MOISTURE	3.87
FC	39.83
VM	24.7
ASH	31.6

8) Setting of Operating parameters for the Blocks (Reactors, Cyclones, Mixer, Heat exchangers, etc.) included in the flowsheet.

9) For sensitivity analysis in simulation, Sensitivity option is selected under the Modal analysis tools.





☑ Active ☑ Case study

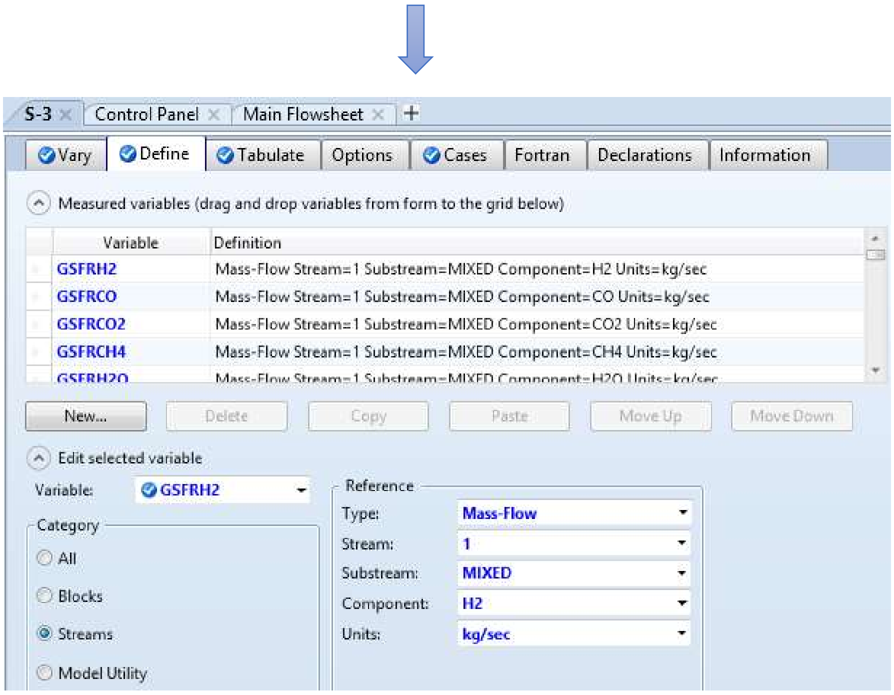
Manipulated variables (drag and drop variables from form to the grid below)

Variable	Active	Manipulated variable	Units
1	☑	Mass-Flow Stream=O2AIR1 Substream=MIXED Component=O2	kg/sec
2	☑	Mass-Flow Stream=OC Substream=CISOLID Component=FE2O3	kg/sec

Edit selected variable

Manipulated variable

Variable: 1
Type: Mass-Flow
Stream: O2AIR1
Substream: MIXED
Component: O2
Units: kg/sec



Measured variables (drag and drop variables from form to the grid below)

Variable	Definition
GSFRH2	Mass-Flow Stream=1 Substream=MIXED Component=H2 Units=kg/sec
GSFRCO	Mass-Flow Stream=1 Substream=MIXED Component=CO Units=kg/sec
GSFRCO2	Mass-Flow Stream=1 Substream=MIXED Component=CO2 Units=kg/sec
GSFRCH4	Mass-Flow Stream=1 Substream=MIXED Component=CH4 Units=kg/sec
GSFRH2O	Mass-Flow Stream=1 Substream=MIXED Component=H2O Units=kg/sec

Edit selected variable

Variable: GSFRH2

Category
○ All
○ Blocks
● Streams
○ Model Utility

Reference
Type: Mass-Flow
Stream: 1
Substream: MIXED
Component: H2
Units: kg/sec

Table 4.5: Model type and operating conditions of the Blocks used in the ASPEN Plus Simulation.[14],[24]

Block Name	**Block type**	**Operating condition**	
		Temperature (^0C)	**Pressure (bar)**
Fuel reactor (3 in series)	RGibbs model	750 - 900	30
Gasifier reactor	RGibbs model	1000	1 atm
Reduction reactors	RStoic model	750-900	30
Oxidation reactors	RStoic model	500	30
Combustion reactors	RStoic model	1000	1
Cyclone-separator	Cyclone model	-	-

Fig 3.3 ASPEN PLUS Process Flow Diagram MODEL for SCL system:

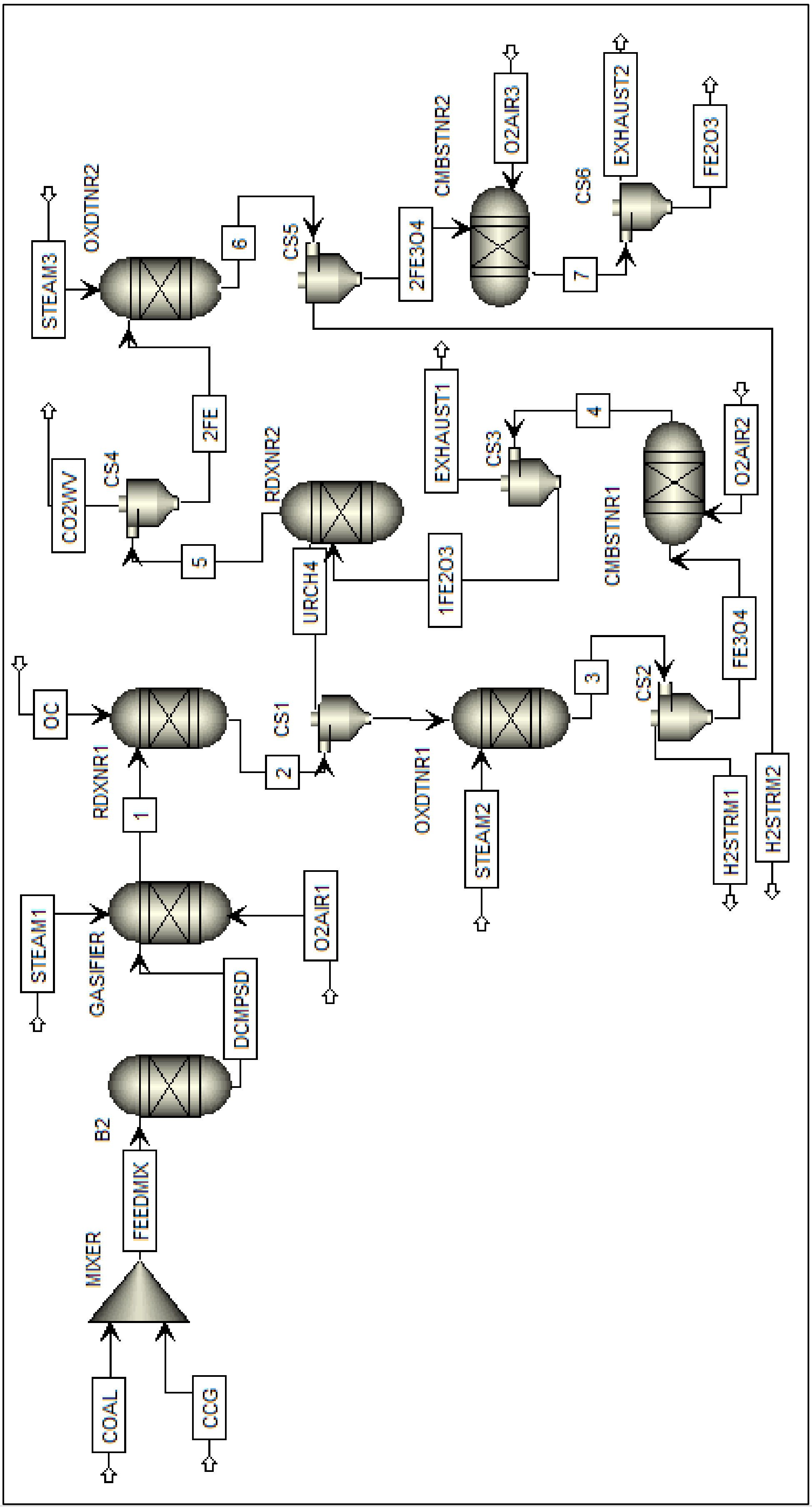
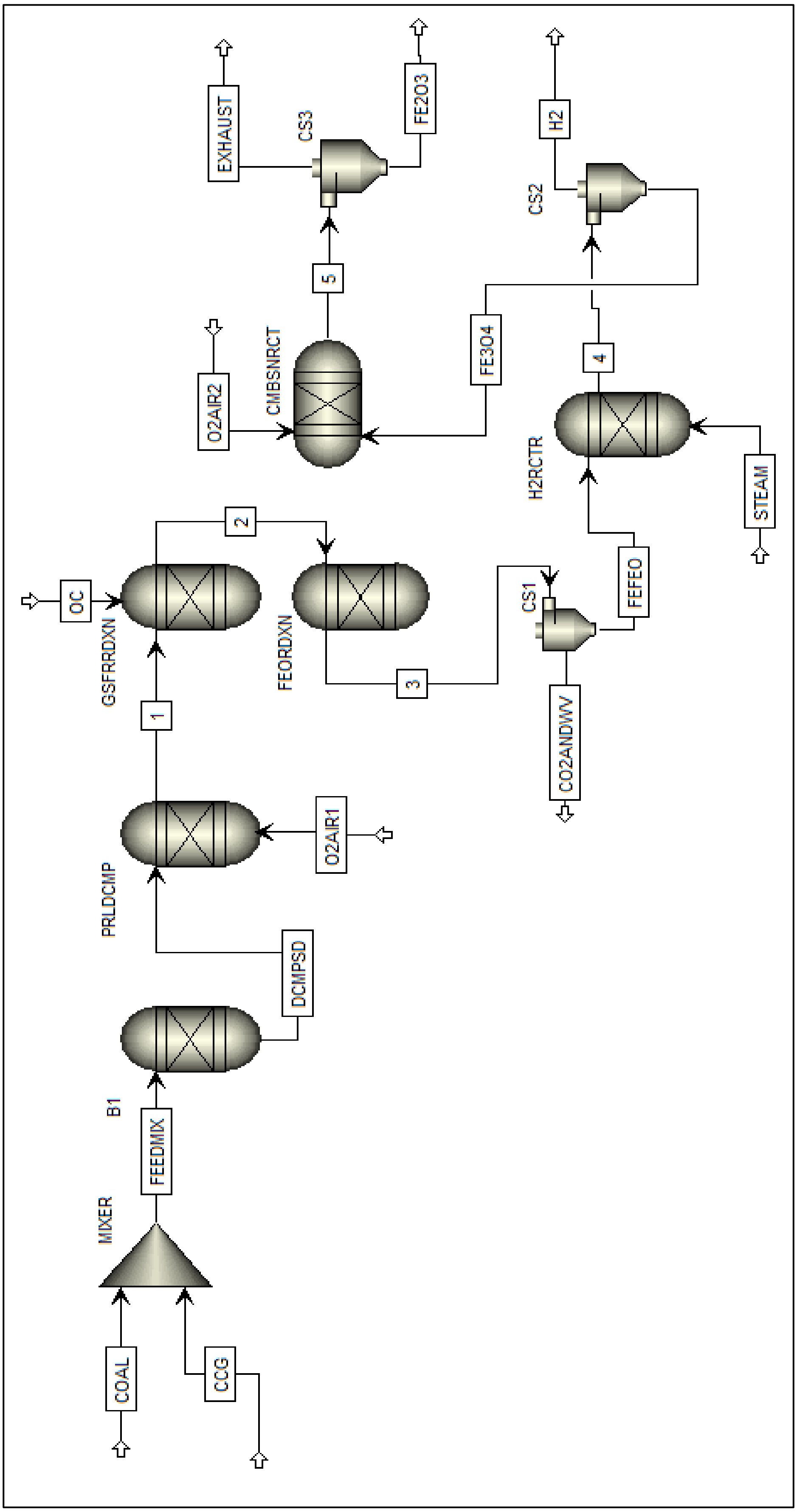


Fig. 3.4 ASPEN PLUS Process Flow Diagram MODEL for CDCL system:



In this Chapter, results of the Simulations run over ASPEN Plus process models developed in present investigation are presented and discussed. In the present work, simulation for Coal Direct Chemical Looping process and Syngas Chemical Looping process based on the process design and operating parameters described by [14] has been carried out in two segments, the first segment is devoted to validation of data of both the Chemical Looping processes with its published data using present ASPEN Plus model and the second segment of the investigation is an extension of present ASPEN Plus model to study the Product composition at outlet of each Reactor in either of the processes. Furthermore, the second segment includes the investigation of the effect of Coal Carrier gas, and Main Reactor temperature (Fuel reactor in CDCL & Gasifier in SCL). The first segment of study for model validation, the process model is validated using reactions proposed by [14] while in the second segment, other significant reactions (other than the reactions proposed by [14]) are also included. The present ASPEN Plus models are described in Chapter 4.

For simulation purpose, as described in Chapter 4, the Fuel reactor of the CDCL process has been divided in three different reactors. The first reactor, simulate the coal devolitilization and partial combustion process at the fuel entrance of the fuel reactor. The second reactor, simulate the process of char gasification and oxygen carrier (Fe_2O_3) at top section of fuel reactor. While the third reactor, simulate the Wustite (FeO) reduction at the bottom of the fuel reactor.

The main difference between the two processes which would differ the output results, is the Gasifier and Reducer of the SCL process is replaced by Single reactor i.e. the Fuel reactor in the CDCL process. The fuel reactor behaves like a reducer as well as a Partial combustor. The Partial combustion in Fuel reactor only includes the oxidation. Whereas, the Gasifier of SCL process includes partial oxidation whose heat of reaction is used in the gasification which includes redox reactions.

5.1 Results Segment 1: Validation of the two processes proposed by [14]

In this section, the present ASPEN Plus process models are validated for the *Pittsburgh# 8* Coal which was used in the Study done by [14].

According to [14], all the results have been plotted against the Oxygen flowrate to Fuel reactor in case of CDCL process. While in case of SCL process, Oxygen input flowrate to Gasifier is being used. The Input flowrate of oxygen has been varied from 3.48 kg/s to 5.8 kg/s.

5.1.1 Comparison of Simulation results of the present CDCL process model with the simulated data of the CDCL process published in [14]:

Figure 5.1 shows variation in Final product (Gas output) composition with inlet mass flow rate of Oxygen to the fuel reactor for the present model for the CDCL process. The results described by the [14] has been included in the Figure 5.2 which shows the variation in Gas outputs with the inlet mass flowrate of Oxygen to the fuel reactor. The Input variation (requirement) in Steam and Iron oxide (oxygen carrier) are also provided in the Figures 5.1 and 5.2.

From Figure 5.1, it can be seen Hydrogen production decreasing from a maximum value 86 Nm^3/h to a minimum value 60 Nm^3/h with the increasing input mass flowrate of oxygen to fuel reactor. While CO_2 emission remains constant at 60 Nm^3/h throughout input flowrate range of oxygen. Considering the Resource requirement in Figure 5.1, oxygen carrier required input flowrate decreases from 26 kg/s to 19 kg/s. While Steam requirement also decreases from around 8 kg/s to 5kg/s.

While in Figure 5.2, which shows the results published in [14], Hydrogen production decreasing from 97 Nm^3/h to 72 Nm^3/h. Here also CO_2 emission remains constant but at 67 Nm^3/h. Resource requirements in Figure 5.2 shows that Oxygen carrier required decreases from 30 kg/s to 22.5 kg/s. While Steam requirement decreases from around 9 kg/s to 6.5 kg/s.

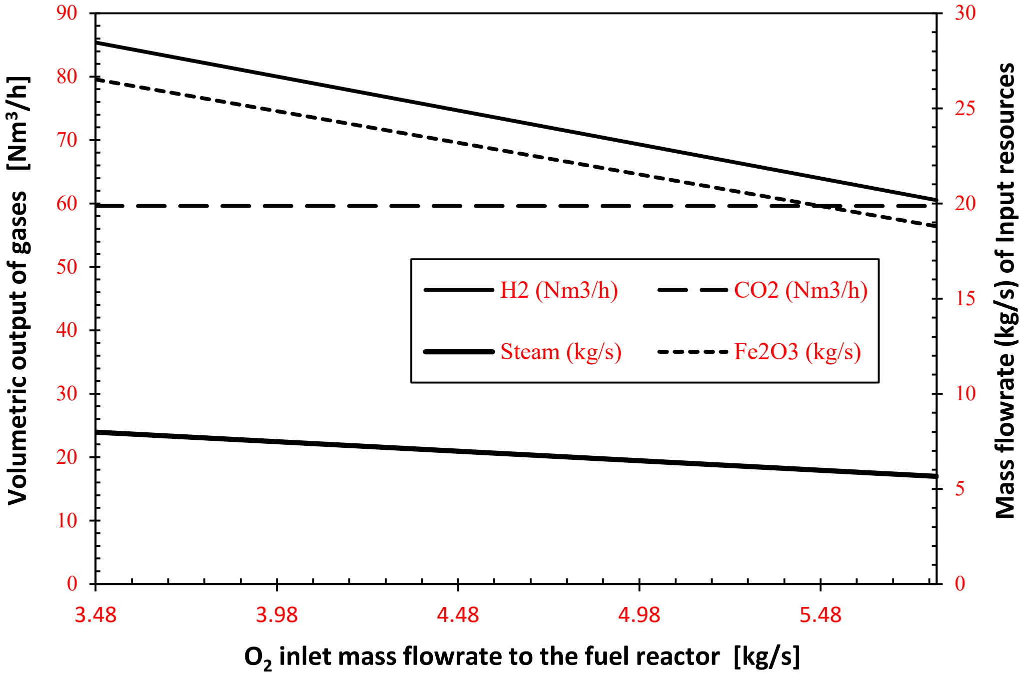


Fig.5.1: (CDCL) Output variation and resource requirements with O_2 inlet mass flowrate for the present ASPEN plus model.

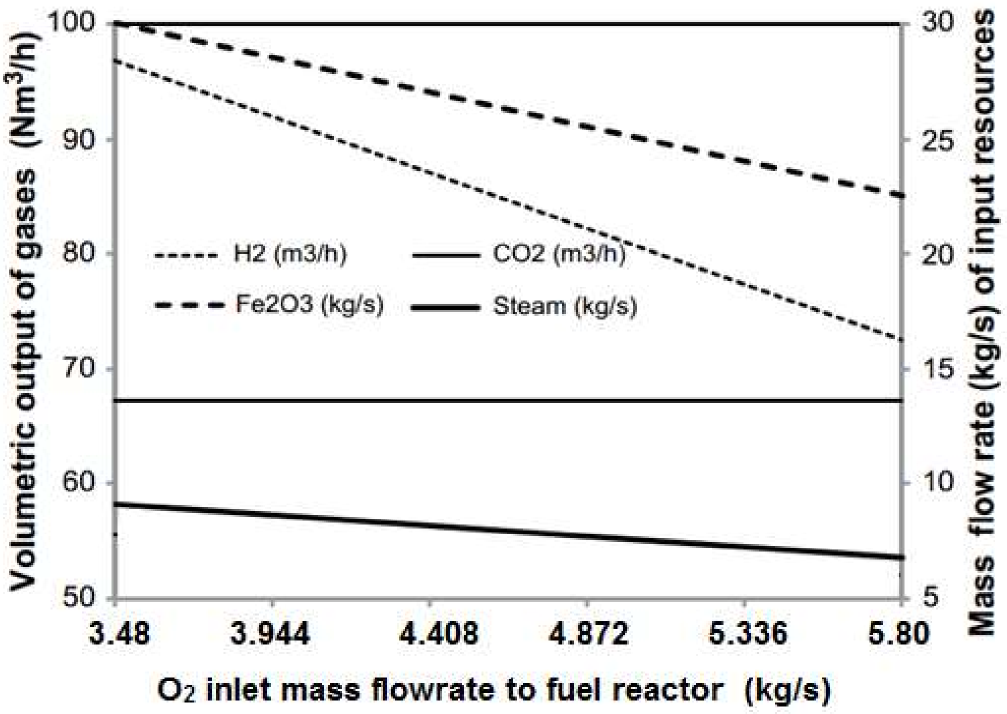


Fig. 5.2: (CDCL) Output variation and resource requirements with O_2 inlet mass flowrate as published in [14].

5.1.2 Comparison of Simulation results of the present SCL process model with the simulated data of the SCL process described by [14]:

In the previous sub-section 5.1.1, results of the CDCL comparing the present Model with published in the [14] are shown. In this section, results of the SCL process are shown. Figure 5.3 shows variation in Final product (Gas output) composition with inlet mass flow rate of Oxygen to the Gasifier in the present model for the SCL process. The results described by the [14] has been included in the Figure 5.4 which shows the variation in Gas outputs with the inlet mass flowrate of Oxygen to the Gasifier. The Input variation (requirement) in Steam and Iron oxide (oxygen carrier) are also provided in the Figures 5.3 and 5.4.

From Figure 5.3, it can be seen Hydrogen production decreasing from a maximum value 63.7 Nm^3/h to a minimum value 45.35 Nm^3/h with the increasing input mass flowrate of oxygen to fuel reactor. While CO_2 emission remains constant at 59.5 Nm^3/h throughout input flowrate range of oxygen. Considering the Resource requirement in Figure 5.3, oxygen carrier required input flowrate decreases from 39.56 kg/s to 28.17 kg/s. While Steam requirement also decreases from around 17.35 kg/s to 15.35 kg/s.

While in Figure 5.4, which shows the results published in [14], Hydrogen production decreasing from 92 Nm^3/h to 67 Nm^3/h. Here also CO_2 emission remains constant but at 66.5 Nm^3/h. Resource requirements in Figure 5.4 shows that Oxygen carrier required decreases from 40 kg/s to 32.5kg/s. While Steam requirement decreases from around 18.5 kg/s to 16.5 kg/s.

As it can be seen from Figures 5.3 and 5.4, There is much difference in Product output in the Present model in comparison to the results published in the [14]. The possible reason could the negligence of the methanation along-with other significant reactions, as described in Chapter 4, in the simulation described in [14]. Whereas, these significant reaction have been taken into account while modeling of the Present model. Apart from this, the coal properties used in simulations by [14] is different from the Coal type written in the publication.

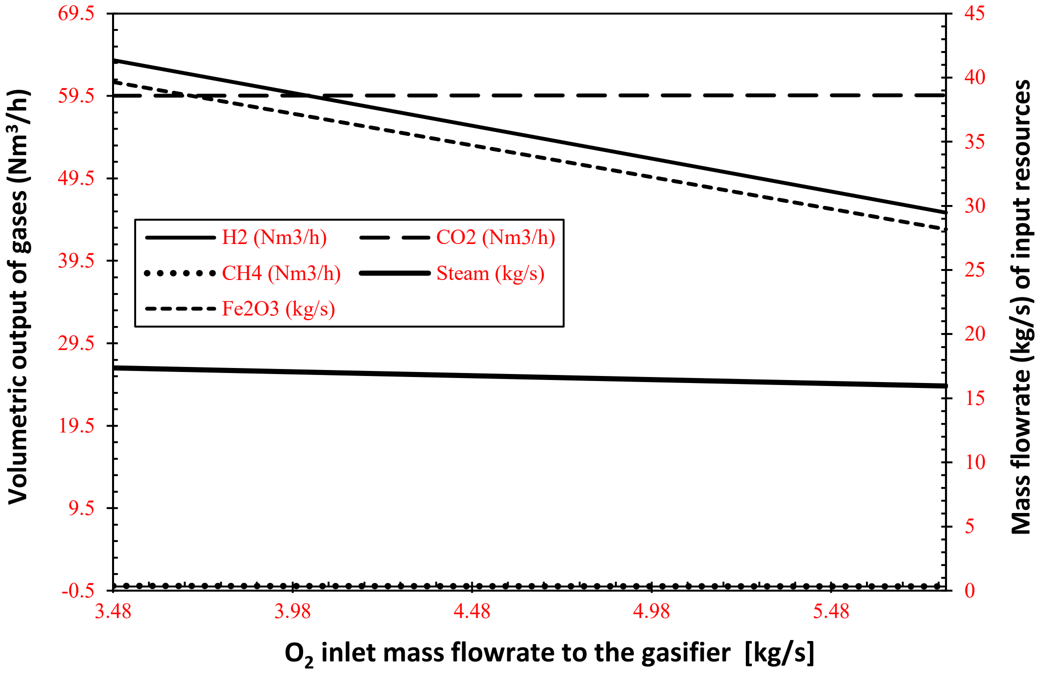


Fig. 5.3: (SCL) Output variation and resource requirements with O_2 inlet mass flowrate in the present Model

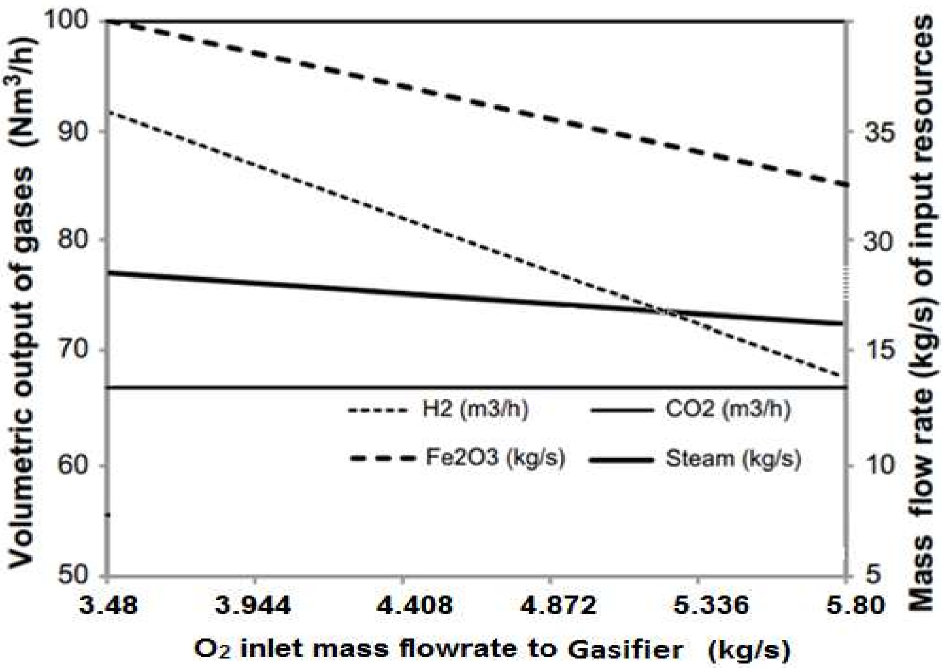


Fig. 5.4: (SCL) Output variation and resource requirements with O_2 inlet mass flowrate as published in [14].

5.1.3 Comparison of results of both the processes with the present models as well as results published in [14]

Figure 5.5 shows the Comparison of Hydrogen production and Carbon dioxide emission for both processes using the present Models. The Comparison hydrogen production and Carbon dioxide emission for the both the processes as described in the [14] is shown in Figure 5.6. It can be seen from the Figure 5.5 and 5.6, the Hydrogen production is always higher in CDCL process than the SCL process. Whereas, the Carbon dioxide emission is seem to be same for the process. But the difference in Hydrogen production for CDCL and SCL using present Models is greater than the results published in [14]. As described in the previous sub-section 5.1.2, the reason for the above could be the use of other significant reactions as described in chapter 4 and the use of coal properties different from the Coal type written in the [14].

Results also describes that the Carbon emission, which is constant throughtout the input mass flowrate range of oxygen, contains the 100 percent of the Carbon input to the process as Coal. This means both processes, Coal direct chemical looping and Syngas chemical looping are efficient for 100% carbon capture.

Figure 5.7 shows the Comparison of the Resource requirements for both the processes in the present models. As can be seen from this figure, the oxygen carrier as well as the Steam requirement is higher in CDCL than the SCL process throughout the input mass flowrate range of the oxygen to the Main reactors. The reason for higher steam required in SCL could be the use of Steam in the Gasifier along-with Oxygen. Apart from this, SCL process includes two stage reduction hence extra steam is required in the second stage of oxidation reactor.

The Hydrogen to CO_2 (product volumetric ratio) variation with input mass flowrate of oxygen to main reactors for present Models is shown in Figure 5.8. It can be seen from the figure that the product volumetric ratio for CDCL process decreases from a maximum value 1.43 to a minimum value 1.01. While in case of SCL process, the product volumetric ratio decreases from 1.07 to 0.76. This shows that both the processes which are efficient in 100% carbon capture are not as equally efficient in case of Hydrogen production where CDCL process is more efficient than SCL process. Therefore, the product volumetric ratio for CDCL is always higher than the SCL process.

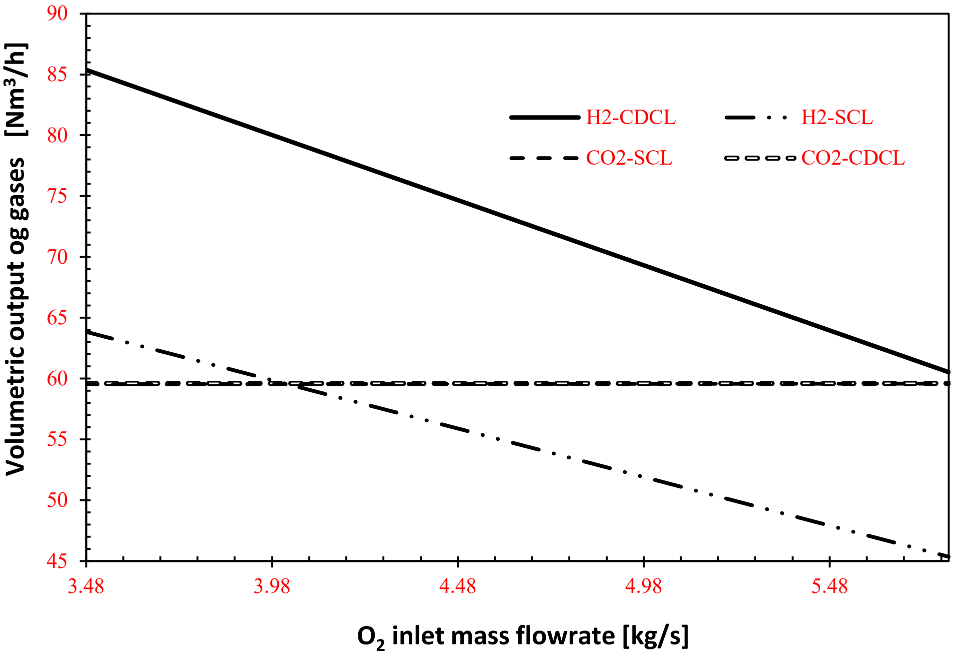


Fig. 5.5: Comparison of CDCL and SCL process on the basis of Product output with O_2 inlet mass flowrate in the present Models.

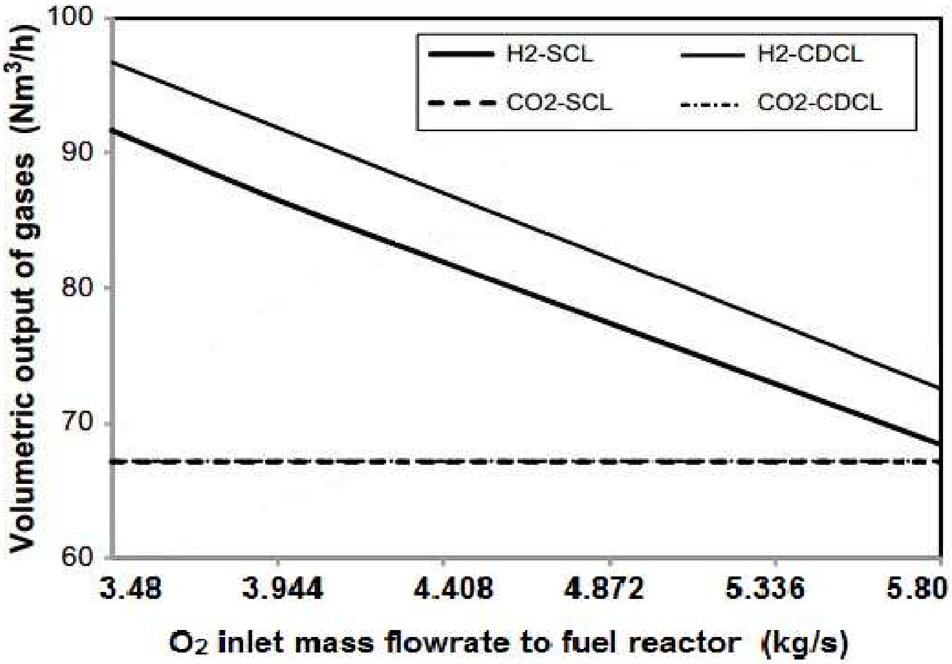


Fig. 5.6: Comparison of CDCL and SCL process on the basis of Product output with O_2 inlet mass flowrate published in [14].

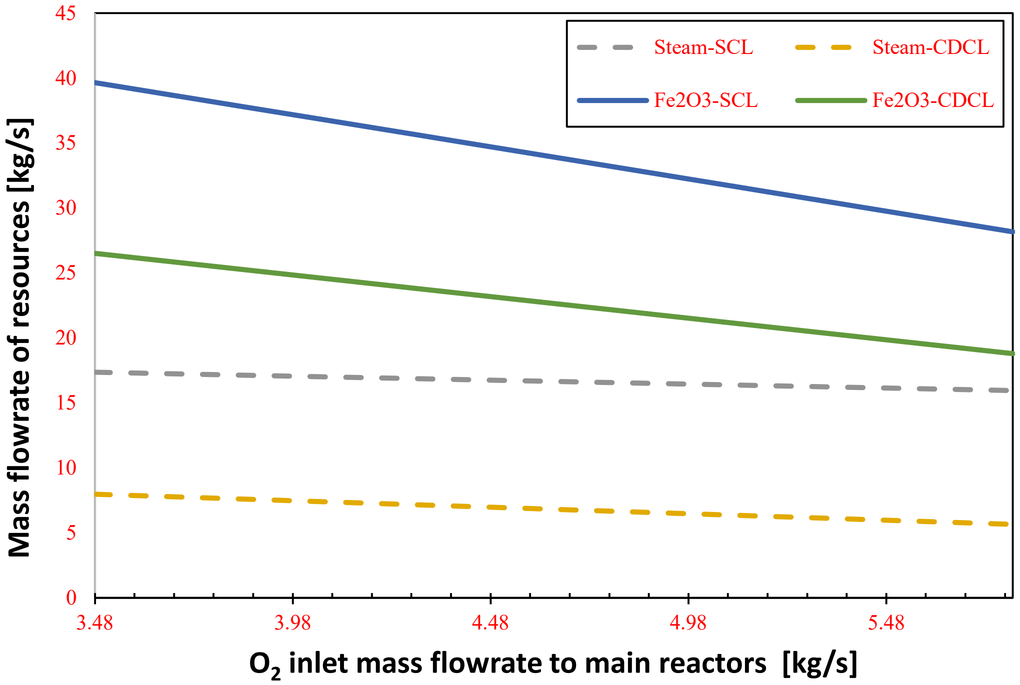


Fig. 5.7: Comparison of CDCL and SCL process on the basis of resource requirement with O_2 inlet mass flowrate in the present Models.

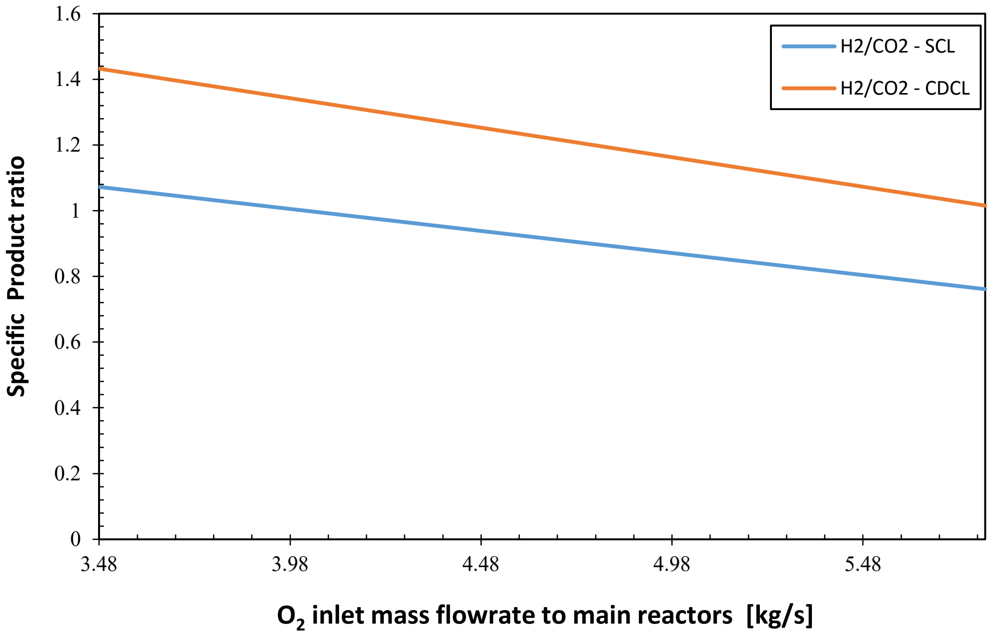


Fig. 5.8: Comparison of CDCL and SCL process on the basis of Hydrogen production to Carbon dioxide (specific ratio) with O_2 inlet mass flowrate in the present Models.

5.2 Results Segment 2: Simulation Results of the Present models when it is extended to Indian coal

In this segment, the ASPEN plus models developed in the Segment-1 study is improved in respect of Indian coal which generally contains high Ash amount. To study the effect of Coal carrier gas and Temperature of the main reactors sensitivity analysis has been done in ASPEN Plus software. Gas composition and solids (oxygen carrier and its other reduced states) outputs at each of the Reactors of both the processes have also been analyzed with the input flowrate of the Oxygen to the main reactors (Fuel reactor in CDCL and Gasifier in SCL).

Study in this segment includes set of reactions other than described by [14]. The set of reactions described by [14], included in the segment-1 study, is mentioned in Table 4.1. The set of other significant reactions is shown in Table 4.2. Thermodynamic parameters to check feasibility of the reactions are tabulated in Table 4.3 and 4.4.

All the results consider variations against the input mass flowrate of Oxygen. For the present study, the limiting range of oxygen flowrate is found to be 0.1 kg/s to 4.1 kg/s. The upper limit is due to the complete oxidation of coal along-with material imbalance after crossing 4.1 kg/s of oxygen flowrate.

The study in this segment is divided in three parts. In the first part, each of reactors of both the Processes has been studied to find the general trend of the Gas and Solid composition at the outlets of each of the reactors. As Coal carrier gas, CO_2 is used in this study. Simulations have been run at certain operating condition of temperature and pressure in the reactors which are shown in Table 3.1.

Second part of the study includes the effect of Coal carrier gas on the Over-all final results of the Processes which includes final Products output flowrate variation with Oxygen input flowrate at the same operating condition as used in the first part.

While in the third part, the Effect of variation in Temperature of the Fuel reactor and the Gasifier on the Hydrogen production in both the respective processes is investigated.

5.2.1 Results of the Variation in Gas along-with Solids (oxygen carrier) composition at the outlets of each of the Reactors in either of the processes.

Figures 5.9, 5.10, 5.11 and 5.12 shows the Gas composition alongwith solids at the outlets of each of the main reactors involved in the CDCL process. The solids here describe the Oxygen carrier and its other reduced states. Fig 5.9 describes the Gas composition and unburned Carbon at outlet of the Fuel reactor's partial combustor. According to the figure, Unburned carbon decreases from around 80kg/min at 0.1 kg/s of input mass flowrate of oxygen to 0 kg/min at 3.7 kg/s of oxygen flowrate. Carbon dioxide composition increases from 5.95 kg/s to 14.56 kg/s. But this includes the incoming Carbon dioxide as Coal carrier gas coming at flowrate of 10 kg/s. Initially the Coal carrier Carbon dioxide gets reacted and used up until the oxygen flowrate reaches 2 kg/s after which net CO_2 gets produced in the reactor. In case of Carbon monoxide, it decreases from 7.13 kg/s to 2.12 kg/s. It is obvious to see that the composition of CO decreases and CO_2 increases with increasing oxygen flowrate. Due to deficiency of oxygen, Methane composition is higher at lower oxygen flowrate. As the oxygen flowrate increases methane converts into CO, CO_2, and H_2 & H_2O. Therefore, Hydrogen initially increases but after enough oxygen flowrate it again decreases and converts to H_2O. Due to this, H_2O initially increases at slower rate than after enough oxygen flowrate increases at faster rate.

Figure 5.10 describes the Gas and Solid composition at the outlet of the Fuel reactor –Top section. Due to Char gasification in this reactor, all the Unburned carbon is converted to CO. Apart from this, Reduction of oxygen carrier from Fe_2O_3 to FeO lead to formation of CO_2 and H_2O. As the oxygen flowrate increases, requirement of oxygen carrier decreases. Therefore the FeO composition at the outlet is decreasing with increasing oxygen flowrate. Also the composition of Carbon dioxide increases and Carbon monoxide decreases with oxygen flowrate.

Figure 5.11 shows the products composition at the outlet of the Fuel reactor – Bottom section. It can be seen that all of the FeO produced in the Top section due to reduction of oxygen carrier has been converted to Fe. As the FeO composition decreases at outlet of Top-section, similarly the composition of Fe is decreasing with oxygen flowrate to fuel reactor. Due to the reduction of FeO all carbon containing components converted to CO_2 and all of the Hydrogen converted to H_2O. Cyclone separator is added at the outlet of the Fuel reactor to separate the solid Fe from gases CO_2 and H_2O which would further be separated by partial condensation of the Gas stream. Now the Fe is sent to the Hydrogen reactor for its oxidation using Steam which would lead to formation of Hydrogen and Iron (ii iii) oxide (hematite). So, the Product composition at the outlet of the Hydrogen reactor is shown in Figure 5.12.

Figures 5.13, 5.14, 5.15 and 5.16 shows the Gas composition along-with solids at the outlets of each of the main reactors involved in the SCL process. Oxygen carrier and its reduced states have been termed as solids. Fig 5.13 describes the Gas composition and unburned Carbon at outlet of the Gasifier. According to this Figure, There is no Unburned carbon remaining at the outlet of the gasifier. This means that all of the Carbon oxidizes in the Gasifier which is due to the fact that Gasification is done using both Oxygen and Steam. Carbon dioxide composition increases from 10 kg/s to 15.5 kg/s. But this includes the incoming Carbon dioxide as Coal carrier gas coming at flowrate of 10 kg/s. Unlike the Fuel reactor-partial combustor, here net Carbon dioxide is produced in the Gasifier. In case of Carbon monoxide, it decreases from 5.02 kg/s to 1.53 kg/s. It is obvious to see that the composition of CO decreases and CO_2 increases with increasing oxygen flowrate. Due to deficiency of oxygen, Methane composition is higher at lower oxygen flowrate but it is negligible as its composition varies in the range of 10^{-8}. As the oxygen flowrate increases methane converts into CO, CO_2, and H_2.

Figure 5.14 describes the Gas and Solid composition at the outlet of the Reduction reactor-1. Reduction of oxygen carrier from Fe_2O_3 to FeO lead to formation of CO_2 and H_2O. As the oxygen flowrate increases, requirement of oxygen carrier decreases. Therefore the FeO composition at the outlet is decreasing with increasing oxygen flowrate. Also the composition of Carbon dioxide increases and Carbon monoxide decreases with oxygen flowrate.

Figure 5.15 shows the products composition at the outlet of the Oxidation reactor-1. Cyclone separator is added at the outlet of the Reduction reactor-1 to separate the solids Fe/FeO from gases CO, CO_2, H_2 and H_2O which would further sent to second stage Reduction reactor. Fe/FeO is sent to the Oxidation reactor-1 for oxidation using Steam which would lead to formation of Hydrogen and Hematite. Fe_3O_4 is sent to the Air combustor -1 where it is oxidized to Fe_2O_3. In the Reduction reactor-2, Fe_2O_3 is again reduced by the unreacted syngas from reduction reacto-1. After separation of solids from the Gaseous product using the Cyclone separator, Fe/FeO and unreacted Fe_2O_3 sent to the Oxidation reactor-2 for further production of Hydrogen using steam along-with regeneration of Fe_2O_3 The Product composition at the outlet of the Oxidation reactor-2 is shown in Figure 5.16.

Figures 5.17, 5.18, 5.19 and 5.20 show the Final product output of the CDCL and SCL processes. Figures 5.17 and 5.18 describe the variation in Product output of the CDCL process when the Coal carrier gas used is CO_2 and N_2, respectively. Figures 5.19 and 5.20 describe the variation in Product output of the SCL process when the Coal carrier gas used is CO_2 and N_2, respectively. It can be seen from the Figures that Hydrogen production is higher at lower oxygen flowrate to main reactors and decreases with increasing oxygen flowrate. Whereas, the Carbon dioxide emission remains constant throughout the mass flowrate range of the Oxygen. In case of SCL process, there is emission of Methane in very little amount in range 0 to 0.03 Std.m^3/hr which is negligible amount.

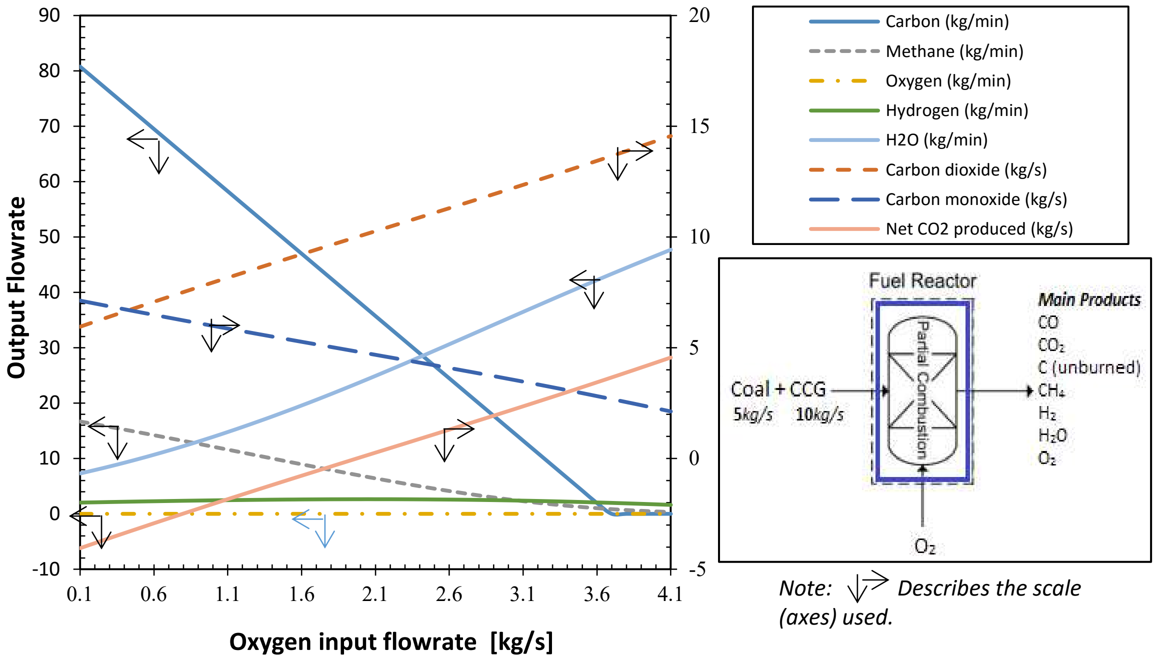
Figures 5.21, 5.22, 5.23 and 5.24 show the Resource requirement for the CDCL and SCL processes. Figures 5.21 and 5.22 describe the variation in resource requirement in CDCL process when the Coal carrier gas used is CO_2 and N_2, respectively. Figures 5.23 and 5.24 describe the variation in resource requirement in SCL process when the Coal carrier gas is CO_2 and N_2, respectively. As can be seen from figures, oxygen carrier (Fe_2O_3) requirement decreases with increasing oxygen flowrate. Similarly the Steam requirement also decreases with increasing oxygen flowrate. Unlike the CDCL process, in SCL process after a certain oxygen flowrate the oxygen carrier requirement is same. The possible reason could be unreacted oxygen increasing at outlet of Gasifier after a certain oxygen flowrate.

Comparing the Figures 5.17 and 5.19 or 5.18 and 5.20, it is observed that the Hydrogen production plot crosses the Carbon emission at higher oxygen flowrate in CDCL process than the SCL process. This means Hydrogen to Carbon dioxide emission (product volumetric ratio) is Higher in CDCL than SCL process. Apart from this, it is also observed that there is negligible effect of Coal carrier gas on the Product output and resources requirement in CDCL process.

Figure 5.25 and 5.26 show the Variation in Final product- Hydrogen production due to the effect of Temperature change of Gasifier of SCL process when the Coal carrier gas used is CO_2 and N_2, respectively. The variation in case of CDCL found to be very less due to the fact that the fuel reactor has been divided in three parts for simulation purpose. It can be seen from the Figures 5.21 and 5.22 that the hydrogen production increases with Temperature change. The other important observation is the variation in Hydrogen production with temperature is higher at lower oxygen flowrate and gradually decreases as the oxygen flowrate increases.

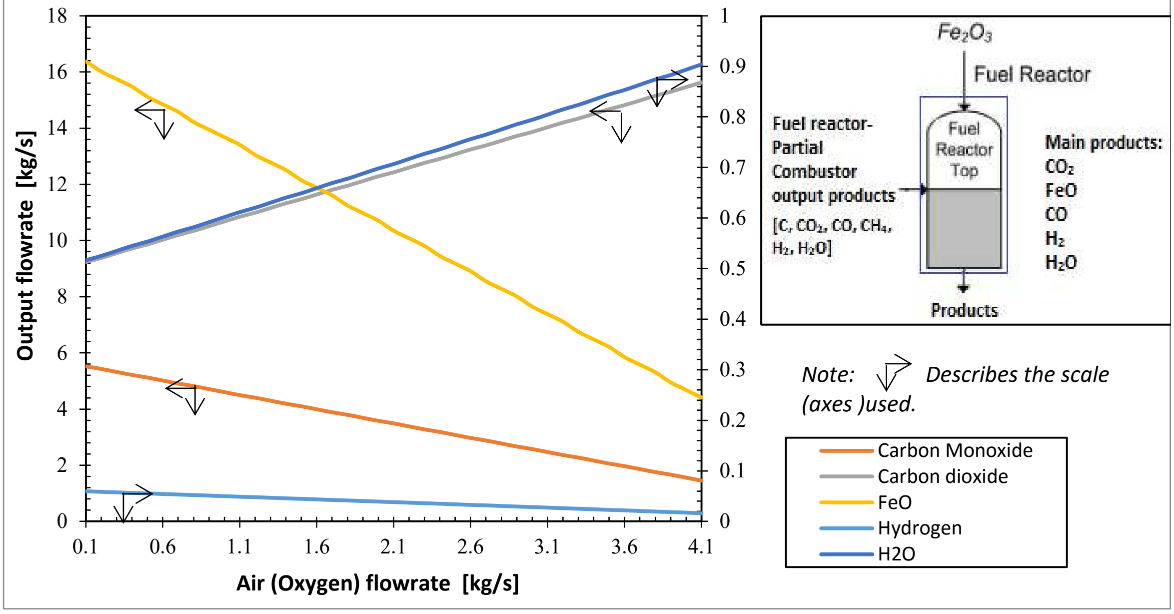
The reactions taking place at different temperatures can be found from the thermodynamics data shown in the Tables 4.3 and 4.4. According to these tables, from 400^0C to 475^0C reactions 4.1, 4.2, 4.3, 4.13, 4.14, 4.15, 4.17, 4.19 and 4.22 are feasible and spontaneous. In range of temperature from 475^0C to 650^0C, reactions that are feasible and spontaneous are 4.1, 4.2, 4.3, 4.13, 4.14, 4.15, 4.17, 4.19 and 4.22. While in the temperature range of 650^0C to 707^0C, reactions 4.1, 4.2, 4.3, 4.13, 4.15, 4.16, 4.19 and 4.22 are feasible. And in the range greater than 707^0C till 1000^0C, reactions 4.1, 4.2, 4.3, 4.4, 4.5, 4.13, 4.14, 4.15, 4.17, 4.19 and 4.22.

Fig.5.9: Gas composition at the outlet of the Fuel reactor-Partial Combustor in CDCL when input is 5kg/s Coal with Coal carrier gas as CO_2 (10kg/s)



Note: Describes the scale (axes) used.

Fig.5.10: Gas composition at the outlet of the Fuel reactor- Top section (Gasification and Oxygen Carrier reduction) when Process input is Coal 5kg/s with Coal carrier gas as CO_2 (10kg/s)



Note: Describes the scale (axes)used.

Fig.5.11: Product composition at the outlet of the Fuel reactor- Bottom section (FeO reduction) when Process input is 5kg/s Coal with Coal carrier gas as CO_2 (10kg/s)

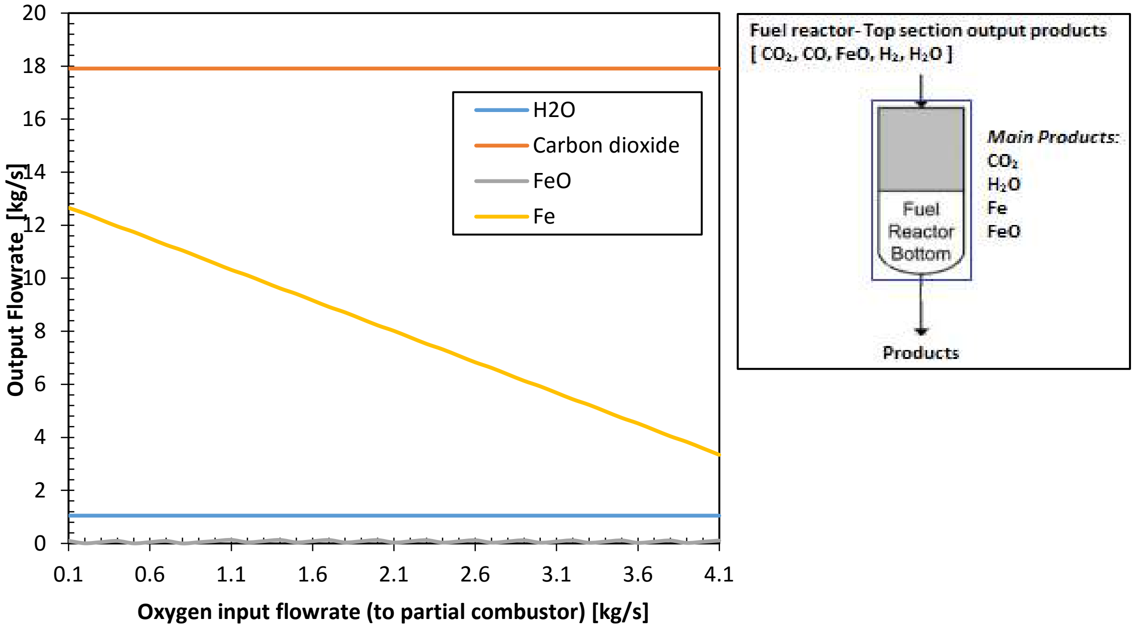
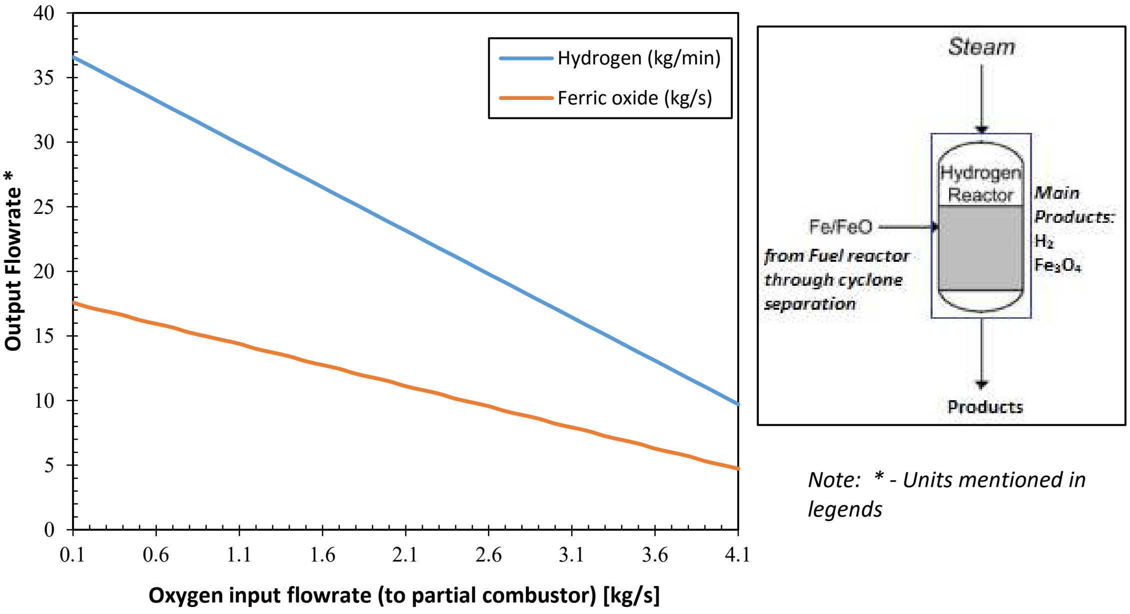
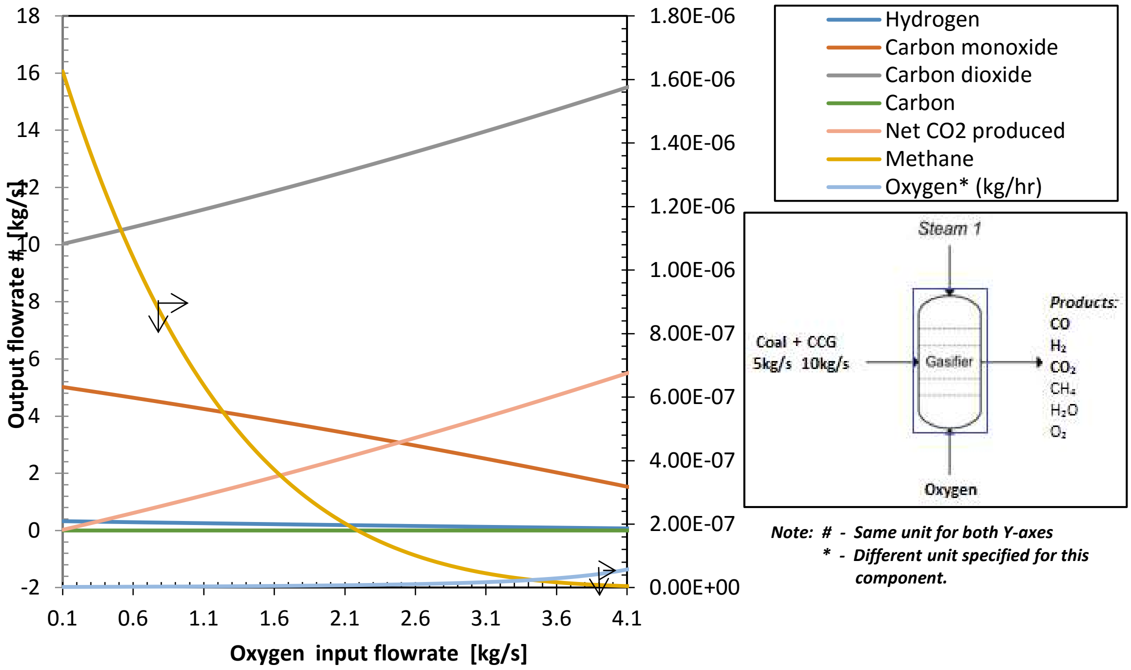


Fig. 5.12: Product composition at the outlet of Hydrogen reactor when Process input is 5kg/s Coal with Coal carrier gas as CO_2 (10kg/s)



*Note: * - Units mentioned in legends*

Fig.5.13 SCL process: Gas composition at the outlet of the Gasifier when input is 5kg/s Coal with Coal carrier gas as CO_2 (10kg/s)



Note: # - Same unit for both Y-axes
** - Different unit specified for this component.*

Fig.5.14 SCL process: Product composition at the outlet of the Reduction reactor-1 when input is 5kg/s Coal with Coal carrier gas as CO_2 (10kg/s)

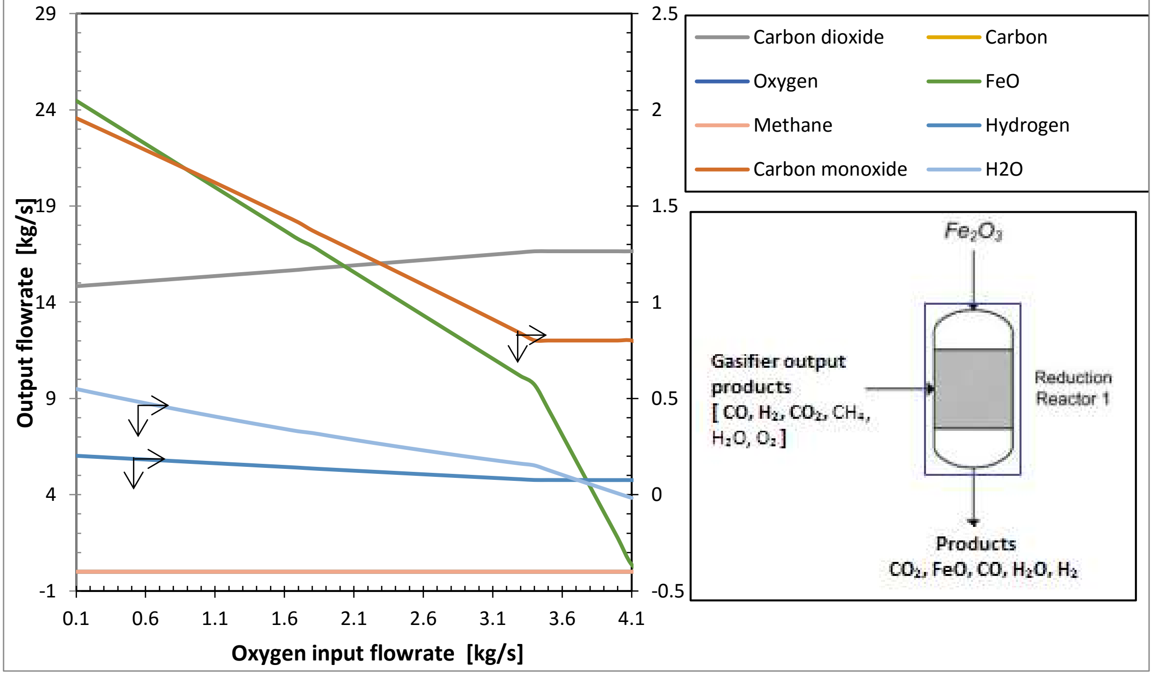


Fig.5.15 SCL process: Product composition at the outlet of the Oxidation reactor-1 when input is 5kg/s Coal with Coal carrier gas as CO_2 (10kg/s)

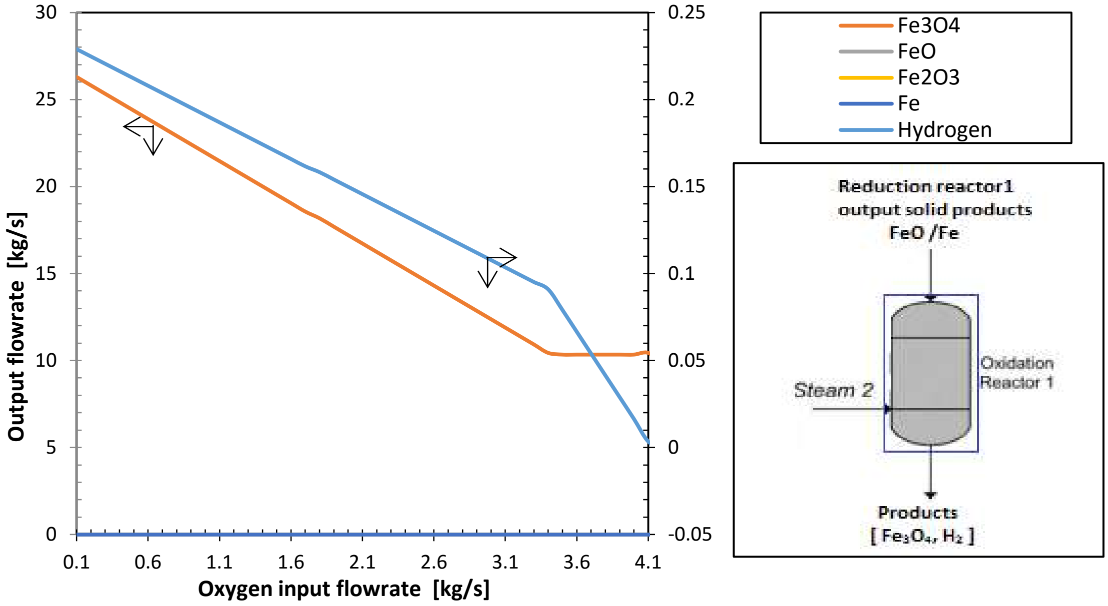


Fig.5.16 SCL process: Product composition at the outlet of the Oxidation reactor-2 when input is 5kg/s Coal with Coal carrier gas as CO_2 (10kg/s)

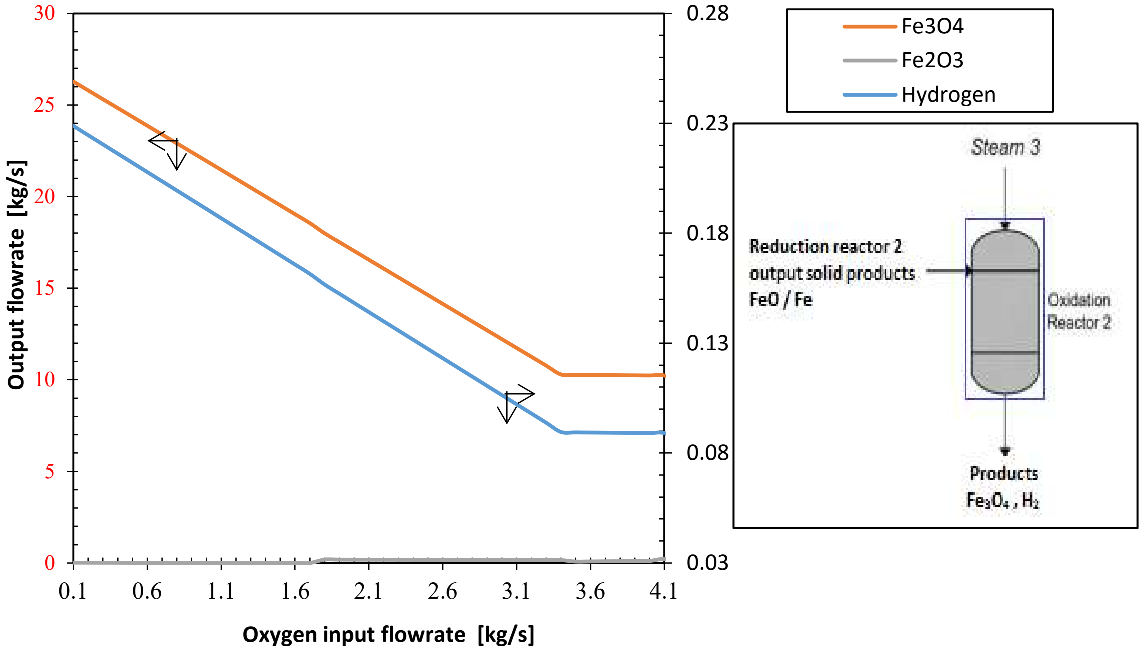


Fig.5.17: Overall process output product composition of the Coal Direct Chemical Looping Process when input is 5kg/s Coal and 10kg/s Coal carrier gas (CO_2)

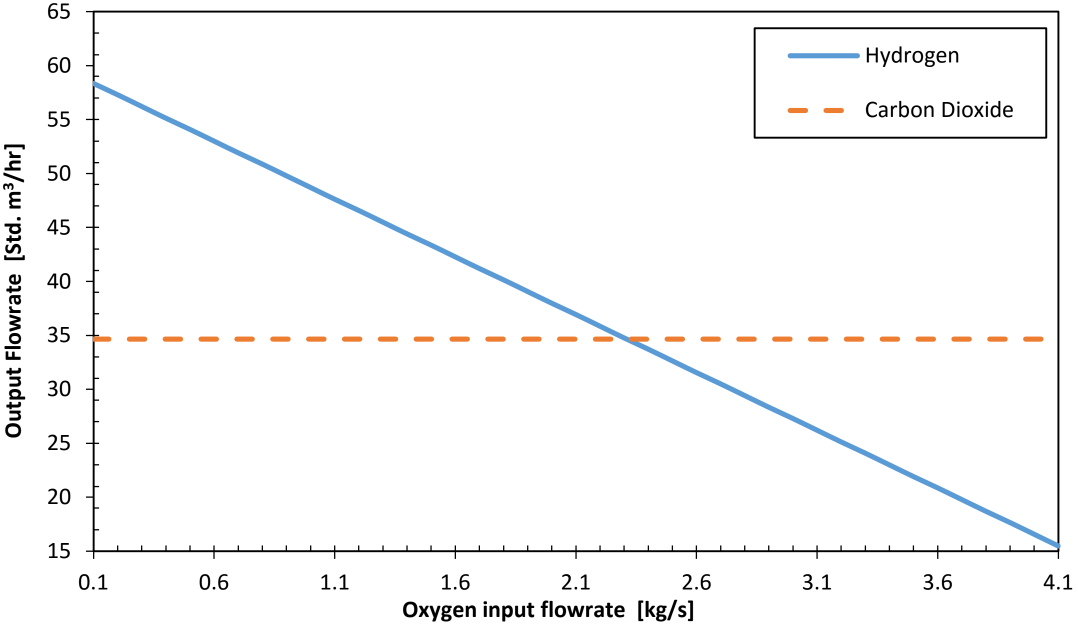


Fig. 5.18: Overall process output product composition of the Coal Direct Chemical Looping Process when input is 5kg/s Coal with 10kg/s Coal carrier gas (N_2)

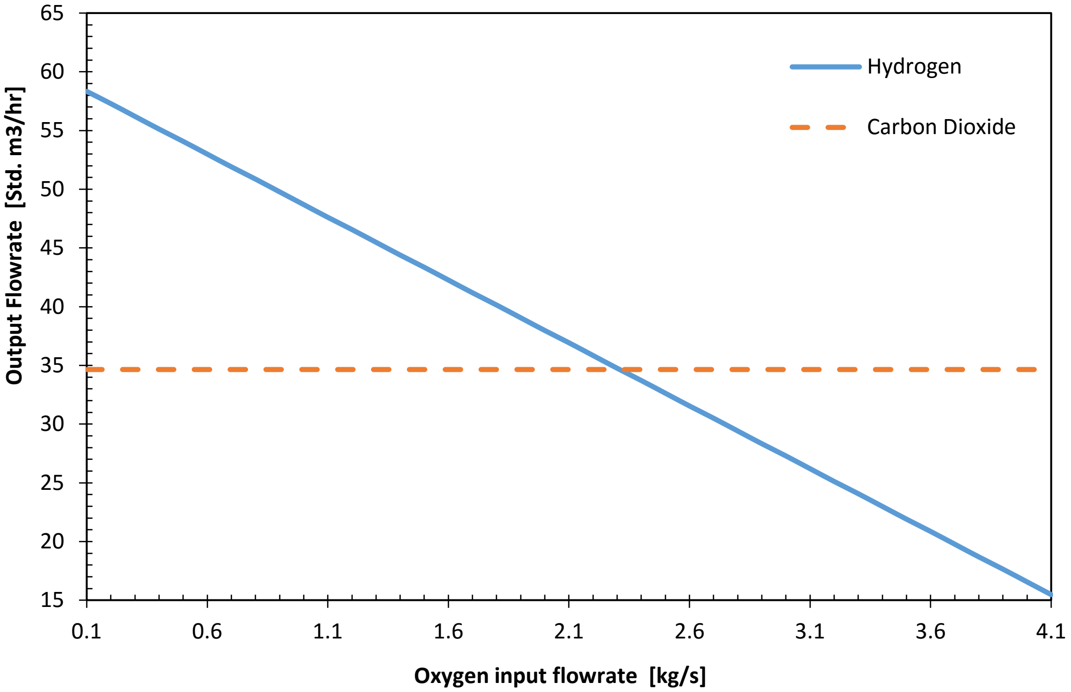


Fig. 5.19: Overall process - output product composition of the Syngas Chemical Looping Process when input is 5kg/s Coal and 10kg/s Coal carrier gas (CO_2)

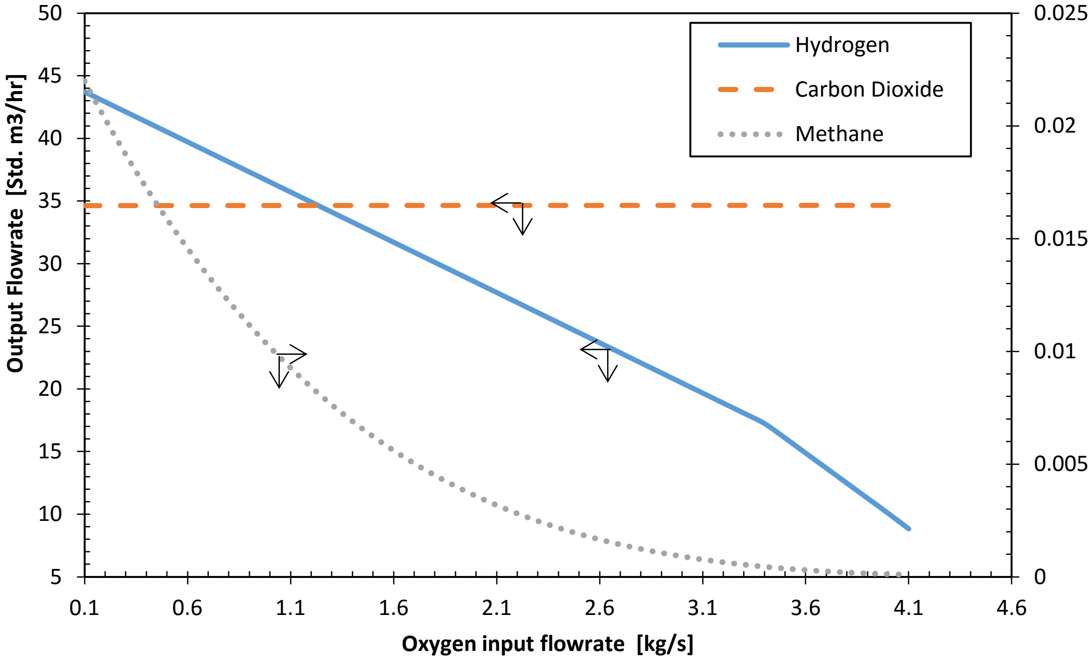


Fig. 5.20: Overall process - output product composition of the Syngas Chemical Looping Process when input is 5kg/s Coal and 10kg/s Coal carrier gas (N_2)

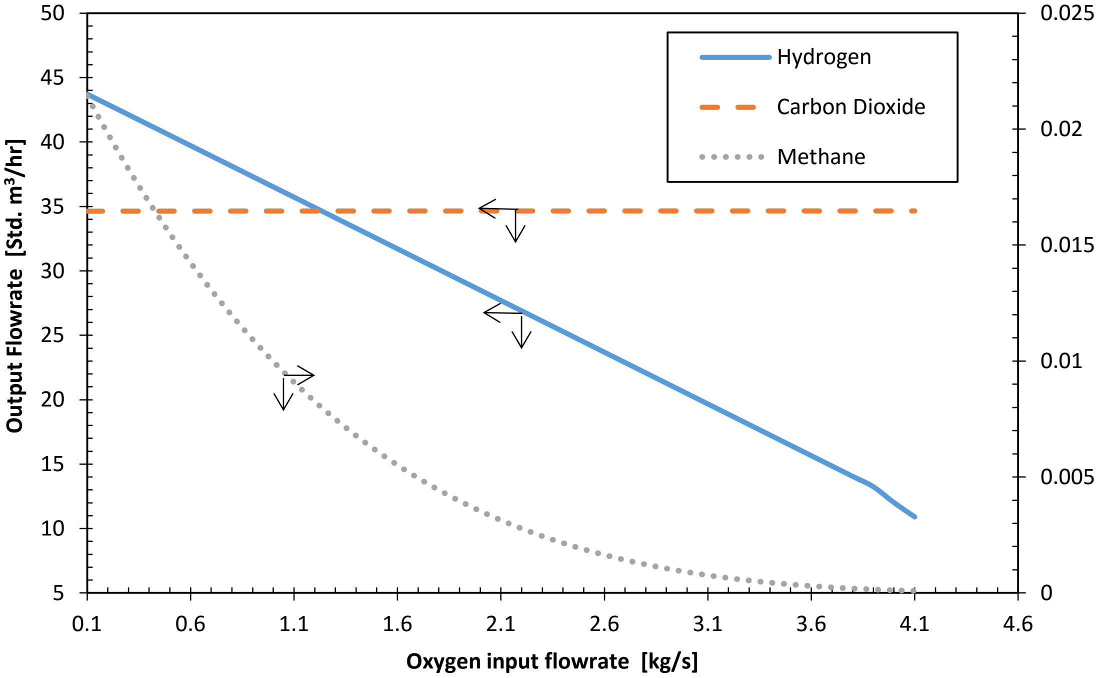


Fig. 5.21: Utilities requirement for the Coal Direct Chemical Looping Process when input is 5kg/s Coal and 10kg/s Coal carrier gas (CO_2)

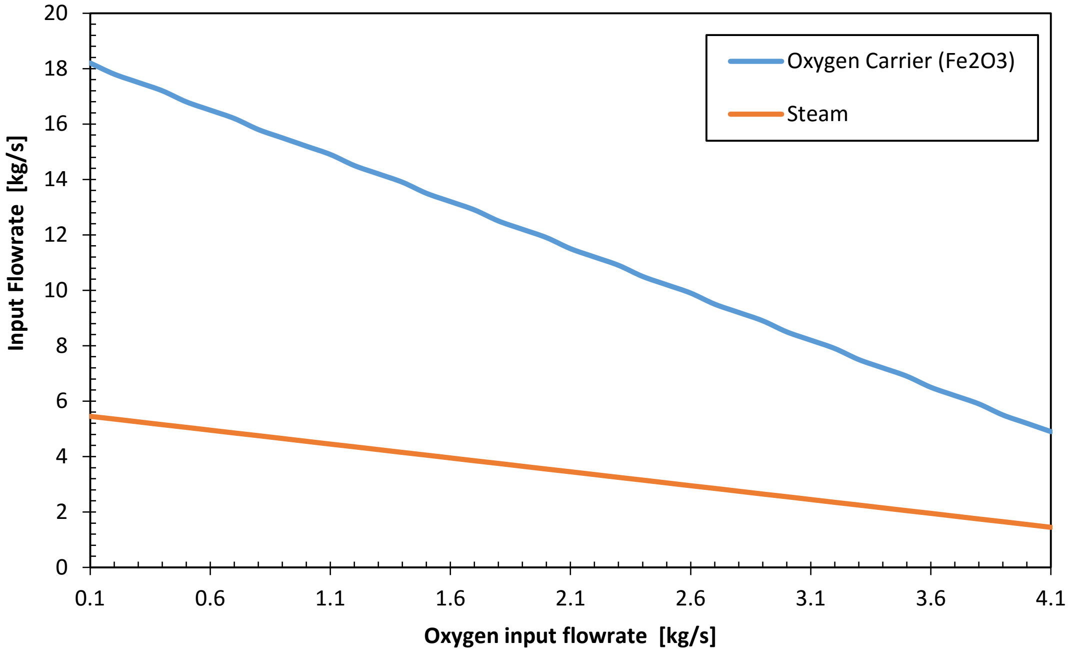


Fig. 5.22: Utilities requirement for the Coal Direct Chemical Looping Process when input is 5kg/s Coal and 10kg/s Coal carrier gas (N_2)

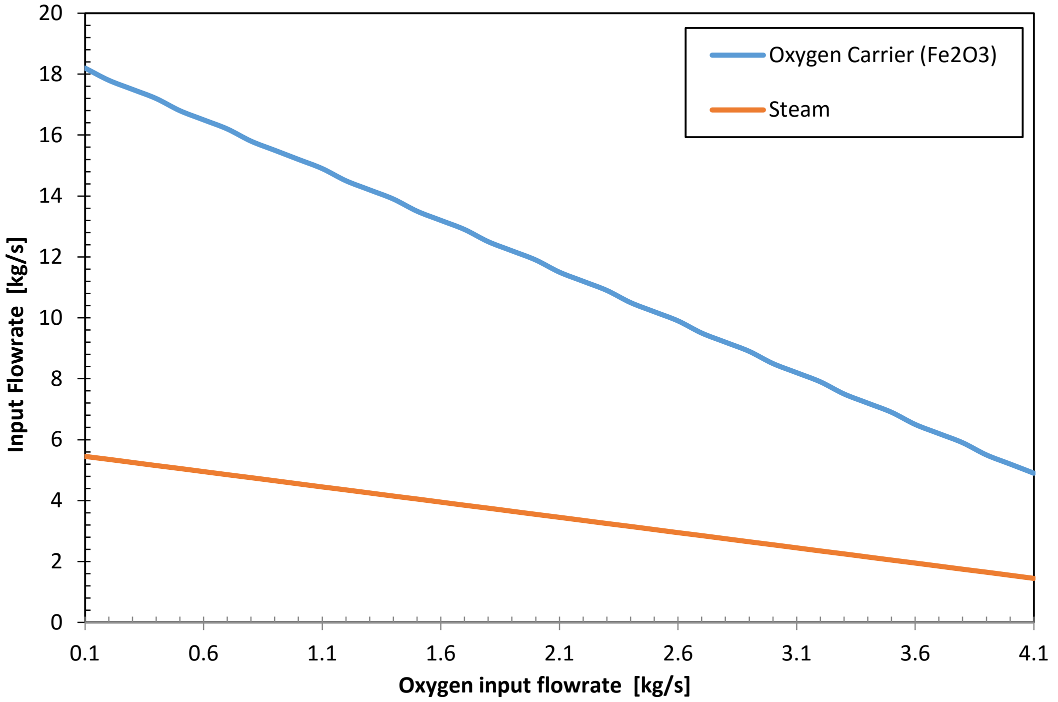


Fig. 5.23: Utilities requirement for the Syngas Chemical Looping Process when input is 5kg/s Coal and 10kg/s Coal carrier gas (CO_2)

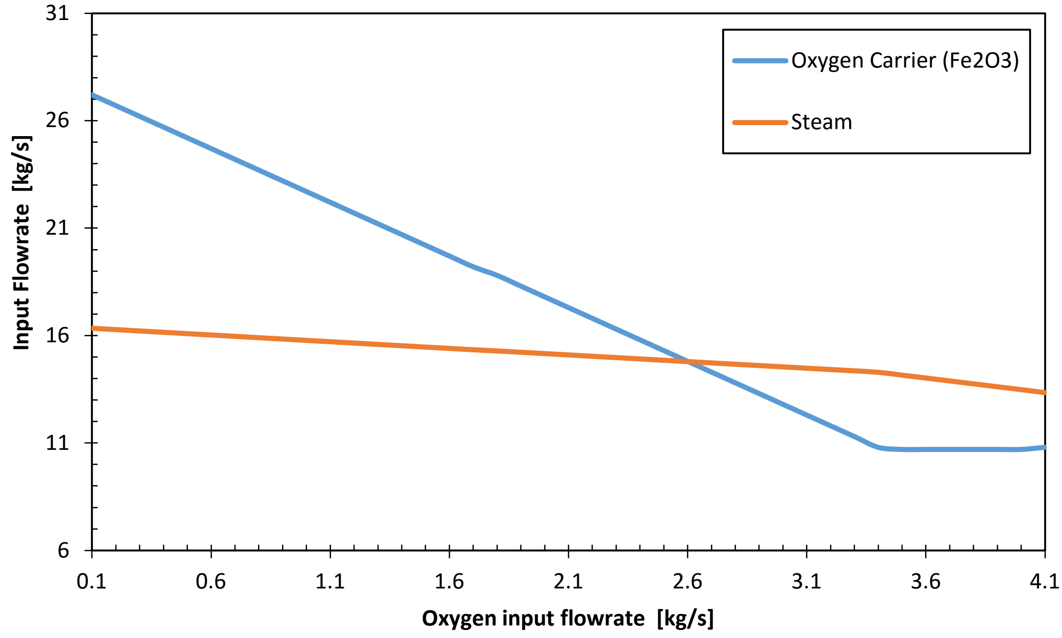


Fig. 5.24: Utilities requirement for the Syngas Chemical Looping Process when input is 5kg/s Coal and 10kg/s Coal carrier gas (N_2)

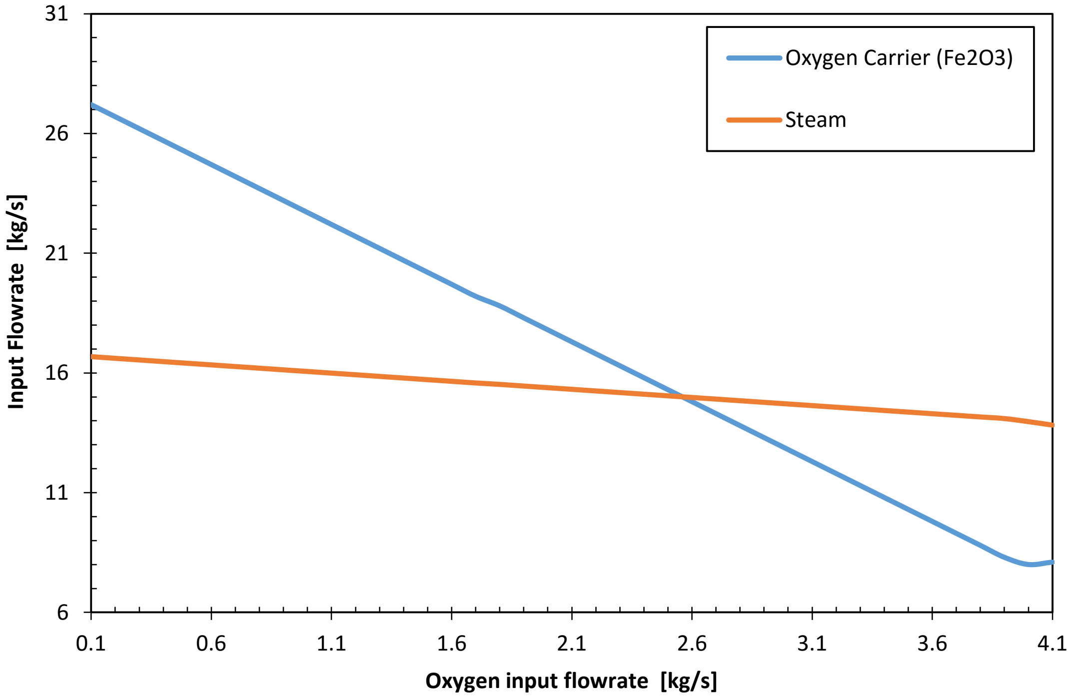


Fig 5.25 **SCL Process: Effect of Gasifier Temperature variation on Overall process Hydrogen Production** when **input is *5kg/s* Coal** with **Coal carrier gas** as **CO_2 *(10kg/s)***

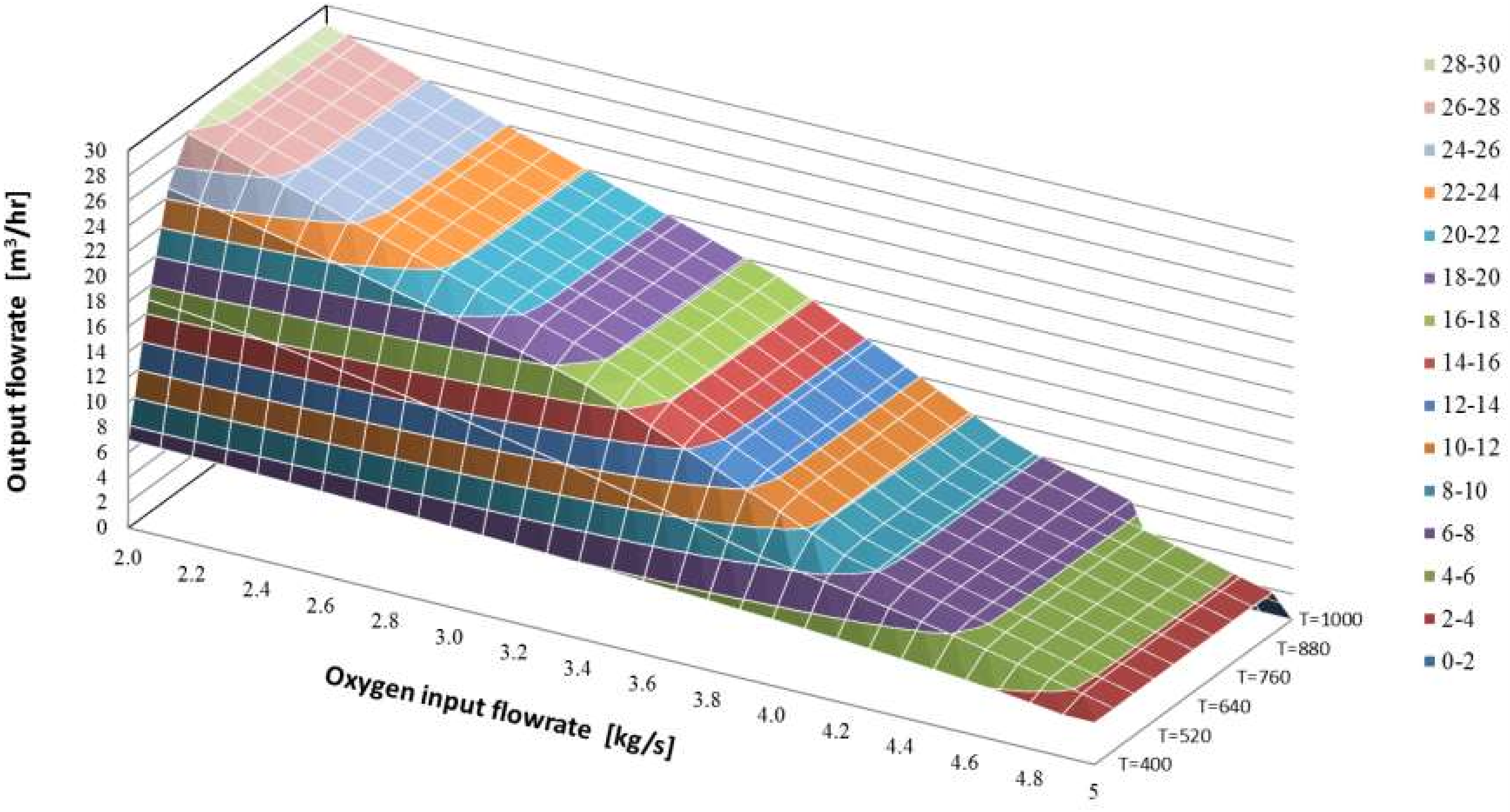
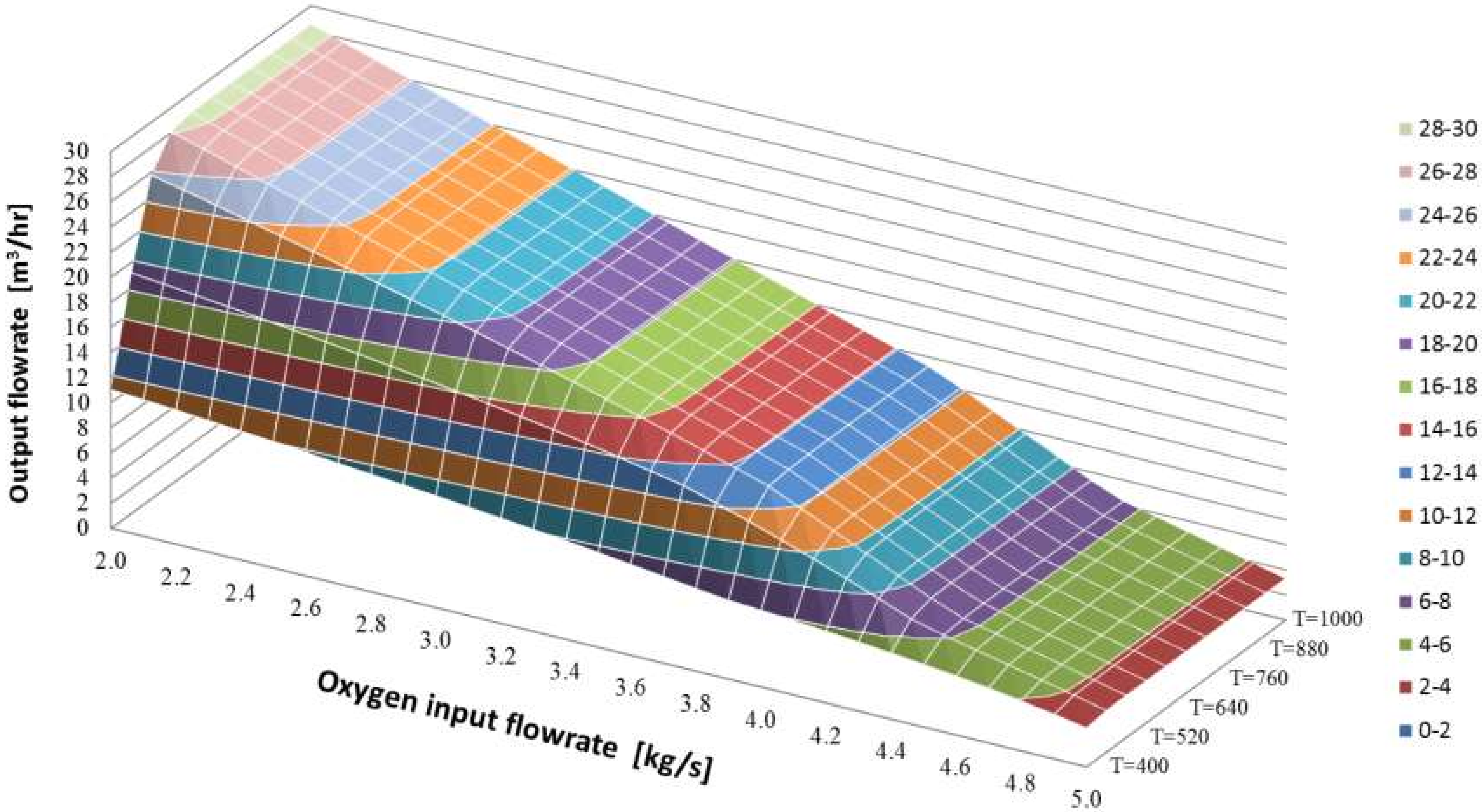


Fig 5.26 SCL Process: Effect of Gasifier Temperature variation on Overall process Hydrogen Production when **input is *5kg/s* Coal** with **Coal carrier gas** as **N_2** ***(10kg/s)***



Chapter 6 *CONCLUSIONS & RECOMMENDATIONS*

The salient conclusions of the present ASPEN Plus models simulation of coal direct chemical looping and syngas chemical looping processes are as follows:

Conclusions from First segment of study

1. Results of present ASPEN Plus model for CDCL process taking into account the reactions used in first segment are in good agreement with the results published in the [14]. The simulated Hydrogen production, and Carbon dioxide emission where CO_2 is used as Coal carrier gas show error equal to 11.34%, and 10.45%, respectively, at the maximum hydrogen production.

2. Further, results of present ASPEN Plus model for SCL process taking into account the reactions used in first segment are also in fine agreement with the results published in the [14]. The simulated Hydrogen production, and Carbon dioxide emission where CO_2 is used as Coal carrier gas shows error equal to 30.76%, and 10.53%, respectively, at the maximum hydrogen production.

3. The possible reason for the errors could be the Coal properties used by [14] for simulations is different from the one indicated in [14]. This statement of using different coal for simulation has been mentioned in [14] by the authors. Apart from this, the reactions considered in the present Models are the set of other significant reactions in addition to the reactions mentioned in [14]. Another valid reason for results of SCL process could be the methane has been set as inert in the publication whereas, it is considered in the set of reactions.

4. The conclusions given above in points 1 & 2 and the justification described in the point 3 clearly indicates that the present ASPEN Plus models are sufficiently good enough and can be used for CDCL and SCL processes simulation if the above error limits can be tolerated.

5. Further, from the results of Carbon dioxide emission which is throughout constant and same for both the processes, it can be concluded that both the processes are capable of total carbon capture.

Conclusions from Second segment of study

The ASPEN models developed, incorporating thirteen reactions as proposed by [14] and nine more reactions, which has been validated with the simulated results of the [14] is used in second segment to study the Gas and Solid (oxygen carrier and its other states) composition at the outlet of each of the important reactors of both the processes. The effect of Coal carrier gas on the product output and Temperature in the main reactors (Gasifier in the SCL process and Fuel reactor in CDCL process) on the Hydrogen production is also studied in this segment. The salient conclusions of this study are listed below:

1. Hydrogen production for the CDCL process is higher than that of SCL process when Coal carrier gas used is same.

2. Carbon dioxide emission is around same and constant for both the processes. As mentioned in the conclusions of first segment, it concludes that both the processes are capable total carbon capture (about 100%).

3. For the set operating conditions of Temperature and Pressure, the effect of Coal carrier gas on final product output is negligible for both the processes.

4. The results of the Gas and Solid composition at the outlet of each of the important reactors involved in the processes follows the general trend anticipated from the thermodynamic feasibility of the reactions mentioned in chapter 4.

5. The effect of temperature on hydrogen production in SCL process describes that hydrogen production increases with increase in temperature till temperature of about 580^0C. After this, the temperature effect is negligible.

6. The combined effect of Coal carrier gas and temperature shows that Hydrogen production is higher at lower temperature when N_2 is used as coal carrier gas as compared to when CO_2 is used.

Recommendations

Further, in development of ASPEN Plus model for coal direct chemical looping technology, research on following topics is recommended:

1. Development of process model using the recently found cost-effective oxygen carrier Red mud-bauxite waste produced from the Bayer’s alumina production process.

2. Attempt should be made to develop ASPEN Plus process model incorporating the effect of Ash content in solid fuel Coal.

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