# Increased Use of Natural Gas in Blast Furnace Iron-making

Submitted in partial fulfillment of the requirements for

the degree of

Doctor of Philosophy

in

Materials Science & Engineering

Megha Jampani

B.Tech. in Metallurgical Engineering, Jawaharlal Nehru Technological University M.S. in Materials Science and Engineering, Carnegie Mellon University

> Carnegie Mellon University Pittsburgh, PA

> > August, 2016

#### Acknowledgements

I would like to express my gratitude to Dr. Chris Pistorius, for his patience, encouragement and guidance throughout the course of this work. I am extremely privileged to be working with him. Dr. Pistorius truly inspires his students to not just be diligent at work, but to be better people.

My family has been the biggest support for me, throughout my life. The distance between us these last few years, only made all the love and support stronger. I owe everything to my mother- whose hard work is the reason I am here.

One of the best things that happened to me in the past few years, was getting to know Jorge Gibson, Ph.d. His support cannot be quantified in this acknowledgement section. I will always cherish all the fun I was allowed to (and will continue to) poke at him.

I would also like to thank Ming Tang, Deepoo Kumar, Dai Tang, Farzin Fatollahi-Fard, Stephano Piva, Mauro Elias, Karina Assis, Andre Assis and all my colleagues for the numerous group meetings, dry-runs and for all the help they provided.

I extend my love and gratitude to Baljeet Yadav, for making this journey more amazing. Aditya Jampani, Nikita Roy, Tugce Ozturk, Ashwin Govindarajan, Kritika Ramani, Prashanth Jampani, thank you all for being there always.

I am grateful to my committee members, Dr. Richard Fruehan, Dr. Bryan Webler and Dr. Michael Riley for their valuable critique and support. Their input has been invaluable and greatly appreciated.

I would like to thank the industrial members of the Center for Iron and Steelmaking Research (CISR) for the financial support and the direction they provided at every step. I would also like to thank all the MSE staff and faculty, especially Roxann Eckman, Jeanna Pekarcik, Suzanne Smith, Adam Wise, William Pingitore and Tom Nuhfer for their continuous help.

#### Abstract

Steelmaking is a highly carbon intensive process. Most of the CO<sub>2</sub> emissions in steelmaking are from the blast furnace. Coke has been the major reductant used in a blast furnace since 1750. The recent boom in the US energy outputs due to shale rock formations has motivated the need to look at natural gas as a partial replacement for coke in a blast furnace. During the course of this project, the impact of higher natural gas utilization has been studied in detail. Theoretical models suggesting the injection of natural gas as a viable method to replace coke partially have been used. These theoretical claims have then been tested experimentally and the results have been discussed. The experimental work described includes reduction of hematite to wüstite, followed by the study of interaction of natural gas with a bed of iron pellets replicating the wüstite reserve zone of a blast furnace. Furthermore, the reforming of methane over metallic iron pellets was investigated and these reactions were tested under blast furnace conditions. Mass and energy balance calculations, along with experimental results were used to support the proposed shaft injection of natural gas.

Ac	knov	wle	dgementsii
Ab	ostra	ct.	iii
Та	ble o	of C	ontentsiv
Lis	st of	Tal	bles viii
Lis	st of	Fig	gures xii
1.	In	tro	duction2
-	1.1	Blas	st furnace iron-making 2
-	1.2	В	last furnace reactions
2.	Mo	otiv	vation4
2	2.1	N	atural gas utilization history4
3.	Те	chr	nical Background7
	3.1	Iı	ncreasing natural gas utilization7
	3.2	D	Pirect reduction of Iron
	3.2	2.1	HYL Zero Reforming process9
	3.2	2.2	MIDREX reformer
	3.2	.3	Ultra-low CO2 Steelmaking13
ļ	3.3	W	Vüstite reserve zone14
	3.3	.1	Expected reactions in the wüstite reserve zone15
	3.4	Т	he 'Rist' mass and energy balance17
	3.4	.1	Raceway Adiabatic Flame Temperature18
	3.4	1,2	Blast temperature19
	3.4	1.3	Top Gas temperature19

# **Table of Contents**

4. Obje	ective and Hypotheses 20
4.1	Objective 20
4.2	Hypotheses
5. Mas	s and energy balance calculations22
5.1	Background 22
5.2	Tuyère injection of natural gas 23
5.2.1	Operating window and TCE26
5.3	Shaft injection of natural gas
5.3.1	Shaft injection and TCE31
5.3.2	2 Coke Replacement Ratio
5.3.3	3 Production rate
5.3.4	4 Endothermic Effect of Shaft Injection37
5.3.5	5 Overall Consumption of Oxygen
5.3.6	5 Unreacted natural gas
6. Con	nbustion of methane 42
6.1	Literature review
6.2	'Kintecus' combustion modeling 43
6.3	Methane combustion calculations using Kintecus 45
6.3.1	Discussion
6.3.2	2 Step-wise combustion of methane
6.4	Safe mixing distance
6.5	Pre-heating methane
6.5.1	Pre-heat energy calculations56
7. Exp	erimental work59
7.1	Background

7	.2	The experimental setup	0
	7.2.1	Modified experimental setup6	4
7	.3	Experimental parameters	5
	7.3.1	Gas flowrates	5
	7.3.2	2 Blast furnace pellets	5
8.	Res	ults and Discussion6	7
8	.1	Reduction of hematite to wüstite	7
8	.2	Methane- wüstite interaction experiments7	'1
	8.2.1	1 Literature review: Methane and iron oxides7	'1
	8.2.2	2 Experimental work	4
8	9.3	Modifying the proposed shaft injection7	8
	8.3.1	Impact of lower shaft injection on mass and energy balance calculations 7	9
8	3.4	Reduction of hematite to metallic iron	0
8	5.5	Methane Reforming	D
	8.5.1	1 Literature review8	1
	8.5.2	2 Dry reforming of methane over metallic iron pellets	6
	8.5.3	3 Steam reforming of methane over iron pellets	3
	8.5.4	4 Post-experiment sample analysis 10	0
8	8.6	Reforming over cementite pellets10	5
8	.7	Mixed reforming and Blast furnace gas10	7
	8.7.1	1 Background	7
	8.7.2	2 Experimental work	8
	8.7.3	3 Experiment #2 10	9
	8.7.4	4 Experiment #311	1
8	8.8	Comparison with blast furnace conditions 11	7

9. C	ost estimate	
9.1	Capital investment	
9.2	Operating costs	
9.3	Cost benefit	
10.	Review of hypotheses	
11.	Conclusion	
12.	References	

## List of Tables

Table 1: Assumed compositions of inputs, slag and hot metal (mass percentages). These
compositions are typical values taken from previous calculations [36]18
Table 2: Table summarizing the impact on coke replacement ratio when the temperature
of methane is increased from 298K to 1200K. These calculations are done at zero
oxygen enrichment of blast and 1000°C blast temperature
Table 3: Table summarizing the blast rate, raceway gas rate and top gas rates at different
natural gas injection rates for the three scenarios considered – all tuyère injection,
1:1 shaft to tuyère injection and all shaft injection. These calculations are for a
1000°C blast temperature and the flame temperature was set at 1800°C. (It must be
noted that 200 kg/THM of natural gas injection for complete tuyère injection, lies
outside the operating window for a furnace and has been shown here only for
comparison)
Table 4: Table shows the total oxygen added to a furnace, based on the point of injection
of 100 kg/THM of natural gas. The shaft $O_2/CH_4$ molar ratio is assumed to be 0.5.
The calculations were done for a 1000°C blast and the flame temperature was set at
1800°C40
Table 5: Top gas compositions for natural gas injection rate of 100kg/THM through
different points of injection. These calculations are for 1000°C blast temperature
and flame temperature was set at 1800°C41
Table 8: Summary of conditions used for Kintecus calculations.    46
Table 9: Gas composition pre and post combustion. Both single step combustion and
step-wise combustion results are shown. For the case of step-wise combustion, each
percentage of species at each step is of the total gas at that step. As $\mathrm{CH}_4$ was added
in parts, there is an increase in gas volume from step 1 to step 2

Table 10: For a case of 100 kg/THM of $CH_4$ to be injected through the furnace shaft. The
$CH_4$ to $O_2$ molar ratio is 4:1. The speed of gas through each pipe has been calculated.
The hot metal produced has been estimated using the 'Rist' mass and energy
balance. Additionally, the gases $CH_4$ and $O_2$ have been assumed to be at 1200K and
2atm pressure
Table 11: Calculation of the safe mixing distance for Cases 1 and 2 ( See page 53). Both
cases consider the injection of 100 kg/THM of $CH_4$ through the furnace shaft and
no tuyère injection. The cases only differ in the molar ratio of $CH_4$ to $O_2$ considered.
The delay in ignition calculations have been done using Kintecus
Table 12: Calculations showing energy available from top gas of the blast furnace and
energy required to heat the blast air and shaft reductant stream to 1273K and 1200K
respectively. Calculations have been performed using the 'Rist' mass and energy
balance
Table 13: Table showing the composition of the pellets that have been used for the
experimental work done as part of this project66
Table 4.4 Henry tite to a fightite and parties are adjusted by table (0)
Table 14: Hematite to wustite reduction experimental details
Table 14: Hematite to wustite reduction experimental details
Table 14: Hematite to wustite reduction experimental details
Table 14: Hematite to wustite reduction experimental details
<ul> <li>Table 14: Hematite to wustite reduction experimental details</li></ul>
<ul> <li>Table 14: Hematite to wustite reduction experimental details</li></ul>
<ul> <li>Table 14: Hematite to wustite reduction experimental details</li></ul>
<ul> <li>Table 14: Hematite to wustite reduction experimental details</li></ul>
<ul> <li>Table 14: Hematite to wustite reduction experimental details</li></ul>

ix

Tab	le 20: Details of the injected gas mixture used in the experiment conducted to
	measure activation energy of steam reforming of methane over a single metallic iron
	pellet

Table 21: Activation energy calculated for each stage of the experiment. The step labels correspond to the change in temperature cycles as shown in Figure 52...... 100

Table 22: Table showing the % weight gained by pellets in 5 dry reforming experiments. The calculated percentage weight gain/pellet is the weight gained by metallic iron pellets. The expected metallic iron weight shows the weight of the pellets after losing 27% of their weight on reduction in a 50%H<sub>2</sub>-50% N<sub>2</sub> atmosphere for 1 hour.

Table 23: Table showing the % weight gained by pellets in 5 steam reforming
experiments. The calculated percentage weight gain/pellet is the weight gained by
metallic iron pellets. The expected metallic iron weight shows the weight of the
pellets after losing 27% of their weight on reduction in a 50%H <sub>2</sub> -50% $\rm N_2$
atmosphere for 1 hour 102
Table 24: Summary of LECO analysis results compared with measured percentage
weight gain in the laboratory. (It must be noted that only part of the actual sample
was sent for LECO testing and the remainder was retained for SEM imaging, XRD,
etc.)105
Table 25: Experimental details of one of methane dry reforming reaction over cementite
pellets
Table 26: Experimental details of interaction of a metallic iron pellet with a gas of
composition similar to a blast furnace gas with shaft injection of methane 109

piping would be done directly from the casting floor [56]. .....123

# List of Figures

Figure 1: Schematic of a blast furnace [3] 2
Figure 2: Natural gas utilization by the North American Blast furnaces from 1997-2015
[6], [9] in comparison with the prices of natural gas, both industrial and
commercial5
Figure 3: Comparison of natural gas used per ton of hot metal in North American
furnaces. The natural gas usage is normalized with respect to the hot metal
produced in the furnaces actually injecting natural gas (dashed line), and with
respect to total hot metal production (dotted line)6
Figure 4: Schematic of a blast furnace showing the currently practiced tuyère injection
and the proposed shaft injection of natural gas7
Figure 5: ENERGIRON ZR Technology [12]: In situ reforming
Figure (, Cinerlified asherestic showing the relevant restion of the UNU Zero referming
Figure 6: Simplified schematic showing the relevant portion of the HYL Zero reforming
process [14]
Figure 6: Simplified schematic showing the relevant portion of the HYL Zero reforming         process [14].         Figure 7: The MIDREX NG <sup>™</sup> Plant : Schematic showing the utilization of natural gas in
Figure 6: Simplified schematic showing the relevant portion of the HYL Zero reforming         process [14].         10         Figure 7: The MIDREX NG <sup>™</sup> Plant : Schematic showing the utilization of natural gas in         the MIDREX reformer [16].
<ul> <li>Figure 6: Simplified schematic showing the relevant portion of the HYL Zero reforming process [14].</li> <li>Figure 7: The MIDREX NG<sup>™</sup> Plant : Schematic showing the utilization of natural gas in the MIDREX reformer [16].</li> <li>Figure 8: Schematic of the top gas recycling experimental furnace of the ULCOS program</li> </ul>
<ul> <li>Figure 6: Simplified schematic showing the relevant portion of the HYL Zero reforming process [14].</li> <li>Figure 7: The MIDREX NG<sup>™</sup> Plant : Schematic showing the utilization of natural gas in the MIDREX reformer [16].</li> <li>Figure 8: Schematic of the top gas recycling experimental furnace of the ULCOS program [25] , showing injection both at the tuyères and the lower shaft of the furnace.</li> </ul>
<ul> <li>Figure 6: Simplified schematic showing the relevant portion of the HYL Zero reforming process [14]</li></ul>
<ul> <li>Figure 6: Simplified schematic showing the relevant portion of the HYL Zero reforming process [14].</li> <li>figure 7: The MIDREX NG<sup>™</sup> Plant : Schematic showing the utilization of natural gas in the MIDREX reformer [16].</li> <li>Figure 8: Schematic of the top gas recycling experimental furnace of the ULCOS program [25] , showing injection both at the tuyères and the lower shaft of the furnace.</li> <li>Figure 9: Simplified sketch of Reichardt's diagram showing the gas-solid thermal equilibrium at the thermal reserve zone in the blast furnace [26].</li> </ul>
<ul> <li>Figure 6: Simplified schematic showing the relevant portion of the HYL Zero reforming process [14]</li></ul>
<ul> <li>Figure 6: Simplified schematic showing the relevant portion of the HYL Zero reforming process [14]</li></ul>
<ul> <li>Figure 6: Simplified schematic showing the relevant portion of the HYL Zero reforming process [14]</li></ul>
<ul> <li>Figure 6: Simplified schematic showing the relevant portion of the HYL Zero reforming process [14]</li></ul>

- Figure 16: Plot showing the impact of a TCE limit on the new operating window. The dashed dot dot line labeled 'TCE = 1GJ' represents the TCE limit for the case with half natural gas injected through the furnace shaft and half through the tuyères; which is the new lower limit for the operating window represented by the shaded

xiii

- Figure 18: Production rate calculations for the three natural gas injection scenarios all tuyère injection, 1:1 shaft to tuyère injection and all shaft injection. The calculations were done for a 1000°C blast temperature and 1800°C flame temperature. The open data points represent the absence of oxygen enrichment of the blast air. The filled data points represent oxygen enrichment of the blast. (It must be noted that 200 kg/THM of natural gas injection for complete tuyère injection, lies outside the operating window for a furnace and has been shown here only for comparison). For all tuyère injection and 1:1 shaft to tuyère injection cases; at natural gas injection rate < 67.5 kg/THM, the O<sub>2</sub> enrichment of blast is zero, i.e. O<sub>2</sub> percentage of blast is 21%. Above 67.5 kg/THM of natural gas injection, enrichment of blast is allowed.

xiv

- Figure 28: Kintecus results showing the concentration of individual gas species as the combustion of methane proceeds. (a)  $CH_4/O_2$  molar ratio is 2:1 at an initial temperature of 1000K, (b)  $CH_4/O_2$  molar ratio is 2:1 at an initial temperature of 1200K, (c)  $CH_4/O_2$  molar ratio is 4:1 at an initial temperature of 1000K, (d)  $CH_4/O_2$  molar ratio is 4:1 at an initial temperature of 1200K, (d)  $CH_4/O_2$  molar ratio is 4:1 at an initial temperature of 1200K, (d)  $CH_4/O_2$  molar ratio is 4:1 at an initial temperature of 1200K, (d)  $CH_4/O_2$  molar ratio is 4:1 at an initial temperature of 1200K, (d)  $CH_4/O_2$  molar ratio is 4:1 at an initial temperature of 1200K, (d)  $CH_4/O_2$  molar ratio is 4:1 at an initial temperature of 1200K.
- Figure 23: Schematic of the step-wise combustion reaction. Here, 1 denotes the initial combustion reaction between 20% of the fuel stream with the oxygen and 2-5 denote the steps in which parts of the fuel stream are added to the product stream.

ΧV

Figure 30: Temperature profile for Step 1 in the step-wise combustion of methane. When
compared to Figure 27 (b), it was seen that the ignition delay considerably reduced
with step-wise combustion. Thus oxygen is consumed faster when the fuel stream is
added in parts
Figure 31: Comparison of the product stream temperatures when $CH_4$ and $O_2$ are reacted
in a single step and in a step-wise manner. The step-wise condition shows that
ignition occurs faster and a higher temperature is achieved with ignition53
Figure 32: Schematic showing the mixing of $CH_4$ and $O_2$ at a safe mixing distance to
ensure complete consumption of oxygen before injection into the blast furnace 54
Figure 33: The complete experimental setup used to study gas interactions with iron ore
pellet bed60
Figure 34: The actual picture and the schematic of the quartz glass reactor used for
studying gas interactions with a bed of iron ore pellets61
Figure 35: Schematic of the modified experimental setup. The $N_2$ gas tank was linked to a
water vapor generator to allow for wetting of N₂. Additionally, a bypass valve was
provided in case dry $N_2$ is required64
Figure 36: Photograph of the North American Blast furnace acid pellets used for the
experimental work
Figure 37: Schematic of the pellet bed used
Figure 38: XRD pattern of unreduced pellets (Cu-Kα radiation was used)
Figure 39: XRD pattern of pellets after (a) Experiment 3 and (b) Experiment 4, both
show a pure wüstite composition. (Cu-Kα radiation was used)
Figure 40: The iron-iron oxides equilibrium diagram in the Fe-CO-CO <sub>2</sub> system was
calculated using FactSage [70]75
Figure 41: Equilibrium constant for decomposition of methane to carbon and hydrogen
[70]75 xvi

Figure 42: Mass spectrum of the gas mixture as (a) injected for experiment 3 (inlet gas as
seen by reactor) (b) after completion of experiment 3 (off-gas)
Figure 43: XRD of pellets post reduction – Experiment 3 (Cu-Kα radiation was used)77
Figure 44: Schematic of the modified proposal of natural gas injection
Figure 45: Schematic representing the region considered for the mass and energy
balance calculations80
Figure 46: Results from Münster and Grabke [71], showing comparable catalytic
behavior of nickel, iron and iron-nickel alloys. 'v' gives the rate of reaction in the
plot. In this work, the rate of steam reforming over iron catalysts was found to be of
the order of $2 \times 10^{-9}$ mol/cm <sup>2</sup> s at 800°C for $P_{H_{2O}}/P_{H_{2}}$ =0.006. The catalysts were in
the form of a foil
Figure 47: Off gas analysis done using the Infrared Spectrometer shows the presence of
higher amounts of CO and the production of $H_2$ as compared to the inlet gas
mixture (the latter is shown by the horizontal dotted lines)
Figure 48: Plot of $\ln(\text{rate})$ vs. $\ln([CH_4])$ where the rate of reaction is in moles/sec per
gram of pellet and $[CH_4]$ is the concentration of $CH_4$ in moles/m <sup>3</sup> . The slope of the
plot gives the order of the reaction with respect to $CH_4$ . Here, the rate is represented
both in terms of CO produced (open diamond markers) and $CH_4$ consumed (filled
circular markers). It must be noted that the rate in terms of CH <sub>4</sub> consumed,
overestimates the rate due to some carbon deposition
Figure 49: Rate constant (in m <sup>6</sup> /mol.s.gram) for the dry reforming of methane is given
for each temperature cycle. Each temperature was maintained for approximately 45
minutes and the off-gas analysis data from the infrared spectrometer was used to
calculate the rate constant. The rate constant was calculated in terms of $\mathrm{CH}_4$
consumed

- Figure 52: Rate constant for the steam reforming of methane is given for each temperature cycle. Each temperature was maintained for approximately 30 minutes and the off-gas analysis data from the infrared spectrometer was used to calculate the rate constant. The rate constant was calculated in terms of CH<sub>4</sub> consumed. .... 99
- Figure 54: SEM images of pellets after completion of experiments. These images are BSE images taken at 10Kv and 2000X magnification. (a) Post-reduction iron pellet surface (b) Pellet surface after dry reforming experiment (c) Pellet surface after steam reforming. The bright regions are metallic iron and the darker regions represent gangue. The black region shows the pores in the pellet. SEM analysis shows no change in pellet surface after dry and steam reforming. ......103

Figure 55: XRD pattern of a metallic iron pellet, which was reduced from hematite in a
50% $\rm H_2$ -50% $\rm N_2$ atmosphere for 1 hour. (Cu-Ka radiation was used) 104
Figure 56: XRD pattern of iron pellets post (a) dry reforming and (b) steam reforming.
The pattern shows presence of graphite and cementite along with metallic iron [92].
(Cu-Kα radiation was used)104
Figure 57: Infrared spectrometer data showing the inlet gas composition in comparison
with the off-gas composition during methane dry reforming over cementite pellets.
Figure 58: Infrared spectrometer analysis of the off-gas in Experiment 2; showing the
interaction of a metallic iron pellet with a methane rich blast furnace gas. (It must
be noted that $H_2$ and $H_2O$ were introduced gradually into the reaction mixture,
hence, in the initial stages the contribution of the CO, $CH_4$ , $CO_2$ appears to
decrease) 110
Figure 59: Infrared spectrometer data for Experiment 3a; from 0-1100 seconds, the inlet
gas mixture is a dry reforming mixture with no $H_2$ , $H_2O$ added. After 1100 seconds,
$\mathrm{H}_2$ and $\mathrm{H}_2\mathrm{O}$ were introduced into the inlet mixture114
Figure 60: Infrared spectrometer data for Experiment 3b; from 0-1100 seconds, the inlet
gas mixture is a steam reforming mixture with no CO, $CO_2$ added. After 1100
seconds, CO, CO $_2$ were introduced into the inlet mixture
Figure 61: X-ray Diffraction patterns of pellets after experiments 3a and 3b. (The peak
denoted by the star represents gangue and the peaks denoted by the dots are
representative of the aluminum sample holder and may be neglected) 116
Figure 62: Top view of the interaction volume considered for the purpose of kinetic
calculations. The penetration distance of methane into the furnace was assumed to
be 1m [97]

#### 1. Introduction

#### 1.1 Blast furnace iron-making

A blast furnace is a vertical shaft furnace lined with refractory bricks. Coke, iron ore and flux are charged into the furnace at the top and a hot blast of air is blown into the furnace at the bottom through "tuyères". The blast furnace acts as a counter-current heat and mass exchanger. The solids take about 6 to 8 hours to descend through the furnace and the hot gases take about 6 to 8 seconds to rise to the top. During this time, a series of chemical reactions occur at various levels in the furnace, which finally reduce the iron ore to pig iron of typical composition Fe-4%C-1% Si. The hot metal and slag produced are tapped from the furnace at the bottom. The blast furnace iron-making process is a continuous process and the furnace runs for 4 - 10 years with occasional shut down for maintenance [1], [2].



Figure 1: Schematic of a blast furnace [3]

Though coke acts as the major source of carbon in the furnace, additional fuels such as pulverized coal and natural gas are also injected into the furnace through the tuyères.

### 1.2 Blast furnace reactions

As the hot blast of air rises through the furnace, it undergoes a number of reactions. The following list summarizes the reaction of gases inside the furnace under current practice conditions [4] :

i. Oxidation of carbon by air in front of the tuyères

$$C + O_2 = CO_2$$
  $\Delta H^{o}_{298} = -394 \text{ kJ/mol of } CO_2$ 

ii. Coke gasification

$$CO_2 + C = 2CO$$
  $\Delta H^{0}_{298} = +172 \text{ kJ/mol of } CO_2$ 

iii. Reduction of oxides

$Fe_{0.947}O + CO = 0.947Fe + CO_2$	$\Delta H_{298}^{o}$ = -17 kJ/mol of CO
$1.2 Fe_3O_4 + CO = 3.8 Fe_{0.947}O + CO_2$	$\Delta H_{298}^{o}$ = +50 kJ/mol of CO
$3\mathrm{Fe}_{2}\mathrm{O}_{3} + \mathrm{CO} = 2\mathrm{Fe}_{3}\mathrm{O}_{4} + \mathrm{CO}_{2}$	$\Delta H_{298}^{o}$ = -48 kJ/mol of CO

#### 2. Motivation

Steelmaking is a highly carbon intensive process with approximately 1.8 tons of  $CO_2$  emitted per ton of hot metal produced [5]. Most of this carbon is consumed by the blast furnace in the form of coke. Coke acts as the fuel, reductant and provides structural support to the furnace. However, the rising coal and coke prices along with the recent boom in the U.S. energy output from shale rock formations, motivates the need to look at natural gas as a partial replacement of coke.

#### 2.1 Natural gas utilization history

The total usage of natural gas (in billion lbs) per year by blast furnaces during the period between 1996-2014 [6] is shown in Figure 2. (It should be noted that the rates shown here refer to tuyère injection of natural gas, which is the only method currently practiced at North American blast furnaces.) For comparison purposes, the industrial and commercial price of natural gas, during the period from 2001-2015 and 1997-2015, as reported by the EIA [7] has also been plotted on the same graph. It is interesting to note the almost mirror-like trend visible for most part of the period. Hence, as natural gas prices dropped, the utilization increased.

Figure 2 indicates that the total use of natural gas in blast furnace ironmaking is now at a similar level to the previous maximum around 1998. However, the total U.S. blast furnace iron production has decreased markedly over this period (from 49.6 million tonnes in 1997, to 30.4 million tonnes in 2013) [8] and hence the intensity of natural gas usage (natural gas used per ton of hot metal produced) has increased considerably.



Figure 2: Natural gas utilization by the North American Blast furnaces from 1997-2015 [6], [9] in comparison with the prices of natural gas, both industrial and commercial.

To illustrate the change in intensity of natural-gas use, Figure 3 shows the natural gas used per net ton of hot metal produced. The dashed line gives the natural gas utilization per net ton hot metal produced in those U.S. furnaces that used natural gas. The dotted line shows the utilization of natural gas per total net ton hot metal produced in all US furnaces, including those that did not use natural gas. Both trends show the remarkable increase in natural gas utilization over the past few years. Although the increase appears to have leveled off, substantial scope remains for further increases in utilization: the estimated maximum rate of tuyère injection is around 125 kg/THM (250 lb/NTHM) [9], approximately twice the current average rate.



Figure 3: Comparison of natural gas used per ton of hot metal in North American furnaces. The natural gas usage is normalized with respect to the hot metal produced in the furnaces actually injecting natural gas (dashed line), and with respect to total hot metal production (dotted line)

#### 3. Technical Background



Figure 4: Schematic of a blast furnace showing the currently practiced tuyère injection and the proposed shaft injection of natural gas.

#### 3.1 Increasing natural gas utilization

North American blast furnaces such as AK Steel Middletown-3 use up to 125kg of natural gas per tonne (metric ton) of hot metal (THM) [9]. Significantly higher natural gas injection rates (through the tuyères) are not feasible because injection of natural gas in the tuyères has an endothermic effect on the raceway flame temperature. This strongly limits the quantity of natural gas that can be injected through the tuyères. To compensate for this reduction in the flame temperature, the blast must be enriched with oxygen. However, the increase in the oxygen content of the blast reduces the nitrogen content, which in turn causes the top gas temperature to drop. The top gas temperature must always be above the dew point to prevent any undesirable condensation in the upper part of the furnace. Hence, a minimum raceway adiabatic flame temperature (typically in the range of 1700-

1900°C) and a minimum top gas temperature (typically greater than 100°C on average) must be maintained to ensure stable functioning of the furnace [9], [10].

Because of the dual constraints of flame temperature and top-gas temperature, the amount of natural gas that can be injected at the tuyères is limited. A different approach is necessary if the utilization of natural gas in blast furnace ironmaking is to be increased; this project investigates the possibility of injecting natural gas higher in the shaft of the furnace, above the tuyères, specifically in the thermal reserve zone or the wüstite reserve zone. The injection of natural gas in the shaft of the blast furnace is expected to result in cracking of methane over iron/iron oxide, which is known to act as a catalyst for carbon deposition [11].

The concept of shaft injection of methane in the blast furnace has some similarities with the HYL ENERGIRON Zero-reforming process. The next section discusses this process and other similar processes in more depth.

#### 3.2 Direct reduction of Iron

#### 3.2.1 HYL Zero Reforming process



Figure 5: ENERGIRON ZR Technology [12]: In situ reforming

### 3.2.1.1 Overview

The concept of injecting natural gas in the shaft furnace is currently utilized in the HYL Direct Reduction technology [13]. The HYL ENERGIRON ZR process (Zeroreforming) [14] optimizes its overall energy efficiency by integrating high reduction temperature (above 1050°C) and 'in-situ' reforming inside the shaft furnace. Figure 5 shows the reactions involved in the in-situ reforming of natural gas and the reduction of iron ore that follows. The HYL DR shaft is operated under a pressure of 6-8 bar and the working temperature is approximately 1050°C. The natural gas injected into the DR shaft undergoes 'in-situ' reforming to produce CO and H<sub>2</sub> which in turn promote the reduction of iron ore to metallic iron pellets. The injected methane also assists in carburizing the pellets. The product of the DR shaft is then used mainly in EAF steelmaking [15].

#### 3.2.1.2 Process details

Figure 6 shows the schematic of the Zero reforming process, emphasizing the top gas recycling and the reductant stream. The DRI shaft utilizes a reductant stream comprising  $CH_4$ , CO,  $H_2$  and  $H_2O$  to reduce and further carburize the iron ore pellets in the shaft furnace. The top gas from the furnace is then recirculated after condensation of water and  $CO_2$  removal and mixed with additional required quantities of  $CH_4$ . The stream is initially heated to approximately 930°C and further mixed with  $O_2$  to increase the temperature further to about 1050°C by partial combustion.



Figure 6: Simplified schematic showing the relevant portion of the HYL Zero reforming process [14].

The current project aims at adopting a similar concept, in the case of a blast furnace. The DR technology is of relevance as the interaction of the reformed natural gas with the solid phase iron/iron oxide in a DR shaft is similar to what is expected in the interaction of methane with a bed of wüstite at similar temperatures in a blast furnace. However, the DR shaft differs from the blast furnace to a certain extent as far as its operating conditions are

concerned. The higher pressure in the DR shaft results in a longer effective residence time of the gases. The blast furnace on the other hand has a pressure drop of approximately 1-3 atm over the total height of the furnace. Additionally, the DR shaft diameter is typically smaller than a blast furnace. This is of relevance when considering the extent of penetration of the reductant stream into the furnace.

#### 3.2.2 MIDREX reformer

The MIDREX NG<sup>TM</sup> [16] process, on the other hand, reforms natural gas in the MIDREX reformer over a Ni-based catalyst [17], [18] bed before injecting the reformed gas into the DRI shaft for reduction of iron-ore. The natural gas is heated in the MIDREX reformer and catalytically reformed with the aid of the recycled  $CO_2$  and  $H_2O$  that are obtained as a by-product in the top gas of the shaft:

Steam reforming:

$$CH_4 + H_2O = CO + 3H_2$$

Reforming with CO2:

 $CH_4 + CO_2 = 2CO + 2H_2$ 

2



Figure 7: The MIDREX NG<sup>™</sup> Plant : Schematic showing the utilization of natural gas in the MIDREX reformer [16]

The reducing gas quality produced by the MIDREX reformer typically has a ratio of reductants (CO and H<sub>2</sub>) to oxidants (CO<sub>2</sub> and H<sub>2</sub>O) of 10:1 [19]. It is enriched with natural gas and injected into the MIDREX shaft furnace in the form of *bustle gas*. The temperature of this bustle gas is typically about 920°C – without O<sub>2</sub> injection. The presence of metallic iron in the shaft catalyzes the reforming of the unreacted methane with the oxidants present (in-situ reforming).

One of the major issues faced by the MIDREX reformers is carbon formation. The nickel catalyst used in the reformer catalyzes reactions to form carbon from carbon monoxide and these reactions are favored at lower temperatures [20]. The reactions involved in the carbon formation are [20]:

• Boudouard Reaction

 $2\text{CO} = \text{C} + \text{CO}_2$ 

3

Beggs Reaction

$$CO + H_2 = C + H_2O$$

Hydrocarbon cracking reaction

$$C_nH_{(2n+2)} = nC + (n+1)H_2$$
 5

The issue of carbon formation is mostly dealt by (1) Removing heavy hydrocarbons from natural gas, (2) Controlling operating conditions of the reformer and (3) Changing catalyst loading profiles (magnesia carriers are better than alumina carriers to prevent carbon formation) [20].

Kinetic studies on methane steam reforming over commercial catalysts concluded that the steam methane reforming is a first order reaction (with respect to methane concentration) at low methane conversion rates and low temperatures [21], [22]. Temperature and steam to methane ratio have a significant impact on steam reforming of methane and a high steam to methane ratio favors production of synthesis gas (CO+ H<sub>2</sub>) [17]. Kaihu et. al [17] experimentally studied the kinetic parameters of the steam methane reforming catalyst by carrying out the reverse water gas shift reaction at low temperatures on the same catalyst. This could be accomplished as the water gas shift reaction is essentially at thermodynamic equilibrium during high temperature steam reforming [19]. Their work concluded that steam reforming of methane produces CO and  $H_2$  as products at high temperatures, whereas the formation of CO<sub>2</sub> is favored at lower temperatures.

#### 3.2.3 Ultra-low CO<sub>2</sub> Steelmaking

In another shaft injection approach, the Ultra-low  $CO_2$  Steelmaking program [23] (ULCOS) demonstrated a new process at an experimental blast furnace in Sweden. This top gas recycling blast furnace (ULCOS-TGRBF) has been used to separate CO and  $CO_2$ from the top gas of the furnace and re-inject the CO along with  $H_2$  at the hearth tuyères and the lower shaft region of the blast furnace. The final results of these tests have confirmed successful running of the trial blast furnace with 25% fossil carbon saving through top gas recycling [23]. An attempt to conduct similar runs on a commercial scale blast furnace was announced [24].



Figure 8: Schematic of the top gas recycling experimental furnace of the ULCOS program [25], showing injection both at the tuyères and the lower shaft of the furnace.

#### 3.3 Wüstite reserve zone

Since it is proposed to inject natural gas into the wüstite reserve zone, this is reviewed briefly.

A high temperature thermal reserve zone forms in the furnace when the burden temperature is approximately 1200K, which is the temperature below which reaction of coke is insignificant. The height of this zone may vary from 1m to 4m [26]. The sequence of blast furnace reactions as discussed earlier, favor the reduction of higher iron oxides to wüstite below the 1200K. This results in the iron-bearing material in the thermal reserve zone to be in the wüstite phase completely [26].



Figure 9: Simplified sketch of Reichardt's diagram showing the gas-solid thermal equilibrium at the thermal reserve zone in the blast furnace [26].

# 3.3.1 Expected reactions in the wüstite reserve zone

The expected reactions on injecting natural gas into the blast furnace shaft are as follows:

i. Methane cracking [27]

$$CH_4 = C + 2H_2$$
  $\Delta H^{o}_{298} = +75.6 \text{ kJ/mol of } CH_4$  6

ii. CO<sub>2</sub> reforming of methane [28]

$$CH_4 + CO_2 - 2CO + 2H_2$$
  $\Delta H^{o}_{298} = 247 \text{ kJ/mol of } CH_4$  7

iii. Steam reforming of methane [29]

$$CH_4 + H_2O = CO + 3H_2$$
  $\Delta H^{0}_{298} = 206 \text{ kJ/mol of } CH_4$  8

Injection of natural gas into the shaft of the furnace is expected to result in the cracking of methane at elevated temperatures (above 800K). Additionally, the presence of  $CO_2$  and  $H_2O$  in these regions is expected to reform the methane and produce CO and  $H_2$ . The concentrations of CO,  $CO_2$ ,  $H_2$  and  $H_2O$  are expected to be controlled by the water-gas shift reaction [30].

iv. Water gas shift reaction [31]:

$$CO + H_2O = CO_2 + H_2$$
  $\Delta H^{o}_{298} = -41.1 \text{ kJ/mol}$  9

According to Smith et al. [31] the water gas shift reaction is kinetically favored at high temperatures and thermodynamically favored at low temperatures as the equilibrium constant of the reaction decreases with increasing temperature. Since there is no change in the volume from the reactants to the products, the reaction equilibrium is unaffected by change in pressure. It has been experimentally shown by Meschter et al. [32] that  $H_2$  is a more reactive reducing agent for reduction of wüstite than CO and a major role of CO during gas-solid reduction reactions is to regenerate  $H_2$  [33]. High concentrations of  $CO_2$  and  $H_2$  in the gas mixtures favor the reverse water gas reaction, producing more CO and  $H_2O$  at higher temperatures. This weakens the reducing power of the gas mixture as demonstrated by the Jiaxin et al. experimentally [30].

The above mentioned reactions, specifically the methane reforming reactions were studied in detail for this work. These are discussed in the later sections of this document.
The kinetics of the water gas shift reaction were not part of this work. The work done by Gibson [34] discussed the water gas shift reaction under conditions similar to the blast furnace.

### 3.4 The 'Rist' mass and energy balance

Thermodynamic, kinetic and energy-balance considerations are expected to affect the feasibility of shaft injection of methane. To evaluate the energy balance, a blast furnace 'Rist' mass and energy balance [35] was used to predict combinations of tuyère natural gas injection rates and oxygen enrichment that would satisfy both the flame-temperature and the top-gas temperature constraints, and to calculate the thermal effect of shaft injection of methane. The Rist balance is based on the observation that in the wüstite reserve zone where the gases equilibrate thermally and chemically with metallic iron and wüstite (approximate composition  $FeO_{1.05}$ ); the equilibration temperature is approximately 1200 K. At and below this temperature coke is essentially chemically inert, and hence all the coke that is charged to the furnace reaches the wüstite reserve zone without reacting, whereas all the iron oxide in the feed has been reduced to wüstite when it enters the wüstite reserve zone. The combined thermal and chemical equilibrium in the wüstite reserve zone allows predictive mass and energy balances to be performed for blast furnace operations. Specifically, the coke rate and blast air rate of the furnace are calculated. The input values include the blast temperature, composition and rate of injectants into the furnace, temperature of the wüstite reserve zone (typically 1200K) and the composition and temperature (typically 1800K) of the hot metal product. For this work, calculations are made for an assumed furnace hearth diameter of 12 m. The hearth diameter affects heat losses from the furnace and the furnace production rate [4]. Based on previous work, the bosh gas flow rate was assumed to follow a simple (approximately quadratic) power-law relationship with the furnace diameter [36]. The furnace productivity was assumed to be

controlled by the bosh gas flow rate. The top-gas temperature is calculated using a simple mass and energy balance for the upper part of the furnace (from the upper boundary of the wüstite reserve zone to the stockline). The adiabatic flame temperature is also calculated with an energy balance, [4] assuming full reaction of the blast air with injectants and with coke at 1800 K, yielding  $N_2$ , CO and  $H_2$  as products.

The compositions which were assumed in the calculations are listed in Table 1.

Table 1: Assumed compositions of inputs, slag and hot metal (mass percentages). These compositions are typical values taken from previous calculations [36]

Iron ore: 71.2% Fe<sub>2</sub>O<sub>3</sub>; 22.8% Fe<sub>3</sub>O<sub>4</sub>; 4.2% SiO<sub>2</sub>; 0.4% Al<sub>2</sub>O<sub>3</sub>; 1.1% CaO; 0.3% MgO Coke: 12.5% ash (composition 65% SiO<sub>2</sub>, 25% Al<sub>2</sub>O<sub>3</sub>, 6% CaO, 4% MgO); balance carbon Blast air: variable oxygen content; moisture content 18 g per Nm<sup>3</sup> dry blast Natural gas injectant: approximated as 100% CH<sub>4</sub> Flux: 100% CaO Hot metal: 4.4% C; 0.5% Si; balance Fe Slag basicity: (%CaO)/(%SiO<sub>2</sub>) = 1

# 3.4.1 Raceway Adiabatic Flame Temperature

The raceway adiabatic flame temperature is a theoretical temperature that develops in the raceway as a result of the combustion reactions that occur in front of the tuyères. The combustion is a result of burning of fuel by the oxidants (air) injected at an elevated temperature. The conditions in the furnace raceway are assumed to be adiabatic, i.e. no external heat losses are considered. The temperature of the raceway gases is directly converted to the energy available in this region, to heat the burden in that regions, i.e. the hot metal. This is done by taking into account the specific heat of the combustion products. In order to maintain sufficiently high temperatures that ensure molten state of the hot metal, the furnace needs to operate at a certain minimum raceway adiabatic flame temperature to prevent chilling of the hearth. Excessively high flame temperatures could prove to be undesirable by causing damage to the tuyères and affecting bed permeability by supplying excess heat to the furnace.

## 3.4.2 Blast temperature

Blast temperature is the temperature to which the blast air is pre-heated before injecting it through the tuyères into the furnace. The pre-heating of the blast air is done using blast furnace gas stoves [2]. The air and additional additives such as fuel, oxygen, etc. are heated to desired temperatures in order to facilitate combustion of coke and other fuel sources in front of the furnace tuyères. Lower blast temperatures require higher coke rates to balance the energy requirements of the furnace. However, blast temperatures that are excessively high require additional materials for tuyère construction, that can withstand higher temperatures. This then increases the overall cost of production.

## 3.4.3 Top Gas temperature

Mass and energy balance calculations determine the composition and temperature of gases that leave the raceway of the furnace and reduce wüstite to metallic iron, while heating up the burden. The upper limit of this region is formed by the wüstite reserve zone which is approximately at 1200K (discussed in the section on 'Wüstite reserve zone'). Once the gases leave the wüstite reserve zone, they enter the region that determines the top gas temperature. This temperature is calculated by taking into account the energy spent on heating the burden to 1200K. The composition of the gas is determined by the oxygen removed from the burden to reduce hematite and magnetite to wüstite [35]. The top gas temperature is an important value as the top gas needs to be maintained at a certain minimum temperature to prevent condensation at the top of the furnace (discussed in the section on 'Increasing natural gas utilization').

## 4. Objective and Hypotheses

## 4.1 Objective

This work aims at finding a practical solution to reducing dependence on the amount of coke used in a blast furnace for the production of iron. Reducing coke rates would prove to be economically and environmentally beneficial. As part of this research, detailed analysis of the interaction of methane with wüstite and iron pellets has been conducted. In addition to assessing the effects on furnace operation, methane reforming over metallic iron pellets has been studied. The underlying principles that have been investigated in this work, lay emphasis on the conversion of methane over porous metallic iron catalysts in a counter-current heat and mass exchanger-type reactor.

# 4.2 Hypotheses

The current project aims at testing the interaction of a methane rich blast furnace gas with a bed of iron ore pellets, specifically in the wüstite reserve zone. As discussed previously, the pellets in this region of the furnace are almost completely wüstite. The hypotheses being tested are hence as follows:

- Injection of natural gas in the shaft of the blast furnace is theoretically feasible, as far as the energy balance is concerned. The endothermic effect of the natural gas injection can be counteracted with the co-injection of oxygen.
- 2. Wüstite is not a good substrate for methane cracking. Interaction of a bed of wüstite pellets with methane rich blast furnace gas is limited. To improve the interaction of methane with the pellet bed, a more catalytic surface (such as metallic iron) is required.
- 3. Natural gas can instead be injected in the lower shaft of the furnace where the pellet bed comprises of part wüstite and part metallic iron. Injection in the lower shaft of the furnace has little or no impact on the mass and energy balance calculations.

4. Methane conversion over metallic iron pellets would result in production of carbon monoxide and hydrogen, which would in turn be utilized in the reduction of wüstite. Thus the furnace can maintain productivity while functioning at higher natural gas rates and lower coke rates.

### 5. Mass and energy balance calculations

### 5.1 Background

It is expected that two main factors would limit the extent to which methane could be injected into the blast furnace shaft.

The first is related to the energy balance: methane cracking (to C and  $H_2$ ) is endothermic, as are the reforming reactions (oxidation of  $CH_4$  to CO and  $H_2$  by reaction with  $CO_2$  and  $H_2O$ ), and hence injection of methane would tend to lower the temperature in the furnace shaft. This quenching effect could be counteracted by preheating the methane before injection, or by co-injecting oxygen with methane to give partial combustion, or both of these.

The second factor is that of kinetics: the gas residence time in the blast furnace is only a few seconds, and hence reaction of injected methane with the furnace burden would have to be rapid. Flow effects are related to the kinetic effects: sufficient mixing of injected natural gas with the gases in the furnace interior, and subsequent reaction of the resulting CO and  $H_2$  with iron oxide, would be essential for maximal utilization of the injected gas. Detailed consideration of flow effects is not part of the scope of this project; instead, the focus is on the kinetics of the initial cracking and reforming reactions.

Conditions in the blast furnace shaft where the methane would be injected are rather complex. Multiple solid phases are present (coke; metallic iron and wüstite; other oxide phases), and the gas stream contains  $N_2$ , CO, CO<sub>2</sub>, H<sub>2</sub> and H<sub>2</sub>O. The reaction of methane upon injection into such a complex system has been studied in this work. Equilibrium calculations, and mass and energy balances, were used to support the experimental work, to find a starting point for the experimental work. The 'Rist' mass and energy balance was used to calculate the effect of natural gas injection through the furnace shaft on the blast furnace as a whole. It is expected that an increase in natural gas utilization may result in a change in parameters such as the coke replacement ratio, oxygen enrichment of the blast, overall oxygen injected into the furnace, productivity, top gas composition, etc. These calculations have been performed to test the feasibility and efficiency of the proposed shaft injection. The following section compares the impact of the proposed shaft injection of natural gas with the current practice of tuyère injection. Additionally, attempts have been made to suggest practical solutions for any undesired effect of methane injection in the furnace shaft.

## 5.2 Tuyère injection of natural gas

As indicated below, mass and energy balances showed that the tuyère injection rate of natural gas cannot exceed approximately 150 kg/THM. This is shown by calculating allowable levels of  $O_2$  enrichment of the hot blast, for different rates of natural gas injection, such that the conditions of top gas temperature greater than the minimum, and raceway adiabatic flame temperature ("RAFT") greater than its minimum, are both satisfied. These two conditions define an 'operating window' for the generic blast furnace. Real plant data was used to test whether the predictions agree with actual operating conditions.

Figure 10 shows the calculated operating window of a blast furnace for blast temperatures of 900°C and 1100°C. For these calculations, the top-gas temperature limit was assumed to be 110°C, and the adiabatic flame temperature limit was assumed to be 1800°C. In Figure 10, the top-gas temperature would be higher than the minimum if the extent of oxygen enrichment were *less* than the limiting value shown by the plotted line; the adiabatic flame temperature would be higher than the minimum if oxygen enrichment were *more* than the "AFT limit" line. In this way, the region between the two lines gives

the allowable operating window. The maximum allowable natural gas injection rate is found at the rightmost edge of the operating window, where the top-gas and flametemperature constraints coincide. For the examples shown in Figure 10, the maximum rates are approximately 150 kg/THM (900°C blast) and 175 kg/THM (1100°C blast). Figure 11 shows the comparison of the operating window of the blast furnace with actual North American plant data [9] to test the accuracy of the theoretical calculations. It can be concluded that the established operating window is close to actual practices.



Figure 10: Operating window of a generic blast furnace (shaded region), for 900°C and 1100°C blast temperatures. The top gas temperature limit and the flame temperature limit have been set at 110°C and 1800°C respectively.



Figure 11: Comparison of actual plant conditions with the predicted operating window. Each point (with a different symbol) refers to reported conditions in a different operating North American blast furnaces [9]. The top gas temperature limit was set at 110°C and the adiabatic flame temperature limit was set at 1800°C.

The data points that lie outside the 900°C blast temperature operating window, have been accounted for in the 1100°C operating window. This demonstrates the flexibility of the operating window. The blast temperature and adiabatic flame temperature limits of the operating window can be adjusted according to any individual furnace's practice. The operating window is a mere theoretical tool that is flexible to a furnace's conditions and shows the feasible natural gas injection rates for those operating conditions (See Figure 12).



Figure 12: Demonstration of flexibility of operating window. Each point (with a different symbol) refers to reported conditions in a different operating North American blast furnace [9]. The operating windows are as in Figure 10, but also showing the 1800°C adiabatic-temperature constraint if the assumed blast temperature is 1200°C instead of 1100°C.Additionally, for a 1100°C blast, a lower adiabatic limit of 1700°C is shown.

## 5.2.1 Operating window and TCE

In 1991, Agarwal et. al. [37] introduced a concept called the Thermal-plus-Chemical Energy of a blast furnace. Work was done to explain the operation of a blast furnace based on the energy input and requirement of the furnace. Agarwal et. al. proceeded by segmenting the blast furnace into different regions and conducted mass and energy balance calculations for a typical blast furnace. This study laid considerable emphasis on the raceway gas produced after combustion in front of the tuyères. The composition and enthalpy of the raceway gas were compared to the energy required to reduce iron ore. It was found that the raceway gas contains low concentration of hydrogen, thus imposing great thermal load on the furnace as a result of higher dependence on the solution loss reaction, which produces carbon monoxide – the main reagent for reduction.

$$CO_2 + C = 2CO$$
  $\Delta H^{0}_{298} = +172 \text{ kJ/mol of } CO_2$  10

Agarwal et. al. suggested the use of hydrogen for reduction of iron ore, to reduce the energy consumed by the solution loss reaction and hence decrease the energy requirement of the furnace. To increase the concentration of hydrogen in the raceway gas, injection of natural gas through the tuyères was suggested. Injection of natural gas was accompanied by oxygen enrichment of the blast to account for the endothermic effect of natural gas decomposition. This changed the thermal state of the raceway, while increasing hydrogen content, which was available for reduction of iron ore. A benefit was seen in the coke rate of the furnace. However, these changes decreased the raceway gas temperature due to a lower value of the 'RAFT', which was extensively used to measure the operation of the furnace.

Thus Agarwal et. al. introduced the 'TCE' or the 'total thermal plus chemical energy available above 2700°F' in the furnace as a better way to represent the state of a furnace. It was a way to quantify the total available resources – temperature and chemical energy – available to reduce the iron ore. The emphasis on 'above 2700°F' (1482°C) was to ensure that the raceway gases can supply enough energy to keep the hot metal in a molten state, as these calculations assume an adiabatic state where the heat content of the gases is used to provide energy to the burden without external heat losses. The units for this quantity were reported as MMBTU/THM (Million British Thermal Units per ton of hot metal).

The thermal component of TCE involves the enthalpy of the raceway gases, in excess of the energy required to maintain the hot metal temperature (1482°C). The chemical component is calculated by taking into account the hydrogen concentration of the raceway gases and the factor by which hydrogen replaces the solution loss reaction.

TCE is used as a guideline for furnace operations in currently operating blast furnaces that utilize natural gas injection [38].

For this work, the original Rist mass and energy balance was adapted to calculate the 'TCE' quantity and determine the state of the furnace [34]. Gibson [34] reported discrepancies in the original TCE calculations and corrected for them while incorporating the TCE calculations in the Rist mass and energy balance.

Figure 13 shows the effect of TCE on the calculated operating window of a blast furnace. (For convenience, the original TCE units of MMBTU/THM were changed to GJ/THM). The 'TCE=1 GJ' line forms the new lower limit of the operating window. It is evident that for the furnace to operate at a TCE greater than 1GJ/THM, the operating window is further limited when compared to the RAFT limitations. However, at higher rates of natural gas injection, the TCE limit of the operating window, allows for a lower oxygen enrichment of the blast when compared to the RAFT limit (represented by the lighter shaded region). Additionally, the comparison of North American furnace practices with the new operating window with TCE calculations is shown in Figure 14. It can be seen that most furnaces operate within the calculated window formed by the top gas temperature limit of 110°C and close to the TCE limit of 1 GJ.



Figure 13: Plot showing the impact of TCE on the 900°C and 1100°C operating window. The dash dot dot line labeled 'TCE = 1GJ' forms the new lower limit of the operating window. Hence, the shaded region is now the new operating window. The top gas limit is set at 110°C and the flame temperature at 1800°C.



Figure 14: Plot showing the comparison of the new operating with a lower limit set by TCE calculations and data points representing furnace operations in North America. These data points represent those furnaces that use natural gas injection [9]. The top gas limit is set at 110°C and the flame temperature at 1800°C.

# 5.3 Shaft injection of natural gas

To study the effects and possibility of injecting natural gas in the shaft of the blast furnace as opposed to at tuyères, a small change was made in the Rist calculations. The mass and energy balance was used to predict changes in the adiabatic flame temperature if some proportion of the natural gas was injected in the shaft of the blast furnace, with the balance injected at the tuyères. Injecting natural gas in or below the wüstite reserve zone (but not at the tuyères) is expected to have the following effects:

- Shaft injection removes the constraint on the adiabatic flame temperature, as chilling of the flame due to endothermic methane cracking is eliminated. Because less oxygen enrichment would be required, the top gas temperature would increase.
- 2. For a given rate of natural gas injection, the coke rate remains approximately the same, whether natural gas is injected at the tuyères, in the shaft, or both.

Figure 15 shows the results of calculations, which tested the first of these expected effects. The figure shows the relaxation of the AFT limit due to the injection of a part of the natural gas in the shaft of the furnace, instead of the tuyères. The fraction of natural gas injected in the tuyères was considered to be 0.5. (For Figure 15, the blast temperature was taken to be 1100°C; the top-gas temperature limit was 110°C and the adiabatic flame temperature limit was 1800°C.)

Figure 15 shows that, as expected, if a fraction of the total natural gas input were to be injected in the shaft of the furnace, the constraint on the adiabatic flame temperature would be relaxed. In this way, injection of natural gas partially in the shaft of the furnace would increase the operating window of the furnace.



Figure 15: Relaxation of the adiabatic flame temperature constraint by shaft injection of methane, instead of tuyère injection. Calculated for 1100°C blast temperature, 110°C topgas temperature limit, and 1800°C adiabatic flame temperature limit. The line "Old AFT limit" is for injection of all the methane at the tuyères, and the line "New AFT limit" for

injection of half the methane at the tuyères, and the other half in the shaft

### 5.3.1 Shaft injection and TCE

Similar to the previous section on 'Operating window and TCE', where the impact of TCE calculations was projected on the original operating window; the change in the shaft injection operating window due to TCE was calculated. Figure 16 shows the new shaft injection operating window with TCE = 1GJ forming the lower limit. The new operating window is more constrained than the one with a lower RAFT limit. If there is any intersection of the TCE and AFT limits, it is beyond the practical operation conditions of the furnace, according to this work.



Figure 16: Plot showing the impact of a TCE limit on the new operating window. The dashed dot dot line labeled 'TCE = 1GJ' represents the TCE limit for the case with half natural gas injected through the furnace shaft and half through the tuyères; which is the new lower limit for the operating window represented by the shaded region. The AFT limit represents the previous lower constraint for the operating window for the shaft injection scenario.

# 5.3.2 Coke Replacement Ratio

The coke replacement ratio is simply the amount of coke that can be replaced per kilogram of natural gas. The coke replacement ratio for injection of natural gas in the shaft and the tuyères has been calculated. To calculate the coke replacement ratio, the coke rate for each case (shaft + tuyère injection and only tuyère injection of natural gas) was calculated with the help of the "Rist" mass and energy balance. The coke replacement ratio was then calculated using the relation:

Coke replacement ratio = (coke rate at zero natural gas injection – coke rate for either case)/natural gas injection rate

For a blast temperature of 1000°C, the coke rate at zero natural gas injection was found to be approximately 492 kg/THM.

For 100 kg/THM of natural gas injected in the blast furnace at a 1:1 ratio through the shaft and the tuyères, the coke rate is 379 kg/THM.

Therefore, Coke replacement ratio = (492 kg/THM-379 kg/THM)/ 100 kg/THM = 1.13 As seen from Figure 17, as we decrease the natural gas injection through the tuyères, the coke rate of the furnace decreases. This is because, a higher natural gas injection rate through the tuyères, has a higher endothermic effect on the flame temperature. Consequently, lower oxygen enrichment is required to maintain the raceway flame temperature. Hence, the shaft injection of methane favors the coke replacement ratio.



Figure 17: Calculations showing the coke replacement ratio for three natural gas injection scenarios – all tuyère injection, 1:1 shaft to tuyère injection and all shaft injection. The calculations were done using the Rist balance. 'm' represents the coke replacement ratio.

These calculations were done for a blast temperature of 1000°C and the flame temperature was set at 1800°C. The all tuyère injection and the 1:1 shaft to tuyère injection cases were divided based on oxygen enrichment. For both cases, at natural gas injection rate < 67.5 kg/THM, the O<sub>2</sub> enrichment of blast is zero, i.e. O<sub>2</sub> percentage of blast is 21%. Above 67.5 kg/THM of natural gas injection, enrichment of blast is allowed.

All shaft injection case shows no required oxygen enrichment.

It was of interest to test whether the coke rate savings shown by shaft injection of natural gas was due to the methane injection or the energy supplied by pre-heating the methane. To test this, the Rist mass and energy balance was used to estimate the change in coke rate when natural gas is injected cold versus at 1200K through the tuyères. The calculation was done keeping all other parameters constant and only the temperature of the natural gas injected is changed. From Table 2, we can see that the benefit in coke savings from preheating the natural gas to 1200K is much smaller than the chemical role of natural gas.

Table 2: Table summarizing the impact on coke replacement ratio when the temperature of methane is increased from 298K to 1200K. These calculations are done at zero oxygen enrichment of blast and 1000°C blast temperature.

Natural gas injection rate through tuyères (kg/THM)	ral gas injection 298K natural gas - through tuyères coke rate (kg/THM) (kg/THM)	
0	492	492
50	445	432
Coke replacement ratio	0.94	1.2

### 5.3.3 Production rate

Injection of natural gas in the blast furnace shaft is expected to bring about a change in the production rate of the furnace. Figure 18 summarizes the predicted production rates, calculated using the Rist mass and energy balance. The open markers represent conditions that do not require oxygen enrichment of the blast. The results corresponding to complete shaft injection of natural gas, show a considerably higher predicted production rate in the furnace. This is attributed to the reduced blast air rate due to the lower coke rate and the absence of natural gas injection and oxygen enrichment in the tuyères. Additionally, this results in an increased raceway flame temperature. 1:1 shaft to tuyère injection, shows better productivity until the furnace reaches 100kg/THM of natural gas injection; as compared to all tuyère injection. This can once again be attributed to the lower blast air rate of the furnace. However, once oxygen enrichment of the blast begins, the production rate is higher in case of complete tuyère injection, due to the observed direct relation between oxygen enrichment of the blast and its productivity [39]. As more natural gas through tuyères requires a higher oxygen enrichment of the blast; therefore, complete tuyère injection shows better predicted productivity when

natural gas injection rates are greater than 100 kg/THM. It must also be noted that in case of data points which do not require oxygen enrichment of the blast, the oxygen in the blast was assumed to be 21%.



Figure 18: Production rate calculations for the three natural gas injection scenarios – all tuyère injection, 1:1 shaft to tuyère injection and all shaft injection. The calculations were

done for a 1000°C blast temperature and 1800°C flame temperature. The open data points represent the absence of oxygen enrichment of the blast air. The filled data points represent oxygen enrichment of the blast. (It must be noted that 200 kg/THM of natural

gas injection for complete tuyère injection, lies outside the operating window for a furnace and has been shown here only for comparison). For all tuyère injection and 1:1 shaft to tuyère injection cases; at natural gas injection rate < 67.5 kg/THM, the O<sub>2</sub> enrichment of blast is zero, i.e. O<sub>2</sub> percentage of blast is 21%. Above 67.5 kg/THM of natural gas injection, enrichment of blast is allowed. All shaft injection case shows no required oxygen enrichment. Table 3 shows the gas flow rates in different regions of the furnace for different rates and points of natural gas injection. As discussed earlier, injection of natural gas completely in the furnace shaft decreases the blast rate through the tuyères and leads to a high predicted productivity. Additionally, it increases the top gas rate, as expected due to less oxygen enrichment of the blast air.

Table 3: Table summarizing the blast rate, raceway gas rate and top gas rates at different natural gas injection rates for the three scenarios considered – all tuyère injection, 1:1 shaft to tuyère injection and all shaft injection. These calculations are for a 1000°C blast temperature and the flame temperature was set at 1800°C. (It must be noted that 200 kg/THM of natural gas injection for complete tuyère injection, lies outside the operating window for a furnace and has been shown here only for comparison).

All tuyère	Natural gas	Blast rate	Raceway gas	Top gas
injection	kg/THM	Nm <sup>3</sup> /THM	Nm <sup>3</sup> /THM	Nm <sup>3</sup> /THM
	0	1234	1515	1750
	100	1120	1715	1850
	200	334	1219	1266
1:1 shaft : tuvère	Natural gas kg/THM	Blast rate Nm³/THM	Raceway gas Nm³/THM	Top gas Nm³/THM
	0	1234	1515	1750
	100	1257	1682	1997
	200	875	1431	1833
All shaft injection	Natural gas kg/THM	Blast rate Nm³/THM	Raceway gas Nm³/THM	Top gas Nm³/THM
	0	1234	1515	1750
	100	1076	1321	1820
	200	918	1126	1891

### 5.3.4 Endothermic Effect of Shaft Injection

The major constraint on the higher rates of natural gas injection through the tuyères is the endothermic nature of methane on the flame temperature. Similarly, when methane is injected in the shaft of the furnace, we expect a drop in the shaft temperature. Such quenching of the shaft temperature is expected to have an undesirable effect on blast furnace stability and fuel efficiency. However, it is proposed that the drop in temperature could be counteracted by co-injection of oxygen with the methane, and by preheating the methane. Oxygen would give partial combustion of the methane. Such co-injection of oxygen with methane, and preheating, are utilized in the HYL direct-reduction process. Unlike Midrex direct-reduction process, in which natural gas is reformed in a separate reactor, natural gas is introduced directly into the HYL reactor shaft, achieving *in situ* reforming of the methane [13]. Co-injection of oxygen increases the temperature of the injected gas and counteracts the endothermic effect of this *in situ* reforming.

Mass and energy balance calculations were performed to estimate the endothermic effect of shaft injection of natural gas, and the effect of oxygen injection. Additional natural gas and oxygen injections were accounted for in the original 'Rist' mass and energy balance. The amounts of natural gas and oxygen injected were included as inputs in the wüstite reserve zone. The  $O_2/CH_4$  ratio was then adjusted to maintain the temperature in shaft of the furnace. As stated earlier, the wüstite reserve zone in the blast furnace has a temperature of about 1200 K. The following contour plots show the calculated effect of the temperature of natural gas,  $O_2/CH_4$  molar ratio of injection and the temperature of coinjected oxygen on the gas temperature (after reaction of the injected gas with the wüstite burden to form CO,  $CO_2$ ,  $H_2$ ,  $H_2O$  and metallic iron). As seen from Figure 19, co-injection of oxygen is predicted to counteract the drop in temperature due to the endothermic effect of methane cracking. As per these calculations, higher  $O_2/CH_4$  molar ratios and higher preheat temperatures of  $CH_4$  can nullify the endothermic effect and maintain the temperature in the wüstite reserve zone.



Figure 19: Combined effect – of preheating methane and co-injecting oxygen with methane – on the gas temperature after reaction with the furnace burden (wüstite) to produce CO, CO<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>O and metallic iron. The lines give the temperature of the reacted gas. Calculated for a total methane injection rate of 200 kg/THM, half injected in the shaft and half at the tuyères. Oxygen is at an initial temperature of 298K.

## 5.3.5 Overall Consumption of Oxygen

Table 4 shows the overall consumption of oxygen in case of shaft injection of natural gas in comparison with tuyère injection. These calculations have been made using the 'Rist' mass and energy balance. It is evident from these calculations that the overall consumption of oxygen in the blast furnace would increase if the  $CH_4$  is injected at higher temperatures in the shaft of the furnace. These calculations take into account the oxygen co-injection into the furnace shaft at a  $O_2/CH_4$  molar ratio of 0.5. The  $O_2/CH_4$  molar ratio was based on calculations in the previous section on counteracting the endothermic effect of natural gas injection.

Table 4: Table shows the total oxygen added to a furnace, based on the point of injection of 100 kg/THM of natural gas. The shaft  $O_2/CH_4$  molar ratio is assumed to be 0.5. The calculations were done for a 1000°C blast and the flame temperature was set at 1800°C.

	O₂ in blast (%)	O₂ enrichment (kg/THM)	O <sub>2</sub> in the shaft (kg/THM)	Total additional O₂ (kg/THM)
All tuyère injection	26.5	51.2	0	51.2
1:1 shaft : tuyère injection	21	0	50	50
All shaft injection	21	0	100	100

# 5.3.6 Unreacted natural gas

The Rist calculations assume complete conversion of methane in the blast furnace via different reactions discussed in the section on 'Expected reactions in the wüstite reserve zone'. However, this is a major assumption of the mass and energy balance calculations. It is expected that the conversion of methane may be lower. In this case, methane would then appear in the top gas of the furnace. As the blast furnace top gas is used to heat the stoves which then pre-heat the blast air [2], the presence of methane in the top gas, would increase its calorific value. As discussed earlier, to inject methane into the furnace shaft, it would need to be pre-heated (also discussed in a later section on 'Preheating methane'). This can be done by using the top gas of the furnace, which would have a higher calorific value with the presence of unreacted methane.

The Rist mass and energy balance was used to calculate the expected top gas composition and its net calorific value, as shown in Table 5. The calculated heat content of the top gas is in the range of 3-4 MJ/Nm<sup>3</sup>, which is in agreement with the literature [39]. In comparison, the calorific value of natural gas is in the range of 36-38 MJ/Nm<sup>3</sup> [40]. Thus, the presence of unreacted natural gas in the top gas would considerably increase the heat content of the gas.

Table 5: Top gas compositions for natural gas injection rate of 100kg/THM through different points of injection. These calculations are for 1000°C blast temperature and flame temperature was set at 1800°C.

	Top gas composition			Calorific Value (net)			
	$%N_2$	%CO	$%CO_2$	$%H_2$	$%H_2O$	(MJ/THM)	$(MJ/m^3)$
All tuyère injection	43	21	17	8	10	6442	3.89
1:1 shaft : tuyère injection	49	18	16	8	10	6275	3.49
All shaft injection	46	19	16	9	10	5962	3.67

# 6. Combustion of methane

### 6.1 Literature review

The current work on shaft injection of methane in the blast furnace derived the idea from the HYL DRI shaft. The HYL ENERGIRON Zero Reforming process injects natural gas into the DRI shaft; the natural gas undergoes 'in-situ' reforming and reduces the iron ore (See Figure 5). Before injection into the shaft, the stream of natural gas is preheated and then partially combusted using oxygen to raise its temperature by almost 180°C [12]. However, energy balances show that the amount of oxygen required to raise the temperature of the natural gas stream by 180°C would be is enough to combust all the methane to produce CO + H<sub>2</sub> if full equilibration were achieved.

In contrast, as reported by HYL, the reductant stream has approximately 20% methane when it enters the furnace shaft [14]. This is different from what the equilibrium energy balance predicts; hence, combustion kinetics need to be considered. The presence of about 50% H<sub>2</sub> in the reductant stream is expected to assist in raising the temperature of the stream with lower oxygen addition through preferential combustion of hydrogen rather than methane. It has been commonly observed that addition of hydrogen to the methaneair flame increases flame speed indicating preferential combustion of hydrogen [41]. Experimental work done by An et. al. [42] shows the impact of adding hydrogen to hydrocarbon fuels, to reduce ignition delay. Hydrogen is known to have lower ignition energy, higher diffusivity and rapid flame propagation. This makes it a suitable additive for lean oxidant mixtures. This has been supported by considerable work done previously [43], [44], [45]. Early work done by Cheng and Oppenheim [45] suggests that the activation energy of combustion of  $CH_4-H_2-O_2$  mixtures is proportional to the ratio of concentrations of  $CH_4$  and  $H_2$ . The benefit in reducing the ignition delay due to addition of hydrogen to methane-air mixtures was shown experimentally by Zhang et. al. [43]. Their results show a decrease in ignition delay from approximately 2000 $\mu$ s to 40 $\mu$ s when a 100% CH<sub>4</sub> stream is diluted to 60% H<sub>2</sub> – 40% CH<sub>4</sub> while keeping pressure constant. Similar to the improvement in ignition delay, considerable work has been done on the improvement in flame speeds of hydrocarbon due to hydrogen addition. This concept is commonly used in combustion engines to improve fuel efficiency [46].

The mechanism of combustion of methane-air mixtures has also been studied in great detail [47], [48], [49]. An et. al. [42] succinctly summarized the mechanism of hydrocarbon combustion. Hydrocarbons typically exhibit a two staged ignition process which involves the formation of radicals in the first stage and the heat release in the second stage. These lead to elevated pressure and temperature. The radicals formed during the combustion of methane, for instance, is a thoroughly researched field. The radicals formed and the reaction pathway involved in the combustion of hydrocarbons can be found in the work done by Baulch et. al. [50] and Peters et. al. [51].

Studying the combustion of methane is useful in determining the design parameters required for shaft injection of natural gas in a blast furnace. Quantities such as flame speed and ignition delay are expected to determine the required distance of mixing of methane and oxygen from the furnace, in order for complete combustion/partial combustion to occur.

# 6.2 'Kintecus' combustion modeling

Kintecus is an open-source, Excel-based compiler that can model chemical reactions. It has the ability to run Chemkin/SENKIN II/III models without the use of supercomputing power or FORTRAN compiling/linking [52], [53]. Kintecus was used to simulate combustion reactions for the current work. Kintecus uses three main input spreadsheets; the model spreadsheet, the species spreadsheet and the parameter spreadsheet. The model spreadsheet requires the user to enter the combustion model that they desire to use. For example, C1-C2 combustion mechanisms may be used for simulating the combustion of hydrocarbons [54]. Once the model has been entered, the species spreadsheet creates the list of species involved in the reactions. The user can then enter the initial concentrations of each of the species. Additionally, the parameter spreadsheet allows the user to enter the duration, initial temperature and integration time step of the required calculation. Once the parameters have been entered, the compiler runs the code to generate the concentration of all the species involved in the reaction at each time step. This then generates the Kintecus plots or results of the calculation.

The current work proposes the co-injection of oxygen with methane in the shaft of a blast furnace. The co-injection of oxygen is to ensure that the endothermic nature of methane decomposition does not chill the furnace shaft and the reductant stream can be safely injected at a higher temperature to maintain the shaft temperature at approximately 1200K. Direct injection of oxygen into the furnace shaft would cause re-oxidation problems and cannot be done. Hence, partial combustion of methane outside the blast furnace needs to be done in order to raise the temperature of the reductant stream. This concept is used in the HYL ENERGIRON process, where the temperature of the reductant stream is increased by >120°C, by addition of oxygen to the reductant stream, thereby partially combusting the gas mixture (See Figure 20). The final temperature of the gas when injected into the HYL shaft is approximately >1050°C [12]. A similar concept was applied to the proposed shaft injection of methane. Kintecus was used to simulate combustion of methane with oxygen at the required rates of injection.

In order to confirm the reliability and relevance of Kintecus results, a comparison was made between Kintecus calculations and HYL data received via personal communication. The reliability of Kintecus calculations was confirmed before using it for the current work.



Figure 20: Schematic of the HYL ENERGIRON process that shows top gas re-circulation with  $CO_2$  removal. The top gas is then pre-heated to 930°C before oxygen addition is done to increase the temperature of the mixture to >1050°C [12].

# 6.3 Methane combustion calculations using Kintecus

As Kintecus results were confirmed to be reliable with the HYL comparison, the next step involved using Kintecus to simulate the partial combustion of methane to be done before injection into the blast furnace. To establish the initial parameters for the calculations, four different cases were considered. Calculations for all these cases were done under adiabatic and isobaric (2 atm) conditions. Each case assumed injection of 100 kg/THM of natural gas through the furnace shaft. Table 6 shows the conditions assumed for each calculation.

For the cases with  $CH_4/O_2$  molar ratio 2:1, the expected reaction is as follows:  $CH_4 + 0.5O_2 = CO + 2H_2$ 

11

For 4:1  $CH_4/O_2$  molar ratio, the reaction being oxidant starved in this scenario, the final products of the reaction depend on the time after combustion. Production of  $H_2O$  and  $CO_2$  results in subsequent methane reforming reactions which may change the final gas composition, however, at a slow rate.

$$CH_4 + 0.25O_2 = xCO + yH_2 + zCO_2 + pH_2 + qH_2O$$
 12

Case	$CH_4/O_2$ molar ratio	Initial temperature (K)	Pressure (atm)
1	2	1000	2
2	2	1200	2
3	4	1000	2
4	4	1200	2

Table 6: Summary of conditions used for Kintecus calculations.



Figure 21: Kintecus results showing the ignition delay and temperature of the reaction occurring as a result of methane combustion under the given parameters. The gas stream

is assumed to be at a pressure of 2 atmospheres. (a) Initial temperature 1000K, (b)

Initial temperature 1200K.



Figure 22: Kintecus results showing the concentration of individual gas species as the combustion of methane proceeds. (a)  $CH_4/O_2$  molar ratio is 2:1 at an initial temperature of 1000K, (b)  $CH_4/O_2$  molar ratio is 2:1 at an initial temperature of 1200K, (c)  $CH_4/O_2$  molar ratio is 4:1 at an initial temperature of 1000K, (d)  $CH_4/O_2$  molar ratio is 4:1 at an initial temperature of 1200K

# 6.3.1 Discussion

From the above results, it can be seen that at higher initial temperatures, the ignition delay of the combustion is shorter. Thus, at 1200K, for 2:1 CH<sub>4</sub> to  $O_2$  (Figure 21(b)), the combustion reaction is faster and the ignition delay is approximately 0.02 seconds. The delay in ignition here is the time after mixing the fuel and oxidant and before the combustion reaction actually occurs. At 1000K, the ignition delay is almost 0.5 seconds. Detailed analysis of the concentration for each initial temperature shows that the final gas mixture mainly comprises approximately 60% H<sub>2</sub> and 30% CO and negligible CH<sub>4</sub> at 3 seconds after ignition. Thus, the combustion of methane with 2:1 CH<sub>4</sub> to  $O_2$  molar ratio and initial temperatures of 1000 or 1200K, gives a gas stream comprising of mainly

 $H_2$  and CO. The final temperature of the gas with 1200K initial temperature, will be higher than for 1000K initial temperature, as expected.

Similar to Cases 1 & 2, a higher initial temperature reduces the delay in ignition in Cases 3 & 4. For an initial temperature of 1000K, the ignition delay is approximately 1.3 seconds. Whereas, for an initial temperature of 1200K, the ignition delay is 0.04 seconds. Overall, in Case 3 & 4 with a  $CH_4$  to  $O_2$  molar ratio of 4:1, the delay in ignition is higher as compared to Cases 1 & 2 where the  $CH_4$  to  $O_2$  molar ratio is 2:1.

For  $CH_4$  to  $O_2$  molar ratio of 4:1 and initial temperature 1200K, analysis of the concentration of the post-combustion gases showed that the gas comprises 40% H<sub>2</sub>, 10% CO, 15% H<sub>2</sub>O and approximately 30% unreacted  $CH_4$ . After 3 seconds of combustion, the temperature of the gas stream is approximately 1400K. The lower effective temperature increase of the gas stream is attributed to the oxidant starved nature of this case. However, the quantities of oxygen added, are sufficient to increase the gas stream temperature to desired levels for the purpose of this work.

## 6.3.2 Step-wise combustion of methane

The above calculations performed using Kintecus, assume perfect mixing of the oxidant and fuel stream before ignition. As seen from Figure 21 (b), the ignition delay for a 4:1 CH<sub>4</sub> to  $O_2$  mixture with an initial temperature of 1200K is approximately 0.04 seconds. Thus, ignition occurs 0.04 seconds after complete mixing of the two streams. This increases the distance the gas needs to travel before being injected into the shaft furnace (See discussion in section on 'Safe mixing distance'). In order to improve the efficiency of combusting fuel before injection into the furnace, a different approach of stepwise combustion is often applied [55]. In this step-wise combustion, the fuel stream is divided into smaller parts. The combustion is done with the first part which comprises of a fraction of the total fuel stream and the oxygen stream. The product of this initial step is subsequently mixed with the remaining parts of the fuel stream step-wise. This method,

decreases the overall combustion time and sufficient time for the reaction to achieve equilibrium. Figure 23 shows a schematic explaining the step-wise combustion reaction, where the fuel stream was assumed to be added in five parts.



Figure 23: Schematic of the step-wise combustion reaction. Here, 1 denotes the initial combustion reaction between 20% of the fuel stream with the oxygen and 2-5 denote the

steps in which parts of the fuel stream are added to the product stream.

In the case of step-wise combustion, the ignition delay for the complete reaction, is the time to ignite the oxygen stream with the first part (20% in this example) of the fuel stream.

Calculations were done to test the results of step-wise combustion of methane being injected into the furnace shaft. These calculations were performed for the case of  $CH_4$  to  $O_2$  molar ratio of 4 and the initial temperature of  $CH_4$  was 1200K. Due to the smaller flow rates of the  $CH_4$  stream when 100 kg/THM of  $CH_4$  is aimed to be injected through the furnace shaft, the number of steps for this case were reduced to 2. This would allow methane concentration to be greater than the oxygen stream and prevent the temperature post combustion to exceed the practical limitations of the pipes.



Figure 24: Gas composition at each step when methane is reacted with oxygen in a stepwise manner. The methane stream is divided into two parts and only half the methane stream is initially reacted with oxygen – Step 1. The remaining half of the methane stream is then added to the products of Step 1. It must be noted that the total gas volume at each step is different as the fuel stream is added in parts to the product stream. (The connectors between the data markers are thus not a depiction of the trend and are shown to differentiate between the gases) Table 7: Gas composition pre and post combustion. Both single step combustion and step-wise combustion results are shown. For the case of step-wise combustion, each percentage of species at each step is of the total gas at that step. As  $CH_4$  was added in

Gas species	Initial pre- combustion	Step-wise	Step-wise combustion composition (%) - Kintecus			
_	compositio	Step o	Step 1	Step 2	composition (%)	
	n (%)				- Kintecus	
O2	20	33	0	0	0	
H2	0	0	46	37	37	
CO	0	0	17	12	11	
CH4	80	67	4	26	26	
CO2	0	0	2	2	2	
H2O	0	0	21	14	15	
N2	0	0	0	0	0	

parts, there is an increase in gas volume from step 1 to step 2.

Figure 24 shows the composition of the product stream at each step of the reaction. The details of the composition of gas at each step can also be seen in Table 7. Table 7 also shows a comparison of the gas composition between single step and step-wise combustion. It is seen from these results, that step-wise combustion and the single step combustion, give nearly similar results. It must be noted that there was a presence of  $C_2H_2$  and  $C_2H_4$  in the product stream which was neglected for the purpose of this work.

Figure 26 shows the temperature profile for the single step and the step-wise combustion reactions. It was observed that in case of the step-wise reaction, the ignition occurs faster and hence oxygen is consumed faster. Additionally, at the end of 2 seconds, both the single step and step-wise combustion reactions give similar product stream temperature of approximately 1400K. The ignition delay for consumption of oxygen was observed to be 0.02 seconds (See Figure 25) for the step-wise condition which is nearly half as much as that of the single step combustion case (See Figure 21).



Figure 25: Temperature profile for Step 1 in the step-wise combustion of methane. When compared to Figure 21 (b), it was seen that the ignition delay considerably reduced with step-wise combustion. Thus oxygen is consumed faster when the fuel stream is added in

parts.


Figure 26: Comparison of the product stream temperatures when  $CH_4$  and  $O_2$  are reacted in a single step and in a step-wise manner. The step-wise condition shows that ignition occurs faster and a higher temperature is achieved with ignition.

## 6.4 Safe mixing distance

There has been considerable work done on the combustion characteristics of methane. It is generally known that methane has a low flame speed and poor lean-burn capability [56], [41]. This drives the need to mix methane and oxygen well before injection into the furnace, in order to ensure complete reaction of oxygen. For this purpose, a quantity called the 'safe mixing distance' was established. It was concluded that for oxygen to be completely consumed in the combustion reactions, mixing of the two gases needs to be done at a distance sufficiently far from the point of injection, such that the travel time is greater than the time for combustion. This will ensure complete combustion and no residual oxygen in the gas stream, which may cause re-oxidation issues if injected into the furnace. Figure 27 shows a schematic, representing the safe mixing distance.



Figure 27: Schematic showing the mixing of  $CH_4$  and  $O_2$  at a safe mixing distance to ensure complete consumption of oxygen before injection into the blast furnace.

The first step to calculate the safe mixing distance would be to estimate the speed of the gas stream injected. The speed of injection was calculated from the desired flowrates of methane to be injected. Additionally, an assumption was made as to the number of points of injection and the diameter of the pipe. For a constant flowrate, the higher the number of points of injection, the lower would be the safe mixing distance. Similarly, the larger the diameter of the pipe, the lower the safe mixing distance as a larger pipe would require lower speed of gas, at a constant gas flowrate. Table 8 shows the calculation of the speed of gas through each pipe for a case of 100 kg/THM of  $CH_4$  to be injected in the furnace shaft. These calculations assume 10 points of injection in the furnace shaft and the diameter of each pipe was assumed to be 10 cm.

Table 8: For a case of 100 kg/THM of  $CH_4$  to be injected through the furnace shaft. The  $CH_4$  to  $O_2$  molar ratio is 4:1. The speed of gas through each pipe has been calculated. The hot metal produced has been estimated using the 'Rist' mass and energy balance. Additionally, the gases  $CH_4$  and  $O_2$  have been assumed to be at 1200K and 2atm

Production (THM/day)	9355		
Points of injection	10		
Diameter of pipe (m)	0.1	t	
	CH <sub>4</sub> O <sub>2</sub>		
Mass injected (kg/THM)	100	50	
Rate of injection (moles/sec)	677	169	
Concentration (moles/cm <sup>3</sup> )	1.62E-05	4.06E-06	
Total volumetric flow of gas			
$(m^3/sec)$	33	8	
Flow through each pipe (m <sup>3</sup> /sec)	1.7	0.4	
Speed of gas in each pipe (m/sec)	424 106		

#### pressure.

The speed of gas as calculated in Table 8, can be used to estimate the safe mixing distance. In the previous section (Page 45), Kintecus was used to calculate the ignition delay of the methane combustion reactions. In particular, for Case 2, when the gas was at an initial temperature of 1200K, the delay in ignition was found to be 0.04 seconds approximately. Hence, for 0.04 seconds, there is no reaction after mixing  $CH_4$  and  $O_2$ . In Table 8, the speed of  $CH_4$  stream through each pipe was found to be 400 m/s approximately. Hence, at that speed, the gas travels a distance of 17 m in 0.04 seconds. Therefore, the mixing of  $CH_4$  and  $O_2$  must be done at least 17 m away from the furnace, to ensure enough time is allowed for the reaction to occur. Thus, 17 m is the safe mixing distance for the case of single step combustion reaction. The discussion in the section on 'Step-wise combustion of methane' showed that step-wise combustion of methane gives an ignition delay of 0.02 seconds as methane in added in parts. Figure 25 and Figure 26 show a faster reaction when step-wise combustion is done. Thus, with the effective safe mixing distance is reduced and

methane and oxygen can be reacted 5 m away from the furnace (From Table 9). However, a factor of safety must be added as well.

Table 9: Calculation of the safe mixing distance for Cases 1 and 2 (See page 45). Both cases consider the injection of 100 kg/THM of  $CH_4$  through the furnace shaft and no tuyère injection. The cases only differ in the molar ratio of  $CH_4$  to  $O_2$  considered. The

Case	$CH_4 / O_2$ molar ratio	Initial Temperature (K)	Delay in ignition (seconds)	Safe mixing distance (m)
1	2	1000	0.5	215
2	2	1200	0.02	5
3	4	1000	1.3	550
4	4	1200	0.04	17

delay in ignition calculations have been done using Kintecus.

It can be observed from Table 9 that a lower initial gas temperature results in an exponentially higher safe mixing distance. Hence, 1200K initial temperature would be ideal considering the mixing distance. Preheating the gas stream to a higher initial temperature is undesirable as it would result in methane cracking. An initial temperature of 1200K is similar to HYL conditions [12], hence providing evidence that safe pre-heating of methane to these temperatures is possible. Additionally, to achieve higher temperatures, special materials for construction would be required that can withstand the higher temperatures and would increase the overall expense.

## 6.5 Pre-heating methane

#### 6.5.1 Pre-heat energy calculations

As discussed in the previous section, in order to combust methane before injection, at a relatively smaller safe mixing distance, the initial temperature of the gas should ideally be about 1200K. The top gas of the blast furnace can be used to supply this energy to the reductant stream. In the blast furnace process, the top gas, owing to its high calorific value is used to heat the blast air in the stoves [1]. The reductant stream can be provided the required energy in a preheater similar to the stoves used for the blast air. Calculations were done to quantify the energy required to heat the reductant stream to 1200K using the top gas of the furnace. The preheater efficiency was considered to be about 60%, similar to stoves [57]. Table 10 shows the energy required to pre-heat the shaft reductant stream to 1200K. It also shows the top gas composition and the available energy in the preheaters. It can be seen from these calculations that burning the blast furnace gas in the preheaters would be able to generate enough energy to heat both the blast air and the methane stream. Additionally, as seen from the section on 'Unreacted natural gas', any presence of natural gas in the top gas will increase the heat content considerably.

Table 10: Calculations showing energy available from top gas of the blast furnace and energy required to heat the blast air and shaft reductant stream to 1273K and 1200K respectively. Calculations have been performed using the 'Rist' mass and energy balance.

CH <sub>4</sub> injected in the furnace (kg/TH M)	Fracti on of total CH <sub>4</sub> injecte d in the shaft	Top comp or	gas ositi 1	CV net of Top gas (MJ/TH M)	Preheat er efficien cy %	Energy available (MJ/TH M)	Energy required to heat Blast air to 1273K (MJ/TH M)	Energy required to heat reductan t stream to 1200K (MJ/TH M)			
100	1	Gas	%	5962	60	3577	1215	245			
		$N_2$	46								
		CO	19								
		$CO_2$	16								
		$H_2$	9	-							
		H <sub>2</sub> O	10	-							
100	0.5	$N_2$	49	6275	60	3460	1540	125			
		CO	18								
		$CO_2$	16		1	-	1				
		$H_2$	H <sub>2</sub> 8								
		H <sub>2</sub> O	9	1							

## 7. Experimental work

#### 7.1 Background

The previous section dealt with the theoretical calculations to predict the feasibility of natural gas injection in the shaft of the furnace. To practically test the concept, a laboratory setup was used. This setup was used to study the interaction of a bed of ironore pellets with a methane-rich blast furnace gas.

The experiments involved passing a methane-rich gas mixture relevant to blast furnace conditions through a reactor containing the bed of iron-ore pellets. The reactor was heated to desired temperatures and the flow rate of the gas mixture was controlled. The off-gas composition reflected the reactions occurring inside the reactor. The characterization of the pellets provided further information regarding the phases present and the degree of reduction that occurred.

Detail of each component of this experimental setup in the following paragraphs:

## 7.2 The experimental setup



Figure 28: The complete experimental setup used to study gas interactions with iron ore pellet bed.

The experimental setup that was used to conduct the reduction of iron ore to wüstite to metallic iron is shown in Figure 28. Each part of the setup is explained in detail as follows:

- Gas system with flow controllers Gas cylinders for ultra-high purity CO, CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub> and Ar were used. The flow was controlled using mass flow controllers that allow a maximum flow of 2l/min. The laboratory space was equipped with a CO monitor and each user carried a personal LEL monitor to detect any gas leaks.
- 2. Fused-quartz glass reactor A fused-quartz reactor was designed specifically to carry out gas interactions with a bed of pellets as shown in Figure 29. The reactor comprises of two tubes and a cap. The inner tube is provided with a porous frit bottom to allow gas flow. The frit bottom also acts as the base of the bed of pellets. The inlet and the outlet provided in the outer and inner tube of the reactor

determine the direction of flow of gases. The cap allows for the insertion of a bed thermocouple to keep a check on the temperature in the pellet bed. The cap also allows for direct injection of gases such as  $CH_4$  and  $O_2$  if needed (in this work,  $O_2$  addition was not done).



Figure 29: The actual picture and the schematic of the quartz glass reactor used for studying gas interactions with a bed of iron ore pellets

- 3. Furnace A Lindberg Blue M<sup>™</sup> furnace was used to heat the fused-quartz reactor. The bottom of the furnace was closed off using insulation. The opening through which the reactor was inserted was also insulated using alumina wool to minimize any heat losses. The furnace was used to maintain a pellet bed temperature of 900°C - 940°C.
- 4. Tubing system The entire setup utilized PFA (Perfluoroalkoxy alkanes) tubing. The tubing was heated (to approximately 60°C) and insulated in the specific stretch from the outlet of the reactor to the condenser setup to avoid any water

vapor condensation in the tubing. A simple heating cord and fiberglass insulation were used.

- Filter An inline filter (2 microns) was used just after the quartz reactor outlet to filter out any amorphous carbon formed from the off-gas after the reactions. Regular cleaning of the filter was done to ensure there was no back pressure.
- 6. Dew point analyzer A chilled-mirror hygrometer was used to measure the content of water vapor in the off gas of the reactions. The sensor of the hygrometer was mounted remotely in a metallic box, which was heated and insulated. The remote mounting is necessary to maintain the temperature of the sensor a little over the expected dew point for accurate measurement. The temperature inside this box was monitored using a surface thermocouple on the sensor body.
- 7. Water condenser setup A water pump was used to circulate water through a Graham condenser to cool down the off-gas after the water vapor content was measured. The condensed water was collected in a beaker at the bottom of the condenser, while the dry off-gas continued to flow through the tubing.
- 8. Mass Spectrometer The mass spectrometer was initially used for off-gas analysis, to determine the reactions occurring. A mass spectrometer ionizes molecules, splitting them into charged fragments. These fragments are then separated based on their mass to charge ratio by subjecting them to an electric field; since the ions with the same mass to charge ratio undergo the same amount of deflection. The use of the mass spectrometer available, was discontinued due to consistency issues and a new instrument (infrared analyzer) was used for further analysis.
- 9. Infrared Spectrometer The infrared spectrometer was mainly used for the offgas analysis to determine the reactions that occur inside the reactor. The IR spectrometer uses an NDIR (Nondispersive Infrared) detector to measure presence and quantities of CO, CO<sub>2</sub>, CH<sub>4</sub> and thermal conductivity detector (TCD)

to measure  $H_2$  content.  $O_2$  content is measured using an electron capture detector (ECD).

- 10. Remote computer A remote computer communicated with the mass spectrometer and the dew point analyzer. The off-gas mass spectra and the dew point of the gas were stored as data files that were analyzed later.
- 11. Kill switch A kill switch was provided to turn off the flow controllers of each gas cylinder. This allowed cutting off the gas flow in case of an emergency. The  $N_2$  gas cylinder was excluded from this kill switch setup to ensure continued flow of an inert gas in case of uncontrolled energy releases due to a gas leak.
- 12. Mesh An aluminum mesh was placed around the top of the quartz glass reactor that protruded from the furnace. In case of an energy release, this mesh would protect the user from shards of glass.

## 7.2.1 Modified experimental setup



Figure 30: Schematic of the modified experimental setup. The  $N_2$  gas tank was linked to a water vapor generator to allow for wetting of  $N_2$ . Additionally, a bypass valve was provided in case dry  $N_2$  is required.

Figure 30 shows the modified experimental setup. In order to carry out steam reforming reactions over wüstite/metallic iron pellets, the experimental setup was expanded to allow for the addition of water vapor. The water vapor generator comprised a water bath which was heated using a hot plate. The dry gas was passed through the water bath. The wet gas then passed through to the condenser system via heated and insulated pipes. The condenser temperature was adjusted to allow for the required concentration of water vapor to remain in the wet gas. The excess water vapor was condensed and collected in a beaker. The wet gas, now containing the desired concentration of water vapor was then included in the inlet gas mixture.

Down the line, after the dew-point of the off-gas was measured, a water vapor condenser cooled the gas and collected the condensed water. Additionally, the gas was passed through a silica gel tube to ensure that the gas was completely dried before analysis by the infrared spectrometer.

#### 7.3 Experimental parameters

## 7.3.1 Gas flowrates

(all of In the experimental work, mixture а gas or some  $CO+CO_2+H_2+H_2O+CH_4+O_2$ ) with compositions relevant to blast furnace iron making was passed through a bed of iron pellets. The gas residence time and flow rate were scaled down from typical blast furnace conditions. A furnace of 12m diameter has a typical bosh gas flow rate of 7500 Nm<sup>3</sup>/min. Using the power-law relationship between the flow rate and furnace diameter, the equivalent flow rate for the reactor with 0.05m diameter was calculated as approximately 306 Ndm<sup>3</sup>/min. Such a flow rate would give the same residence time in a 0.05m diameter reactor as in a blast furnace, if the height of the reaction zone were the same (assumed to be around 1 m in the blast furnace). However, the experimental reactor is much shorter, around 2-3 cm if several layers of pellets are used. The result is that an equivalent gas residence time would be achieved in the experimental reactor if the gas flow rate is around 3-5 Ndm<sup>3</sup>/min.

#### 7.3.2 Blast furnace pellets

The blast furnace iron ore pellets used for the experimental work that follows in the next section, were typical North American acid pellets, 10-13mm in diameter and weighed 1.5-3.5g. Table 11 summarizes the pellet composition.

Constituents	%
Fe <sub>2</sub> O <sub>3</sub>	93.09
SiO <sub>2</sub>	4.79
Al <sub>2</sub> O <sub>3</sub>	0.41
CaO	0.84
MgO	0.560
Mn	0.220
Р	0.021
S	
TiO <sub>2</sub>	
Na <sub>2</sub> O	0.046
K <sub>2</sub> O	0.022
С	

Table 11: Table showing the composition of the pellets that have been used for the experimental work done as part of this project.



Figure 31: Photograph of the North American Blast furnace acid pellets used for the

experimental work.

## 8. Results and Discussion

## 8.1 Reduction of hematite to wüstite

In order to recreate the reactions occurring in the blast furnace, particularly in the wüstite reserve zone, the initial step was to produce wüstite from the given iron ore pellets. As stated earlier, North American pellets, which contain approximately 93% Fe<sub>2</sub>O<sub>3</sub>, were used as the starting material. A pellet bed of about 15 pellets was used for all the reduction experiments.



Figure 32: Schematic of the pellet bed used.

To reduce the hematite pellets to wüstite, a gas composition of 50% CO and 50% CO<sub>2</sub> was used [58]. The pellets were initially heated to about  $900^{\circ}$ C in a Nitrogen atmosphere. The mixture of CO and CO<sub>2</sub> was then injected for a specified time. The details of the experiments carried out are shown as follows:

Experiment No.	Gas mixture	Temperature (ºC)	Duration (minutes)	Initial weight (g)	Weight loss from hematite(%)
1	50%CO- 50%CO₂	870	60	48.64	7.11
2	65%CO- 35%CO₂	900	90	45.38	6.76
3	50%CO- 50%CO₂	900	120	48.74	7.59
4	50%CO- 50%CO₂	900	210	51.16	7.56

Table 12: Hematite to wüstite reduction experimental details

The expected sequence of reactions is:

- 1.  $3Fe_2O_3 + CO = 2Fe_3O_4 + CO_2$
- 2.  $Fe_3O_4 + CO = 3FeO^a + CO_2$

X-ray Diffraction was done on the pellets before and after the reduction experiments. The XRD pattern of the unreduced pellets is as follows:

<sup>&</sup>lt;sup>a</sup> Wüstite here has been considered to be stoichiometric for simplification.



Figure 33: XRD pattern of unreduced pellets (Cu-Ka radiation was used)

Figure 33 shows that the unreduced pellets largely consist of hematite with minor other peaks [59].



Figure 34: XRD pattern of pellets after (a) Experiment 3 and (b) Experiment 4, both show a pure wüstite composition. (Cu-Kα radiation was used)

Observations from the hematite to wüstite reduction experiments:

- Gas mixtures of 50%CO-50%CO<sub>2</sub> successfully reduced hematite to wüstite. A gas mixture richer in CO does not give better results, as the weight loss seen with a gas mixture of 65%CO-35%CO<sub>2</sub> was lower. It was observed that at higher CO concentrations, carbon was deposited on the walls of the reactor. This carbon formation might be hindering the reduction to wüstite at greater CO concentrations. However, literature suggests that as expected, higher CO/CO<sub>2</sub> ratios increase the reducing power of the gas mixture [30].
- 2. Full reduction to wüstite gave a weight loss of approximately 7.56%. FactSage [38] calculations show that the wüstite formed at the given conditions is expected to be non-stoichiometric with a composition FeO<sub>1.088</sub>. The total expected mass loss for this stoichiometry is approximately 8.3% (from pure hematite) i.e. the expected mass loss for 93% hematite is approximately 7.7%, similar to the measured weight loss.

#### 8.2 Methane- wüstite interaction experiments

Once the method of making wüstite was established, experiments were done to test the interaction of the wüstite pellet bed with a methane rich gas under relevant blast furnace conditions. This aimed to give insight into the possible conversion of methane to carbon monoxide and hydrogen in a blast furnace. This section deals with the experimental work done to test this interaction.

## 8.2.1 Literature review: Methane and iron oxides

The production of hydrogen and syngas is a heavily researched field. There are a number of studies focused on producing hydrogen from catalyzed methane reforming reactions [60], [61], [29]. The steam reforming of methane is the reaction between methane and water vapor to produce carbon monoxide. This is discussed in detail later in the section on 'Methane Reforming'. The current section focusses on evidence in the literature regarding the interaction of methane with iron oxides; specifically, wüstite. The concept of chemical looping combustion (CLC) to catalyze the steam reforming of methane is a well-studied field which focusses on use of oxides as catalysts that provide oxygen to the fuel for combustion and then the reduced metal oxides are regenerated by air. Thus, the metal oxide acts as an oxygen carrier to facilitate fuel combustion [60]. This was shown with the help of the following reactions [60]:

Complete oxidation of methane

$$4Fe_{3}O_{4} + CH_{4} \rightarrow 12FeO + CO_{2} + 2H_{2}O \ (\Delta H^{0}_{298} = +463.7 \text{ kJ/mol})$$
 13

Partial oxidation of methane

$$Fe_{3}O_{4} + CH_{4} \rightarrow 3FeO + CO + 2H_{2} (\Delta H^{o}_{298} = +280.9 \text{ kJ/mol})$$
 14

Reduction of steam

$$3\text{FeO} + \text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + \text{H}_2(\Delta \text{H}_{298}\text{=}-74.7 \text{ kJ/mol})$$
 15

Thus, the above reactions show the use of  $Fe_3O_4$  as an oxygen carrier during which it undergoes reduction to FeO. The  $Fe_3O_4$  is then regenerated from FeO. Similarly, Mattisson et. al. [61] studied the behavior of natural hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) with CH<sub>4</sub> in a chemical looping combustion system at 950°C and studied the reduction and oxidation of the catalyst under multiple cycles. Yamaguchi et. al. [29] conducted studies, comparing the behavior of Fe<sub>2</sub>O<sub>3</sub> and supported Fe<sub>2</sub>O<sub>3</sub> as oxygen donors for methane conversion. It was found that addition of supports such as CeO<sub>2</sub> and ZrO<sub>2</sub> promoted the production of hydrogen, by retarding the formation of Fe and promoting reduction to FeO at lower temperatures (in the range of 650-750°C).

Methane is thermodynamically unstable above  $600^{\circ}$ C (See Figure 36), however, data in the literature reports that methane does not decompose below  $1300^{\circ}$ C, in the absence of a catalyst [62]. Thermo-catalytic decomposition of methane over supported metal catalysts is a well-known phenomenon [62], [63]. Muradov [27], [64] also showed the thermo-catalytic decomposition of methane over metal oxide catalysts such as alumina supported Fe<sub>2</sub>O<sub>3</sub>, in the temperature range of 200-900°C.

It can be seen that recent work focused mainly on the behavior of  $Fe_2O_3$  or  $Fe_3O_4$  as oxygen donors for methane conversion. However, the role of wüstite has not been emphasized greatly. Early work done by Barrett [65] in the 1970's focused on the interaction of wüstite and methane. Barrett conducted experimental work using iron ore pellets which were reduced to ferrous state before passing methane over them in the temperature range of 700-1000°C.The wüstite pellets showed approximately 42% porosity. The conversion of methane was quantified by analyzing the off-gas from the experiment. Barrett concluded that initially, methane reduces wüstite slowly and produces CO,  $H_2$  and  $H_2O$ . The metallic iron layer thus formed on the wüstite then speeds up the process due to the active Fe/FeO interface. Barrett suggested that the active nature of higher iron oxides as oxygen donors was also due to the formation of an Fe/FeO interface. Additionally, Barrett concluded that the overall reaction showed chemical reaction control.

Haas et. al. [66] ranked  $H_2$ , CO and  $CH_4$  in decreasing order of reducing potential for iron ores in the temperature range of 800-1100°C. Work done by Park et. al. [67] reported the increase in the reduction potential of  $CH_4$  at temperatures greater than 1100°C. A detailed kinetic analysis of the reduction of wüstite by methane above 1100°C, showed the reduction of wüstite by the carbon adsorbed on the iron ore surface by methane cracking [67]. The involved reactions were shown as:

$$CH_4(g) = \underline{C} + 2H_2(g)$$
 16

$$FeO(s) + CO(g) = Fe(s) + CO_2(g)$$
17

$$FeO(s) + H_2(g) = Fe(s) + H_2O(g)$$
 18

$$FeO(s) + \underline{C} = Fe(s) + CO(g)$$
 19

Here, <u>C</u> denotes the carbon that dissolved in Fe by the following reaction:

$$C_{adsorbed} + Fe = \underline{C}$$
 20

Similar work done by Nomura et. al. [68] showed 80% reduction in fine ore by a  $CH_4$  gas within one second, at 1300°C.

Thus, there is convincing evidence of reduction potential of  $CH_4$  at higher temperatures (> 1100°C). Also, from the kinetic studies, it is evident that interaction of methane with iron ores proceeds with dissociation of methane as a first step.

#### 8.2.2 Experimental work

The interaction of a methane rich gas with the bed of wüstite formed was tested. The iron ore pellets were first reduced to wüstite by the procedure mentioned in the previous section. The wüstite thus formed, was the starting material for the next step. The gas mixture was switched from 50% CO-50% CO<sub>2</sub> to the different mixtures discussed in Table 13. It must be noted that argon was used instead of nitrogen to simplify the process of off-gas analysis using the mass spectrometer. The reaction was conducted at 900°C for a duration of 20 minutes. The final product was analyzed by X-Ray Diffraction to establish the phases. In Experiments 2 & 3, a methane rich gas was used. In experiment 2, the CO:CO<sub>2</sub> ratio was 1:2 while, in Experiment 3, the CO:CO<sub>2</sub> ratio was 2:1 (both gas compositions favor formation of wüstite – See Figure 35). This was to ensure that the starting material in the reaction would be wüstite. As seen from the results, the final product formed in both Experiment 2 and Experiment 3 was wüstite itself (see Figure 38). Figure 37 shows the mass spectrum of the gas mixture as injected into the reactor. As seen from the significant 15 peak, CH<sub>4</sub> comprises approximately 9% of the gas mixture by volume. However, it can be seen from Figure 37 that the 15 peak persists even after the experiment. This clearly shows that even though the temperatures inside the reactor were around 900°C, cracking of methane over the wüstite bed is limited. This is contrary to what is expected from equilibrium, as methane is unstable above 600°C (See Figure 36).



Figure 35: The iron-iron oxides equilibrium diagram in the Fe-CO-CO<sub>2</sub> system was calculated using FactSage [69].



Figure 36: Equilibrium constant for decomposition of methane to carbon and hydrogen

[69].

No.	com	Gas position	Duratio n (minute s)	Temperatu re (°C)	Weight loss % (from hematite)	Starting material	Final produ ct (XRD)
2		%	20	900	7.62	Wüstite	Wüsti
	Ar	45					te
	CO	26					
	2						
	CO	12					
	$H_2$	8					
	СН	9					
	4						
3	Ar	45	20	900	8.54	Wüstite	Wüsti
	CO	12					te
	2						
	CO	26					
	H <sub>2</sub>	8					
	СН	9					

Table 13: Experimental details of wüstite-methane interaction experiments.



Figure 37: Mass spectrum of the gas mixture as (a) injected for experiment 3 (inlet gas as seen by reactor) (b) after completion of experiment 3 (off-gas)



Figure 38: XRD of pellets post reduction - Experiment 3 (Cu-Ka radiation was used)

FactSage was used to predict the equilibrium compositions of the gas mixtures used in the experimental procedure above with wüstite for comparison with the results obtained. As expected, FactSage calculations predicted complete reforming of the  $CH_4$  injected. However, the analysis of the experimental off-gas shows the presence of unreacted  $CH_4$  (Figure 37).

The observations from the methane- wüstite interaction experiments are summarized as follows:

- The wüstite surface does not seem to provide a favorable catalyzing surface for methane cracking. The persisting methane in the off-gas demonstrated the limited interaction of methane with wüstite.
- 2. FactSage calculations showed that from the laboratory experiments remained far from equilibrium. According to FactSage calculations, all of the methane injected would decompose upon equilibration and very negligible methane should remain in the off-gas.

#### 8.3 Modifying the proposed shaft injection

As seen from the previous section, the interaction of methane with wüstite pellets is limited. If methane were to be injected in the wüstite reserve zone, we would expect the gas to pass through the furnace, unreacted. Hence, modification of the proposed shaft injection scheme was required. The injection of the methane in the lower shaft of the furnace, i.e. below the wüstite reserve zone, was considered. In the lower shaft, the presence of metallic iron along with unreduced wüstite is expected. Pure metals and alloys have been well researched as catalysts for methane reforming reactions [70], [28]. If methane were to be injected in the lower shaft of the blast furnace, some conversion of methane due to the presence of metallic iron is expected. As discussed previously, the HYL ENERGIRON process uses this concept of 'in-situ' reforming of methane over metallic iron to carburize pellets and reduce iron ore [14]. The converted methane would then produce CO and H<sub>2</sub>, both of which are reagents for iron ore reduction in the blast furnace [37]. Figure 39 shows a simplified schematic of the modification in the initial proposal of natural gas injection in the blast furnace. This concept is also similar to the ULCOS top gas recycling program, which has its second set of tuyères in the lower shaft of the experimental furnace [23].



Figure 39: Schematic of the modified proposal of natural gas injection.

# 8.3.1 Impact of lower shaft injection on mass and energy balance calculations

The Rist mass and energy balance broadly divides the blast furnace in three regions; the raceway, the region extending from above the raceway to the top of the wüstite reserve zone and the region above the wüstite reserve zone. As discussed earlier, the composition and temperature of the gases leaving the raceway of the furnace is calculated based on the combustion products in front of the tuyères. The gases leaving the raceway then undergo temperature and composition changes due to reduction of wüstite to metallic iron and the heat exchange involved. Originally, when the injection of methane was considered in the wüstite reserve zone, it was within this region shown in Figure 40. Modifying the proposed injection slightly by injecting the gases below the upper boundary of the wüstite reserve zone, However, the burden material at the point of injection changes as below the wüstite reserve zone, presence of metallic iron is expected. Thus, the mass and energy balance calculations are not expected to be changed by injecting the natural gas lower in the furnace shaft. The presence of metallic iron is expected to change

the interaction of methane with gases in this region. This interaction of methane in the presence of metallic iron is discussed in further sections.



Figure 40: Schematic representing the region considered for the mass and energy balance calculations.

## 8.4 Reduction of hematite to metallic iron

The first step (in testing the behavior of metallic iron pellets as catalysts for reactions occurring in the blast furnace when natural gas in injected in the lower shaft), is the reduction of hematite pellets to metallic iron. To reduce hematite to metallic iron, a gas mixture of composition 50% H<sub>2</sub> – 50% N<sub>2</sub> was used [34]. The total flowrate of the inlet gas was 1 l/min. This gas mixture was passed through a bed of four iron ore pellets for approximately 1 hour at  $900^{\circ}$ C -  $940^{\circ}$ C. After reduction, the pellets were cooled down and weighed. This standard procedure gave a weight loss of approximately 27% relative to the iron ore pellet mass. XRD analysis of the pellets after reduction, showed a complete metallic iron phase, as seen from Figure 50.

## 8.5 Methane Reforming

The section on 'Expected reactions in the wüstite reserve zone' discussed the reactions expected when methane is injected in the blast furnace shaft. As the system is

complex and multiple reactions may be occurring at the same time, the most important reactions were taken into consideration, i.e. the reactions involving methane consumption which are of relevance for this work. These reactions were studied individually over a bed of metallic iron pellets. The later part of this section discusses the overall reaction and the conversion of methane under blast furnace conditions.

#### 8.5.1 Literature review

Dry and steam reforming of methane are the interaction of methane with carbon dioxide and water vapor respectively to produce carbon monoxide and hydrogen. Steam reforming in particular is a popular and commercially established method of hydrogen production [21], [22], [71]. Methane reforming reactions are highly endothermic in nature and hence the reforming reactors are operated at high temperatures with heating [22]. To ensure maximum methane conversion, steam reforming processes are known to use a steam to carbon ratio of 3-5 at 800°C-900°C and 35 atm pressure [27]. For production of hydrogen, alumina supported nickel catalysts are most widely used [21], [28], [70]. Extensive literature is available on the catalysts used for both dry reforming and steam reforming of methane, with detailed analysis of the kinetics of the reactions and the deactivation of catalysts. As supported Ni catalysts have been commercially established as the catalysts for reforming, most of the available literature addresses the kinetics of steam reforming over nickel, nickel-iron alloys and iron as catalysts.

The deactivation of metal catalysts used for methane reforming is a well-known and researched issue [72], [73], [74], [75], [76]. The deactivation of catalysts is due to carbon deposition from methane decomposition or sintering of the catalysts themselves with extensive use [21], [22], [77], [74]. Alumina supported Ni catalysts are widely used for this process due to their low cost and high availability [78], however, nickel based catalysts are also highly susceptible to carbon deposition at high reforming operating temperatures

[79]. Joo et al. [78] studied the activity of Ni/Al<sub>2</sub>O<sub>3</sub> catalysts at different temperatures and concluded that the catalysts remained active for 70 hours at 850°C, but had a higher amount of deposited carbon as compared to catalysts used at 450°C. They attributed the high activity even though the catalysts have high carbon deposition to the type of carbon formed. Amorphous carbon is known to deactivate the surface; however filamentous carbon does not cover the surface, thereby not deactivating it. There have been a number of studies on the behavior of such filamentous carbon on metal surfaces [80], [81]. Fe and Ni alloys are known to be attacked by this 'metal dusting' phenomenon in the critical temperature range of  $400^{\circ}$ C -  $800^{\circ}$ C [80]. The presence of this filamentous carbon was confirmed microscopically by Theofanidis et al. [82] and Bradford et. al. [79]. The work done by Nielsen [83] showed the resistance of reforming catalysts to coking in the presence of sulphur, is a widely accepted concept.

The reactions which have been found to cause carbon deposition during methane reforming are as follows [77]:

$$CO + H_2 = C + H_2O$$

$$2CO = C + CO_2$$

$$CH_4 = C + 2H_2$$

#### 8.5.1.1 Dry reforming of methane

Dry reforming of methane is the reaction between methane and carbon dioxide to give carbon monoxide and hydrogen. This reaction is highly endothermic. Reformers are generally run at temperatures in the range of 1000-1200K.

$$CH_4 + CO_2 = 2CO + 2H_2 [28] \Delta H^{\circ}_{298} = 247 \text{ kJ/mol of } CH_4$$
 24

Pakhare and Spivey [28] reviewed the dry reforming of methane extensively and summarized the kinetics of the reaction over various metal catalysts and supports. The activation energy of dry reforming of methane was found to be in the range of 76-123 kJ/mol over various supported noble metal catalysts [28].

Benrabaa et. al. [84] studied the catalytic behavior of nickel-ferrite oxides for dry reforming of methane and found that such reducible oxides as opposed to supported metal catalysts, show lower activity but are also more resistant to carbon deposition. The surface oxygen promotes the burning of carbon while the cations are reduced. However, the main drawback of these oxides is the high contribution of the reverse water gas shift reaction. Work done by Bradford and Vannice [85] on the kinetics of dry reforming of methane on supported nickel catalysts showed the dependence of the reaction rate on partial pressure of the reactants. They showed that an increase in the partial pressure of methane increased the rate of CO and  $H_2$  formation; however, increases in the partial pressure of the reverse water gas shift reaction.

Wang et. al. [76] suggested that there is a lot of contradictory work on the reaction mechanism involved in the dry reforming of methane reaction and many studies suggest the rate determining step depends on the surface oxygen available. Wang et. al. suggested a simplified reaction mechanism based on previous studies and their experimental work, shown in the following reactions:

$CH_4 + * \rightarrow CH_4^*$	25
$\text{CO}_2 + * \rightarrow \text{CO}_2*$	26

$$CH_4^* \rightarrow CH_3^* + H$$
 27

$$CH_3^* \to CH_2^* + H$$
 28

$CH_2^* \rightarrow CH^* + H$	29
$CH^* \rightarrow C^* + H$	30
$\mathrm{C}^{*} + \mathrm{CO}_{2}^{*} \rightarrow 2\mathrm{CO} + 2^{*}$	31
$CO \rightarrow C + O$	32
$2H + O \rightarrow H_2O$	33

$$H + H \rightarrow H_2$$
 34

Species with the '\*' symbol in the above reaction mechanism show the 'active' state of carbon. The reactions involving active carbon are faster than the other reactions.

Previous work on dry reforming of methane suggests mechanisms similar to the aforementioned reaction mechanism, however, the rate limiting step has been shown to depend on the catalyst used, catalyst surface, temperature and partial pressure of reactants and in a few studies, oxygen activity specifically.

## 8.5.1.2 Steam reforming of methane

Steam reforming of methane is widely used as a method of producing hydrogen. It is the reaction between methane and water vapor to give carbon monoxide and hydrogen. Similar to the dry reforming reaction, steam reforming is highly endothermic in nature.

$$CH_4 + H_2O = CO + 3H_2 [29] \Delta H_{298}^0 = 206 \text{ kJ/mol of } CH_4$$
 35

Münster and Grabke [70] conducted research on the kinetics of steam reforming over nickel, iron and iron-nickel catalysts. Their results show comparable values of reaction rate constant of nickel and iron catalysts, but the rates are lower on iron.



Figure 41: Results from Münster and Grabke [70], showing comparable catalytic behavior of nickel, iron and iron-nickel alloys. 'v' gives the rate of reaction in the plot. In this work, the rate of steam reforming over iron catalysts was found to be of the order of  $2 \times 10^{-9}$  mol/cm<sup>2</sup> s at 800°C for P<sub>H2O</sub>/P<sub>H2</sub>=0.006. The catalysts were in the form of a foil.

The reaction kinetics of steam reforming on metal catalysts, has been studied in great detail [72], [86], [70]. Münster and Grabke [70] found methane decomposition to be the rate limiting step. However, at low oxygen activities, the reaction between adsorbed oxygen and carbon to form carbon monoxide was found to be rate-limiting. Bengaard et. al. [72] conducted detailed experimental and computational analysis to conclude that the steam reforming reaction is extremely sensitive to the catalyst surface and relies on the active sites on the catalyst surface for both  $CH_4$  adsorption reactions and nucleation of graphite.

Hou and Hughes [21] discussed the kinetics of methane reforming over supported nickel catalysts in great detail. The reverse water gas shift, which approaches equilibrium under reforming conditions, was also studied to determine the consumption of CO<sub>2</sub> and H<sub>2</sub>

formed during methane reforming. Hou et. al. concluded that methane reforming follows first-order kinetics with respect to methane at low methane conversion rates and low temperatures. An intrinsic kinetic model was used to verify that both methane and steam adsorb on the catalyst surface by dissociation and the reaction between adsorbed species is rate limiting for the catalyst under consideration. The work of Xu et. al. [71] on the intrinsic kinetics of methane reforming on nickel based catalysts showed that the reaction mechanism largely depends on the type of catalyst used. The use of nickel fibers, for instance, does not provide any diffusional limitations unlike those observed in catalysts with large pores

#### 8.5.2 Dry reforming of methane over metallic iron pellets

In this work, CO<sub>2</sub> reforming of methane was identified as one of the expected reactions when methane is injected into the furnace shaft. Experiments were conducted to measure the rates of dry reforming of methane over metallic iron pellets, under relevant conditions to estimate the extent of reaction in the blast furnace.

### 8.5.2.1 Rate of reaction

To measure the rate of the CO<sub>2</sub> reforming of methane over metallic iron, 4 commercial blast furnace pellets (93% hematite, typical size – 10-12mm, typical mass – 1.5-3.5g) were placed in the fused quartz reactor and heated under nitrogen to approximately 940°C. The pellets were first reduced to metallic iron under a 50% H<sub>2</sub> – 50% N<sub>2</sub> atmosphere for about 1 hour. Once metallic iron was obtained, a reforming gas mixture of controlled composition (varied between experiments) was passed through the reactor. The off-gas analysis obtained using the infrared spectrometer was used to calculate the rate of consumption of methane. The weight of the pellets was measured before and after the reaction to observe any weight gain/loss.

Table 14 shows the experimental details of one such dry reforming reaction conducted over 4 metallic iron pellets. Apart from  $CH_4$  and  $CO_2$ , CO was also injected with the inlet gas mixture, to maintain a reducing atmosphere and prevent the re-oxidation of metallic iron by  $CO_2$ . The off gas analysis obtained during this particular experiment is shown in Figure 42. We can see that the reforming of  $CH_4$  occurred, by the production of  $H_2$  and CO during the experiment. Further analysis also showed the presence of excess CO, which was produced along with the  $H_2$ . Calculations were done to determine the rate of consumption of  $CH_4$  and the rate constant for the reaction was estimated per pellet. For this particular reaction shown in Table 14, the rate constant is estimated as k = rate (mol/s for 1 gram of pellet) / ([ $CH_4$ ]×[ $CO_2$ ] ×(1- $\beta$ )) = 9.5×10<sup>-6</sup> m<sup>6</sup>/mol.s gram, where the concentrations are in mol/m<sup>3</sup> and  $\beta$  is the ratio of the reaction quotient and the equilibrium constant.  $\beta$  was found to be close to 1 for all experiments.

Experiment	Gas compos	Duration (minutes)	
1	$CH_4$	11	40
	$CO_2$	3	
	CO	25	
	$N_2$	61	

Table 14: Experimental details of one of the methane dry reforming reactions



Figure 42: Off gas analysis done using the Infrared Spectrometer shows the presence of higher amounts of CO and the production of  $H_2$  as compared to the inlet gas mixture (the latter is shown by the horizontal dotted lines).

These dry reforming experiments were repeated several times, for different concentrations of methane, to test whether the reaction follows first-order kinetics as was assumed to calculate the rate constant. In each repetition of the experiment, the percentage of  $CO_2$  in the total reaction mixture was kept constant and the  $CH_4$  concentration was changed while maintaining the total flow rate. The order of the reaction was then determined as the slope of the ln(rate) vs. ln([ $CH_4$ ]) plot, where *r* is the rate of the reaction in moles/sec per gram of pellet and [ $CH_4$ ] is the concentration of  $CH_4$  in moles/m<sup>3</sup> (See Figure 43). The reaction does follow first order kinetics with respect to  $CH_4$  (when the rate is calculated in terms of  $CH_4$  consumed), which is in agreement with previous work [76], [87].

The methane concentration in these kinetic studies is the concentration of methane at the pellet surface. The surface concentration of each gas species was estimated using the following equations:
$\dot{n}_{species} = \dot{V}_{gas} * C_{bulk} + m \times A_{ext} \times \Delta C$ 

And

$$\dot{V}_{gas} = \frac{\dot{n}_{reaction^{*R*T}}}{P}$$
 2

Where,

 $\dot{n}_{species}$  is the rate of change of a particular species in moles/sec per pellet,

 $\dot{V}_{species}$  is the volumetric flow of the gas species,

 $\dot{n}_{reaction}$  is the rate of reaction per pellet,

z is the molar ratio of the species consumed and produced with respect to methane, m is the mass transfer coefficient for boundary-layer diffusion around the pellet A<sub>ext</sub> is the external surface area of the pellet

 $\Delta c$  is the difference between the bulk and surface concentrations in moles/m<sup>3</sup>.

Therefore, for each gas species;

$$C_{surface(i)} = C_{bulk(i)} - \frac{z \times \dot{n}_{reaction} * (1 - C_{bulk(i)} * R * \frac{T}{P})}{m_{(i)} \times A_{ext}}$$

$$3$$

Where,

C<sub>bulk</sub> is given by the average of the input and output mole fractions, for each species. The mass transfer coefficients for each gas species in a multi-component system was calculated using Wilke's equation [88] for viscosity and diffusivity of gas mixtures.

1



Figure 43: Plot of ln(rate) vs. ln([CH<sub>4</sub>]) where the rate of reaction is in moles/sec per gram of pellet and [CH<sub>4</sub>] is the concentration of CH<sub>4</sub> in moles/m<sup>3</sup>. The slope of the plot gives the order of the reaction with respect to CH<sub>4</sub>. Here, the rate is represented both in terms of CO produced (open diamond markers) and CH<sub>4</sub> consumed (filled circular markers). It must be noted that the rate in terms of CH<sub>4</sub> consumed, overestimates the

rate due to some carbon deposition.

## 8.5.2.2 Activation Energy

In order to test the rate-controlling step for dry reforming of methane over metallic iron pellets, further experiments were conducted to measure the apparent activation energy of the reforming reactions. To measure the apparent activation energy, a bed of iron ore pellets was first reduced to metallic iron at 900°C under a 50%  $H_2 - 50\% N_2$ atmosphere for approximately 1 hour. The metallic iron thus obtained was then exposed to a relevant reforming gas mixture. While the reforming mixture was flowing through the reactor at 900°C for about 45 minutes, off gas analysis data was recorded using the infrared spectrometer. The temperature was then changed to 970°C and was held for 45 minutes. The temperature was then changed back to 900°C and then 970°C for 45 minutes each. This temperature cycling was expected to bring about physical changes in the pellets themselves due to sintering and the rate of the reaction at each temperature cycle would help determine or observe any such changes.

This experiment was carried out on a bed of 3 pellets weighing approximately 3.53 g each, initially. Figure 44 shows the experimental results.

Table 15. Figure 44 shows the experimental results.

Table 15: Details of the injected gas mixture used in the experiment conducted to measure activation energy of dry reforming of methane.

Experiment	Gas compos	Duration at each stage (minutes)	
3	$CH_4$	13	45
	CO <sub>2</sub>	3	
	CO	26	
	$N_2$	58	



Figure 44: Rate constant (in m<sup>6</sup>/mol.s.gram) for the dry reforming of methane is given for each temperature cycle. Each temperature was maintained for approximately 45 minutes and the off-gas analysis data from the infrared spectrometer was used to calculate the rate constant. The rate constant was calculated in terms of CH<sub>4</sub> consumed.

The Arrhenius equation was used to determine the apparent activation energy:

$$k = A * e^{-\frac{E_a}{RT}}$$

4

Where, k is the rate constant A is a constant  $E_a$  is the activation energy in KJ/mol R is the gas constant in J/mol. K T is the temperature in Kelvin On rearranging, we get:

$$\ln k = \ln A - \frac{E_a}{RT}$$
 5

i.e. 
$$\ln k = \left(-\frac{E_a}{R}\right) * \left(\frac{1}{T}\right) + \ln A$$
 6

Using the above equation and the information from Figure 44, the apparent activation energy for each change in temperature for CO<sub>2</sub> reforming of methane can be calculated. Table 16 shows the calculated values of activation energy for each such step. The apparent activation energy calculated in this work (Table 16) is comparable to those in the literature [28], [85]. The apparent activation energy indicates a chemical controlled reaction. The lower rate of the reaction during the second cycle may have been caused by the carbon pick-up by the pellets or sintering. Thus, the catalytic history of the pellets has some influence on the reaction rate.

Table 16: Activation energy calculated for each stage in both experiments over 3 iron ore pellets. The step labels correspond to the change in temperature cycles as shown in

Step	Step details	Activation Energy (kJ/mol)
а	900°C-970°C ramp up	69
b	970°C-900°C ramp down	157
с	900°C-970°C ramp up 2	127

Figure 44.

# 8.5.3 Steam reforming of methane over iron pellets

The blast furnace gas also contains some water vapor in addition to CO,  $CO_2$ ,  $H_2$  and  $N_2$ . To consider relevant blast furnace gas compositions, the next step was to test the interaction of a methane rich gas with metallic iron pellets, in the presence of water vapor.

# 8.5.3.1 Rate of reaction

The experiments carried out to measure rate of steam reforming of methane over metallic iron pellets were conducted in a way similar to the dry reforming reactions. Hematite pellets were first reduced to metallic iron under a 50%  $H_2 - 50$ %  $N_2$  atmosphere for a duration of 1 hour. A steam reforming gas mixture was then passed through the fusedquartz reactor. A water vapor generator was used to wet the  $N_2$  stream before it entered the reactor. A dew point analyzer (chilled-mirror hygrometer) was used to measure the water vapor content in the off gas. The water vapor was then condensed to dry the off-gas before passing it through the infrared spectrometer for further analysis. Table 17 shows the experimental details of the steam reforming reaction mixture passed over a single metallic iron pellet for a duration of approximately 45 minutes.  $H_2$  was injected along with the steam reforming mixture, to ensure the stability of the metallic iron phase [89]. Figure 45 shows the dry off-gas analysis showing the production of  $H_2$  when compared to the injected  $H_2$  concentration. Also, the dew point of the off-gas was around 15°C, i.e. 1.5% water vapor, whereas, the total water vapor content in the inlet gas mixture was 2.4%. Thus, the consumed water vapor showed up in the off-gas in the form of CO and  $H_2$ .

Kinetic analysis to calculate the rate constant of the steam reforming reactions was done (similar to the dry reforming experiments). The rate constant per pellet in this particular reaction was found to be  $2.0 \times 10^{-5}$  m<sup>6</sup>/mol.s per gram of pellet at 940°C, where the concentrations are in mol/m<sup>3</sup> and the rate of reaction is in moles/s per gram of pellet. The rate of reaction was approximately  $1 \times 10^{-5}$  moles/s.

Gibson [34] reported the BET surface are of reduced iron ore pellets, depending on the degree of reduction. Blast furnace pellets with 99.48% degree of reduction, showed a surface area of approximately  $0.4m^2/g$ . In the current experiment, approximately 2.6g of metallic iron was used as a catalyst. The total surface area of the pellet is thus approximately, 1 m<sup>2</sup>. The rate of the steam reforming reaction can thus be reported as

 $9.5 \times 10^{-10}$  moles/cm<sup>2</sup> s. This value is similar to the data reported in the literature [70] (See Figure 41).

Table 17: Experimental details of a steam reforming reaction carried out over a single metallic iron pellet.

Experiment	Gas composition		Duration	Temperature
	(%)			
1	$CH_4$	10	45 minutes	940°C
	$H_2O$	2.4		
	$H_2$	11		
	$N_2$	76.6		

These experiments were repeated multiple times; each time changing the methane concentration to determine the order of the reaction with respect to methane. Figure 46 shows the relation between the rate of methane consumption and the concentration of methane. The slope of the plot gives the order of the reaction. It can be seen that the steam reforming experiments show first order kinetics with respect to methane (when rate is calculated in terms of CO produced), which is supported by data in the literature [21]. The pellets subjected to steam reforming, picked up carbon during the experiment (See Table 21 and Table 22). Thus, it was concluded that production of CO was a more accurate way of calculating the rate of reaction, than consumption of  $CH_4$ .



Figure 45: Infrared spectrometer analysis of the dry gas after water vapor was condensed out of the off-gas. The off-gas analysis shows a considerable amount of  $H_2$  in the dry gas as compared to the 10%  $H_2$  injected in reactor. The production of CO and the absence of  $CO_2$  in the off-gas also shows that the dominant reaction here is the steam reforming reaction. The off-gas concentrations of  $CH_4$ ,  $H_2$  and CO have been corrected for the presence of 1.5% water vapor which was condensed out before the gas reached the IR spectrometer.



Figure 46: Plot of ln(rate) vs.  $ln([CH_4])$  where the rate of reaction is in moles/sec per gram of pellet and  $[CH_4]$  is the concentration of  $CH_4$  in moles/m<sup>3</sup>. The slope of the plot gives the order of the reaction with respect to  $CH_4$ . Here, the rate is represented both in

terms of CO produced (open diamond markers) and  $CH_4$  consumed (filled circular markers). It must be noted that the rate in terms of  $CH_4$  consumed, overestimates the

rate due to some carbon deposition.

## 8.5.3.2 Activation energy

Similar to the dry reforming reaction, the apparent activation energy of steam reforming over metallic iron pellets was measured. One hematite pellet was first reduced to metallic iron at 900°C under a 50%  $H_2 - 50\%$  N<sub>2</sub> atmosphere for approximately 1 hour. The metallic iron thus obtained was then exposed to a relevant reforming gas mixture. While the reforming mixture was flowing through the reactor at 900°C for about 30 minutes, off gas analysis data was recorded using the infrared spectrometer. The temperature was then changed to 970°C and was held for 30 minutes. The temperature was then changed to 970°C for 30 minutes each. This temperature cycling was expected to bring about physical changes in the pellets themselves due to sintering and the rate of the reaction at each temperature cycle would help determine or observe any such changes.

Table 18 and Figure 47 show the experimental details and also shows the rate constant at each step/temperature cycle.

Table 18: Details of the injected gas mixture used in the experiment conducted to measure activation energy of steam reforming of methane over a single metallic iron

pellet.

Experiment	Gas compos	Duration at each stage (minutes)	
3	CH <sub>4</sub>	6	30
	$H_2$	14	
	H <sub>2</sub> O	2	
	$N_2$	77	

98



Figure 47: Rate constant for the steam reforming of methane is given for each temperature cycle. Each temperature was maintained for approximately 30 minutes and the off-gas analysis data from the infrared spectrometer was used to calculate the rate constant. The rate constant was calculated in terms of CH<sub>4</sub> consumed.

Using  $\ln k = \left(-\frac{E_a}{R}\right) * \left(\frac{1}{T}\right) + \ln A$  (Equation 6), the apparent activation energy for each of the temperature cycles, i.e. (a) ramp up from 900°C to 970°C, (b) ramp down from 970°C to 900°C and (c) second ramp up from 900°C to 970°C was calculated. Table 19 shows the calculated apparent activation energy for each of these temperature cycles. It can be concluded from these results, that steam reforming of methane over metallic iron pellets has a high activation energy and is mostly chemical reaction controlled. These activation energy values agree well with those in the literature [70].

Step	Step details	Activation Energy (kJ/mol)
а	900°C-970°C ramp up	185
b	970°C-900°C ramp down	196
С	900°C-970°C ramp up 2	196

Table 19: Activation energy calculated for each stage of the experiment. The step labels correspond to the change in temperature cycles as shown in Figure 47.

#### 8.5.4 Post-experiment sample analysis

Reduction of hematite to metallic iron was carried out to estimate the expected weight loss. This was determined to be about 27% for the pellets used. Table 20 and Table 21 show the weights of the pellets before and after dry reforming and steam reforming experiments. In each experiment, the pellets were weighed before beginning the experiment, i.e. as hematite pellets, giving the initial weight of the pellets. After each experiment, the pellets were weighed again to give the final weight of the pellets. The weight loss percentage was estimated and in most cases, this was found to be less than 27%. It was concluded that the pellets, which were initially reduced using a standard practice, regained some of the weight during the reforming experiments. The percentage gain in weight was estimated. Carbon pick up by the pellets during reforming was determined to be the reason for the weight gain. Carbon deposition on the catalyst during dry and steam reforming, is a commonly observed phenomena and has been discussed by Theofanidis et. al. [82] and Trimm et. al. [77].

After each experiment, the pellets were weighed and analyzed. LECO combustion tests [90] were also used to detect any carbon pick up in the pellets. The pellets subjected to the activation energy experiments experienced the highest weight gain with respect to metallic iron. Apparently, the temperature cycling contributed to carbon pick up. Additionally, as the activation energy experiments were conducted for a duration of 2-6 hours, the

exposure to the reforming mixtures was the longest in these cases. However, the SEM analysis of the pellet surface did not show any presence of elemental carbon.

As mentioned earlier, analysis of the pellet surface under a scanning electron microscope, showed no visible presence of elemental carbon, even at low voltage backscattered electron imaging, as shown in Figure 49. The surface of a metallic iron pellet, after dry reforming and a pellet after steam reforming look exactly the same. Since the pellets showed a gain in weight, but the SEM images did not show the presence of carbon, the pellets were sent for LECO combustion testing and also analyzed by X-Ray Diffraction.

Table 20: Table showing the % weight gained by pellets in 5 dry reforming experiments. The calculated percentage weight gain/pellet is the weight gained by metallic iron pellets.

The expected metallic iron weight shows the weight of the pellets after losing 27% of

Experiment	Total duration of reforming (minutes)	Initial hematite weight (g)	Expected metallic iron weight (g)	Measured Final weight (g)	% weight gain from Fe/ pellet
1	30	7.578	5.532	5.544	0.22
2	50	10.973	8.010	8.078	0.85
3	60	14.240	10.395	10.540	1.39
4	90	11.295	8.245	8.360	1.39
5	90	10.780	7.869	8.028	2.02

their weight on reduction in a 50%H<sub>2</sub>-50% N<sub>2</sub> atmosphere for 1 hour.

Table 21: Table showing the % weight gained by pellets in 5 steam reforming experiments. The calculated percentage weight gain/pellet is the weight gained by metallic iron pellets. The expected metallic iron weight shows the weight of the pellets after losing 27% of their weight on reduction in a 50%H<sub>2</sub>-50% N<sub>2</sub> atmosphere for 1 hour.

Experiment	Total duration of reforming (minutes)	Initial hematite weight (g)	expected metallic iron weight (g)	Final weight (g)	% weight gain from Fe
1	30	8.700	6.351	6.730	5.97
2	50	3.510	2.562	2.690	4.98
3	50	3.350	2.446	2.490	1.82
4	60	2.920	2.132	2.186	2.55
5	75	2.144	1.565	1.693	8.17



Figure 48: Photographs of pellets after (a) dry reforming and (b) steam reforming experiment.



Figure 49: SEM images of pellets after completion of experiments. These images are BSE images taken at 10Kv and 2000X magnification. (a) Post-reduction iron pellet surface(b) Pellet surface after dry reforming experiment (c) Pellet surface after steam reforming. The bright regions are metallic iron and the darker regions represent gangue. The black region shows the pores in the pellet. SEM analysis shows no change in pellet surface after dry and steam reforming.



Figure 50: XRD pattern of a metallic iron pellet, which was reduced from hematite in a 50% H<sub>2</sub>-50%N<sub>2</sub> atmosphere for 1 hour. (Cu-K $\alpha$  radiation was used)



Figure 51: XRD pattern of iron pellets post (a) dry reforming and (b) steam reforming. The pattern shows presence of graphite and cementite along with metallic iron [91]. (Cu-Kα radiation was used)

As seen Figure 51, the pellets which were used as catalysts for both dry and steam reforming show the presence of graphite and cementite as compared to the metallic iron pellet in Figure 50. However, no carbon was visible on the pellet surface in the backscattered electron imaging. This may be due to the relatively small amount of carbon pick up and/or non-uniform deposition of carbon.

Additionally, selected samples were sent for LECO testing [90] to confirm the presence of carbon using a standardized technique. Table 22 summarizes the results obtained by LECO testing. These results were compared to the measured percentage weight gain of metallic iron pellets. The agreement between the two results, confirmed the carbon pick-up during reforming reactions. Additionally, it can be concluded that pellets pick up more carbon during steam reforming and longer exposure to the reforming atmosphere, leads to greater carbon pick-up.

Table 22: Summary of LECO analysis results compared with measured percentage weight gain in the laboratory. (It must be noted that only part of the actual sample was sent for LECO testing and the remainder was retained for SEM imaging, XRD, etc.)

S. No.	Experiment	Duration	Measured % weight gain (from Fe)	Carbon wt. % (LECO analysis)
1	Dry Reforming-1	155	1.2	2.2
2	Dry reforming (activation energy)-1	145	1	0.6
3	Dry reforming (activation energy)-2	165	4	2.1
4	Steam reforming-1	45	5	5.9
5	Steam reforming-2	75	8.2	8.5
6	Steam reforming (activation energy)	165	15	14

## 8.6 Reforming over cementite pellets

On conducting dry and steam reforming of methane over metallic iron pellets, a weight gain due to carbon pick-up was observed in the pellets. This is a known phenomenon in catalysts used for methane reforming reactions [83]. Thus, during the course of the reaction, the pellet chemistry is changing and cementite (Fe<sub>3</sub>C) is being generated as shown in Figure 51. It was of interest to specifically study the rate of reforming over cementite catalyst to observe if the carbon pick-up slows down the rate of

the reaction considerably. To do so, the blast furnace iron ore pellets were reduced and carburized to cementite as a first step. This involved reducing four iron ore pellets to metallic iron (900°C, 50% H<sub>2</sub>-50%N<sub>2</sub>, 1 hour) and then carburizing them to produce a 4-5% carbon content. This was done by exposing the metallic iron pellets to a mixture of composition 45% CH<sub>4</sub>, 45% H<sub>2</sub> and 10% N<sub>2</sub> at 650°C for approximately 1 hour [91]. Once cementite was formed, the pellets were exposed to a methane reforming atmosphere to observe the conversion of methane over cementite. Table 23 and Figure 52 summarize the experimental details and show the off-gas composition as seen by the infrared spectrometer. The results show conversion of methane over cementite as a production of H<sub>2</sub> and CO is observed, while CH<sub>4</sub> and CO<sub>2</sub> are consumed. The rate of methane consumption was found to be  $2.3 \times 10^{-6}$  moles/s per gram of cementite pellet. In comparison, the rate of dry reforming was found to be  $2.6 \times 10^{-6}$  moles/s per gram of methane consumption is not affected significantly.

Table 23: Experimental details of one of methane dry reforming reaction over cementite

Experiment	Gas compos	Duration (minutes)	
1	$CH_4$	13	30
	$CO_2$	3	
	CO	26	
	$N_2$	58	

pel	lets.
per	icus.



Figure 52: Infrared spectrometer data showing the inlet gas composition in comparison with the off-gas composition during methane dry reforming over cementite pellets.

## 8.7 Mixed reforming and Blast furnace gas

## 8.7.1 Background

A considerable amount of work has been done to study the mechanism behind steam and dry reforming of methane as a method for hydrogen production. Most of these studies emphasize optimizing the catalyst to make the methane conversion to hydrogen most efficient. Mixed reforming on the other hand, has not been researched as extensively. It has been found that mixed reforming does not present optimum conditions for methane conversions [92] and partial-oxidation of methane to directly convert it to syngas may be a more viable option [92], [93]. The work done by Qin et. al. also showed a decreased rate of methane conversion when both  $CO_2$  and  $H_2O$  are present in the feed [92]. Mixed reforming is endothermic and the reverse water gas shift reaction (producing CO and  $H_2O$ ) makes it less attractive an efficient process to produce hydrogen. However, most reforming studies were conducted over reforming catalysts and at lower temperatures in the range of 800°C- 850°C. Wei et. al. [94] presented experimental evidence to support that the conversion of methane over nickel catalysts solely depends on the partial pressure of methane and does not depend on  $CO_2$  and  $H_2O$  concentration. It was suggested that the overall reaction mechanistically behaves similar to decomposition of methane and that breaking the C-H bond was the most relevant step kinetically.

With the previous work done in this field in context, this section deals with interaction of metallic iron with a gas mixture that is relevant to blast furnace conditions and the presence of methane under these conditions.

#### 8.7.2 Experimental work

After testing and studying the methane reforming reactions and their rates over metallic iron pellets, the next step was to combine the two reactions and achieve a gas composition closer to blast furnace gas composition. This was done to finally test the conversion of methane in a blast furnace, when injected through the furnace shaft. The experimental design was similar to previous experiments, with iron ore pellets first being reduced to metallic iron and then passing the reaction mixture over the pellet bed at approximately 940°C. The reaction mixture was estimated in the following way:

- The off-gas composition of the wüstite reserve zone was calculated under the condition that there is no tuyère injection of natural gas. This mixture approximates the proportion of CO, CO<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>O and N<sub>2</sub> in the region of lower shaft injection.
- 2. The gas mixture being injected into the lower shaft of the furnace was estimated. As partial combustion of methane is being considered before injection into the furnace itself, the composition was estimated using Kintecus (discussed in section

on Combustion of methane). As discussed previously, the partial combustion calculations yield a gas mixture comprising  $CH_4$ ,  $H_2$ , CO,  $CO_2$  and  $H_2O$ .

3. The two compositions, i.e. the 'off-gas' from the furnace raceway and the gas mixture being injected into the lower shaft were added and the flowrates were scaled down to laboratory scale.

## 8.7.3 Experiment #2

When 100 kg/THM methane was assumed to be injected through the shaft of the furnace with no tuyère injection, the composition of the resulting gas mixture (shown in Table 24) was calculated using the abovementioned method. Similar to previous experiments, a single iron ore pellet was first reduced to metallic iron  $(50\% H_2 - 50\% N_2, 900^{\circ}C, 1 \text{ hour})$  before being exposed to the gas composition mentioned. The total flow rate of the gas stream was approximately 1.3 l/min. The water vapor content of the off-gas was measured using the dew-point analyzer and the dry gas was analyzed using the infrared spectrometer.

Table 24: Experimental details of interaction of a metallic iron pellet with a gas of composition similar to a blast furnace gas with shaft injection of methane.

Experiment	Gas compos	Duration (minutes)	
2	$CH_4$	6	25
	$CO_2$	7	
	CO	32	_
	$H_2$	16	_
	H <sub>2</sub> O	2	
	$N_2$	38	

Figure 53 shows the off-gas analysis from the experiment, as reported by the infrared spectrometer. It is evident from these results<sup>b</sup> that there was no interaction between the methane rich blast furnace gas with the metallic iron pellets. This was different from the previously obtained reforming results. Even though there were both  $H_2O$  and  $CO_2$  present in the gas mixture, methane conversion was not seen. The reducing potential of the gas was sufficiently strong to maintain the metallic iron phase and some conversion of methane was expected under these conditions. However, these experiments did not show any methane conversion.



Figure 53: Infrared spectrometer analysis of the off-gas in Experiment 2; showing the interaction of a metallic iron pellet with a methane rich blast furnace gas. (It must be noted that H<sub>2</sub> and H<sub>2</sub>O were introduced gradually into the reaction mixture, hence, in the initial stages the contribution of the CO, CH<sub>4</sub>, CO<sub>2</sub> appears to decrease).

<sup>&</sup>lt;sup>b</sup> The results appear to show the consumption of  $CO_2$  and  $H_2$  to produce CO and  $H_2O$  (reverse water gas shift reaction), however, the results are within the range of error shown by the setup (with respect to  $H_2$  specifically) and hence conclusive evidence is not observed.

## 8.7.4 Experiment #3

The absence of any methane conversion in the previous experiment showed the need to tweak the experimental parameters to understand the issue. In the following experiment, the concentration of methane was increased with respect to the  $CO_2$  content. Since the reforming of methane was found to follow first order kinetics with respect to methane concentration, an increase in methane was expected to increase the reaction rate. There was evidence in the literature that supported the increase in methane partial pressure to increase the reaction rate [95]. Additionally, a high  $CO_2$  partial pressure increased the rate of reverse water gas shift reaction. The new gas composition called 'blast furnace gas' is shown in Table 25 and Table 26 under 'Blast furnace gas'.

Experiment 3 was carried out in two separate phases.

**Experiment 3a**: In the first experiment, a bed of four iron ore pellets was first reduced to metallic iron  $(50\%H_2 - 50\%N_2, 900°C, 1 \text{ hour})$ . Once the reduction was complete, the reaction was carried out as follows:

- i. Initially, a gas mixture containing  $CH_4$ ,  $CO_2$ , CO and  $N_2$  was injected.  $H_2$ and  $H_2O$  were not introduced right away. This gas mixture was called 'dry reforming gas'. This mixture was passed over the metallic iron pellet bed for approximately 20 minutes. (See Table 25)
- ii. After 20 minutes, the H<sub>2</sub> and H<sub>2</sub>O were gradually introduced into the mixture (and argon was turned off). The addition of H<sub>2</sub> and H<sub>2</sub>O changed the 'dry reforming gas' to 'Blast furnace gas'. The 'blast furnace gas' was then passed over the pellets for 15 minutes.

This step-wise addition of  $H_2$  and  $H_2O$  showed the change in the rate of methane consumption when the dry reforming mixture was gradually changed to a methane-rich blast furnace mixture.

**Experiment 3b**: In the second phase of the experiment, a bed of four iron ore pellets was first reduced to metallic iron. Once the reduction was complete:

- An inlet gas of composition shown in Table 26 (under 'Steam reforming gas') was introduced. This injected gas comprised of CH<sub>4</sub>, H<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub> and Ar. This reaction mixture was allowed to flow for approximately 20 minutes.
- After 20 minutes, CO and CO<sub>2</sub> were gradually introduced into the mixture. Thus, the 'steam reforming gas' was changed to 'blast furnace gas' after addition of CO and CO<sub>2</sub>. This blast furnace gas was allowed to pass for approximately 15 minutes.

Thus, a change in the methane consumption when the gas mixture changed from a steam reforming to a methane-rich blast furnace gas mixture was observed.

The objective behind carrying out the experiment in this manner was to observe the change in rates of methane consumption between dry reforming, steam reforming and interaction of methane-rich blast furnace gas with metallic iron pellets.

The results of Experiments 3a and 3b are shown in Figure 54 and Figure 55. As compared to experiment 2, clearly, conversion of methane is observed in this reaction. This confirms that when methane concentration was higher than the CO<sub>2</sub> concentration of the blast furnace gas, some conversion of methane was observed.

Step	Name	Gas composition		Duration (minutes)
1	Dry reforming	$CH_4$	11	20
	gas	$CO_2$	6	
		СО	29	
		Ar	17	
		$N_2$	37	
2	Blast furnace	$CH_4$	11	15
	gas	$CO_2$	6	
		CO	29	
		$H_2$	15	
		H <sub>2</sub> O	2	
		$N_2$	37	

Table 25: Details of Experiment 3a (which was carried out in two different steps).

Table 26: Details of Experiment 3b (which was carried out in two steps).

Step	Name	Gas composition		Duration (minutes)
1	Steam reforming gas	$CH_4$	11	20
		$H_2$	15	
		$H_2O$	2	
		Ar	35	
		N <sub>2</sub>	37	
2	Blast furnace	CH <sub>4</sub>	11	15
	gas	CO <sub>2</sub>	6	
		CO	29	
		H2	15	
		H <sub>2</sub> O	2	
		N <sub>2</sub>	37	

Figure 54 shows the change in methane conversion when the gas mixture was changed from a dry reforming mixture to a methane-rich blast furnace gas. The production of CO peaks just as  $H_2$  and  $H_2O$  are introduced in the inlet gas and then quickly stabilizes. However, a similar trend is observed in the  $CH_4$  percentage. This shows that the consumption of  $CH_4$  decreased slightly, however CO was produced. It is highly probable that the peak in CO production was due to the reverse water gas shift reaction.

Within a few minutes, the rate of  $CH_4$  conversion went back to the initially observed rate. Thus, in spite of the presence of  $H_2O$ , the reaction showed a conversion rate similar to the dry reforming reaction. Additionally, both  $CO_2$  and  $CH_4$  showed similar trends of consumption, confirming that the final rate of methane conversion was similar to the rate of dry reforming.



Figure 54: Infrared spectrometer data for Experiment 3a; from 0-1100 seconds, the inlet gas mixture is a dry reforming mixture with no  $H_2$ ,  $H_2O$  added. After 1100 seconds,  $H_2$ and  $H_2O$  were introduced into the inlet mixture.

In the second phase, i.e. experiment 3b, the interaction of the methane-rich blast furnace gas with a steam reforming mixture can be observed. The production of  $H_2$  and the consumption of  $CH_4$  clearly show a drop in the rate of methane conversion. Thus, the rate of methane conversion in steam reforming is evidently faster than the methane-rich blast furnace gas. The two phased experiment 3, thus showed that when methane concentration is greater than the CO<sub>2</sub> concentration under blast furnace conditions, the reaction is likely to proceed at the rate of dry reforming.

Figure 55 also shows the increase in water vapor concentration when CO,  $CO_2$  were introduced, indicating an apparent discontinuation in steam reforming once  $CO_2$  is introduced as the outlet and inlet water vapor concentrations are almost similar. It is likely that steam reforming occurs in parallel with the reverse water gas shift reaction.

Further experiments are kinetic studies are required to separate the reverse water gas shift rates from the reforming rates. However, since the reverse water gas shift will occur under furnace conditions, for the purpose of this work, overall methane consumption provides the better insight.



Figure 55: Infrared spectrometer data for Experiment 3b; from 0-1100 seconds, the inlet gas mixture is a steam reforming mixture with no CO,  $CO_2$  added. After 1100 seconds, CO,  $CO_2$  were introduced into the inlet mixture.

Experiments 3a and 3b were done over different pellet beds and the initial weight of the metallic iron was different. Both experiments showed the same consumption of methane per gram of pellet for the same injected methane concentration. Here, the rate of consumption is simply the overall consumption of methane during the experiment. It was further observed in these experiments that the effective consumption of  $CH_4$  and  $CO_2$  in moles/ sec gram of pellet was in the ratio 1:1. Table 27 shows the pellet weight before the experiments. Post-experiment measurement of pellet weight showed a 27% loss in weight from hematite. Thus, the pellets are expected to be completely metallic iron.

Table 27: Summary of pellet analysis and methane consumption for experiments 3a and

	•
0	h
ັ	$\sim$

Experiment	Initial hematite weight	final weight loss %	Rate of methane consumption (moles/sec per gram)
за	9.74	27	3.00E-06
3b	7.2	27	3.20E-06

X-Ray diffraction analysis of the pellets post experiment, however, showed the presence of additional phases other than ferrite, as shown in Figure 56.



Figure 56: X-ray Diffraction patterns of pellets after experiments 3a and 3b. (The peak denoted by the star represents gangue and the peaks denoted by the dots are representative of the aluminum sample holder and may be neglected)

### 8.8 Comparison with blast furnace conditions

The rates of methane consumption obtained from the above experiments were used to estimate the consumption of methane if injected in a blast furnace, just below the thermal reserve zone. Calculations were done using under the following assumptions:

- 1. The furnace is operated under baseline conditions, without any fuel injection through the tuyères.
- Dry reforming of methane is the dominant reaction and follows first order kinetics; from the experiment reported in Experiment 3 above, the rate constant is estimated as k = rate (mol/s for 1 pellet) / ([CH<sub>4</sub>]×[CO<sub>2</sub>]) = 1.7×10<sup>-5</sup>, where the concentrations are in mol/m<sup>3</sup>.

Calculations were based on a hypothetical 12 m (hearth diameter) furnace (with no oxygen enrichment in the blast air, taken to be at 1273 K). Using the 'Rist' mass and energy balance [35], the production rate was estimated as approximately 8153 THM/day. As a first estimate, the injected methane was assumed to penetrate to 1 m from the outside diameter. Hence, the interaction volume of the pellets with the gas was determined by the penetration of the methane injection.

Interaction volume = 
$$\pi (R^2 - (R - p)^2) * (\Delta z)$$
 7

where R is the radius of the furnace, p is the penetration distance of methane into the furnace (for the current calculations, p=1m), and  $\Delta z$  is the height of the furnace burden available to catalyze methane reaction.

Calculations were performed for a temperature of 1213 K, an assumed pressure of 2 atm and assuming the pellet bed volume to be equivalent to 0.8 pellets per cm<sup>3</sup>. Figure 57 shows the schematic of the top view of the interaction volume. Assuming the reforming reaction to be first-order with respect to the concentrations of methane and carbon dioxide, the initial reaction rate is estimated to be 450 mol/s per meter height of pellet bed.

The gas composition was estimated using the Rist mass and energy balance and the previously done Kintecus calculations (See section on 'Methane combustion calculations using Kintecus'). For a furnace of 12m diameter and methane penetration of 1m into the furnace; the interaction area considered here is approximately 30% of the actual furnace cross-section area. The Rist mass and energy balance was used to estimate the composition of gases that enter the wüstite reserve zone. The quantity of gas as reported by the Rist mass and energy balance is for the entire cross-section of the furnace. This number was then reduced to 30% to obtain the actual flow rate of the gas through the annulus cross-section.

Kintecus calculations were used to estimate the actual composition of the gas being injected in the furnace shaft. The injection of 100 kg/THM of  $CH_4$  needs to be combusted with  $O_2$  before injection and the molar ratio of  $O_2/CH_4$  was established as 0.25. Thus the total mass of gas being injected in the shaft is 150 kg/THM. Kintecus calculations show that after combustion, the gas stream contains 40%  $H_2$ , 10% CO, 15%  $H_2O$ , 5% CO<sub>2</sub> and 30% unreacted  $CH_4$ . This gas was then added to the wüstite reserve zone gas passing though the annulus region. Table 28 shows the effective gas composition that is interacting with the metallic iron pellets in the presence of unreacted methane under blast furnace conditions. Thus unreacted methane injection rates are approximately 250 moles/sec. Figure 58 shows the fraction of methane consumed as a function of the height (or distance travelled by the gas). These calculations assume the absence of lateral mixing of methane when it is injected into the shaft.

Table 28: Summary of the effective gas composition and flow rate that interact with the bed of metallic iron pellets in a blast furnace. The annulus gas composition is specific for the assumption that injected gas penetrates 1 m into the furnace and the furnace diameter is 12m. The injected gas composition is calculated using Kintecus and combusting 100 kg/THM with  $O_2$  in the  $O_2/CH_4$  molar ratio of 0.25 and initial temperature 1200K.

Gas species	Wüstite reserve zone gas (moles/sec)	Annulus gas [30% of wüstite reserve zone gas] (moles/sec)	Injected gas through shaft (moles/sec)	Total gas flow rates (moles/sec)
CO <sub>2</sub>	801	245	16	261
CO	1917	586	51	636
H <sub>2</sub>	819	250	2831	3081
N <sub>2</sub>	3502	1070	0	1070
H <sub>2</sub> O	460	140	118	258
CH <sub>4</sub>	0	0	265	265



Figure 57: Top view of the interaction volume considered for the purpose of kinetic calculations. The penetration distance of methane into the furnace was assumed to be 1m [96].



Figure 58: Plot showing the fraction of methane that will be consumed in the furnace over the height of 2m. This calculation assumes 100 kg/THM of CH<sub>4</sub> is injected completely through the shaft, with partial combustion at O<sub>2</sub>/CH<sub>4</sub> molar ratio of 0.25. The rate of the reaction from experiment 3 was used as the rate of methane consumption.
These calculations were done for a 1000°C blast temperature and the flame temperature was set at 1800°C. (a) The fraction of unreacted methane injected into the furnace is shown. (b) The fraction of total methane (100kg/THM) converted by combustion and reforming is shown.

### 9. Cost estimate

An initial cost estimate was attempted for the proposed shaft injection of natural gas. Currently, blast furnaces do not have any facility in the lower shaft for injection of gases. Installing 10 tuyères for example, would involve many factors and conducting an absolute cost estimate here is not feasible. However, the feasibility of lower shaft tuyères is supported by the ULCOS top gas recycling program. The experimental furnace constructed to facilitate top gas recycling and injection of CO and  $H_2$  into the furnace, allows for injection into the original tuyères and lower shaft tuyères [23]. Here an initial quantitative estimate has been attempted with the available information.

### 9.1 Capital investment

A number of requirements have been identified as a first step to conducting a cost estimate. Personal communication with Dr. M. F. Riley helped narrow down the factors to be considered [55].

- Furnace shut down To be able to install tuyères in the lower shaft, furnace operations will have to be stopped briefly. This may be scheduled with any other maintenance shut down. However, as installing tuyères in the lower shaft is a big undertaking, it might need extra time than regular maintenance.
- 2. Altering the furnace design Currently, furnaces do not have openings in the lower shaft for installing a tuyère. 'Boring holes' in the lower shaft will not be a simple task. It would interfere with the existing design and may need relining of the refractory inside the furnace and the copper staves outside the furnace.
- 3. Tuyère installation Tuyères need to be installed in the furnace shaft. As partial combustion of natural gas is being considered, tuyère diameter of 4 inches or approximately 10cm has been estimated. An estimate of 4 inch tuyère diameter has been made to allow for partial combustion of methane stream down the line. In the

absence of any combustion requirements, typical tuyère diameters are about 1 inch.

- Water-cooled Copper As tuyères are being installed as opposed to simple injection lances, water-cooled copper will be needed to maintain tuyère life.
- 5. Piping Apart from natural gas, oxygen for partial combustion and nitrogen for purging will need to be supplied. This results in laying pipes for the three gases from the nearest source around the furnace. Additionally, to use the top gas as a source of energy for pre-heating the natural gas, pipes need to be laid from the top of the furnace to the preheater. However, the top gas is used in the blast furnace stoves and diverting part of it towards the pre-heater may involve challenges.
- 6. Flow-controls Each tuyère to be installed, requires injection of oxygen down the line to partially combust the natural gas. The ratio of methane to oxygen needs to be controlled and thus each tuyère requires 3 control legs for N<sub>2</sub>, O<sub>2</sub> and CH<sub>4</sub>.
- Pre-heater The natural gas supply is in the range of 300 Nm<sup>3</sup>/THM (assuming 200 kg/THM injection). Accordingly, a pre-heater is required to heat the natural gas supply to approximately 930°C before it is partially combusted.
- 8. Compressor The lower furnace shaft is expected to be at 2 atmospheres pressure, due to the pressure drop across the furnace height [2]. The gases that are injected, thus need to be pressurized before injection. The HYL system uses a compressor in-line, before pre-heating the reductant stream [14].
- 9. Labor cost The process of boring holes into the furnace shaft and installing new tuyères, pipes, pre-heater, compressor system would be a highly labor intensive process. Additionally, labor costs may be higher if the furnace shut-down is scheduled for a shorter time.
- Platform construction A platform may be needed to facilitate servicing of the tuyères.

Table 29: Initial estimate of investment required for tuyère installation, piping and flow controls. The cost of natural gas, oxygen and nitrogen piping is based on pipe lengths of 60m, 180m and 180m respectively. It was considered that natural gas piping would be

<b>Tuyère installation</b>		
Diameter	0.1	m
Installation cost per tuyère	20000	\$
No. of tuyères	10	
Total cost of installation	0.2	Million \$
Piping (N <sub>2</sub> ,O <sub>2</sub> ,NG)		
Cost + engineering cost	36	\$/ ft/ inch of pipe
	480	\$/m of pipe
Cost of NG pipe	28800	\$
Cost of O2 pipe	86400	\$
Cost of N2 pipe	86400	\$
Total piping cost	0.2	Million \$
Flow controls		
No. of control legs/tuyère	3	$(\mathrm{N}_2,\mathrm{O}_2,\mathrm{NG})$
Cost per control leg	60000	\$
Total cost per tuyère	180000	
Total cost of flow controls (10 tuyères)	1.8	Million \$
•		
Total estimated cost	2.2	Million \$

done directly from the casting floor [55].

Table 29 gives an initial estimate of the capital costs of installing 10 tuyères (approximately 4" or 0.1m in diameter). Additionally, the labor cost, cost of pre-heater, compressor, etc. might depend to a great extent on the specific furnace.

Another cost would be the loss in production while the tuyères are being installed. However, installation may be done at the same time as a regular service shut down and might not be directly part of the capital investment. A furnace of 12m diameter, operating at baseline conditions (no fuel injection through tuyères, 1000°C blast temperature and flame temperature set at 1800°C) shows a productivity of approximately 7100 THM/day. At an estimated cost of \$200 /tonne of pig iron [97], the furnace would see a total product cost of approximately \$3 Million for two days of shut down.

## 9.2 Operating costs

In addition to the abovementioned capital costs, installing new tuyères would add to the running cost of the furnace.

- Gas supply A continuous supply of N<sub>2</sub>, CH<sub>4</sub> and O<sub>2</sub> is required to carry out the shaft injection of natural gas. However, this method does not show any excess O<sub>2</sub> requirement than what is already consumed by the furnace.
- Maintenance Installing new tuyères, pre-heater, compressor and piping would require regular maintenance of the system. This adds to the existing maintenance cost of operation.

## 9.3 Cost benefit

According to our mass and energy balance calculations, injecting natural gas in the furnace shaft would require lower coke rate and increase furnace productivity. However, it is difficult to estimate whether these cost benefits would provide a fair trade-off for the initial costs incurred and the additional maintenance required.

The U.S. EIA reported the current price of natural gas and coke as 0.2 \$/kg and 0.26 \$/kg respectively. Therefore, for a coke replacement ratio of 1.3 and a furnace that injects 100 kg/THM of methane, the savings are approximately \$14 /THM with respect to baseline conditions.
It must be noted that the mentioned factors are highly area-specific or furnace-specific. Each furnace has different logistics and would require a more detailed analysis of factors that need to be considered.

## 10. Review of hypotheses

**Hypothesis 1**: Injection of natural gas in the shaft of the blast furnace is theoretically feasible, as far as the energy balance is concerned. The endothermic effect of the natural gas injection can be counteracted with the co-injection of oxygen.

Review: The mass and energy balance calculations supported the feasibility of natural gas injection in the furnace shaft. It was shown that injecting natural gas in the furnace shaft, relaxes the constraint on the adiabatic flame temperature limit. The need for oxygen enrichment of the blast is reduced and instead, oxygen can be injected along with natural gas in the furnace shaft.

However, as initially considered, a  $O_2/CH_4$  molar ratio of 0.5 would result in complete combustion of methane outside the furnace and the injected gas would only comprise CO and  $H_2$ . Instead if the  $O_2/CH_4$  is maintained at 0.25, this would provide sufficient energy to the reductant stream to raise its temperature, while the reductant stream contains unreacted methane.

**Hypothesis 2**: Wüstite is not a good substrate for methane cracking. Interaction of a bed of wüstite pellets with methane rich blast furnace gas is limited. To improve the interaction of methane with the pellet bed, a more catalytic surface (such as metallic iron) is required. Review: The previous work done in this field, did not present convincing evidence of interaction between methane and wüstite. Most of the work done, emphasized the use of  $Fe_2O_3$  as a catalyst for reforming (as an oxygen donor). The experimental work done to confirm this showed the absence of any interaction between a wüstite pellet bed and a methane rich gas under blast furnace conditions. A review of the literature available, showed that metals are better catalysts for methane reforming. Though nickel is commonly used due to its optimum catalytic behavior, iron has been research as a reforming catalysts previously. Hence, it was concluded that a bed of metallic iron would provide the required catalytic surface for conversion of methane.

**Hypothesis 3**: Natural gas can instead be injected in the lower shaft of the furnace where the pellet bed comprises of part wüstite and part metallic iron. Injection in the lower shaft of the furnace has little or no impact on the mass and energy balance calculations.

Review: It was confirmed with the help of experimental work done that wüstite shows limited interaction with a methane rich gas. Injection of methane in the lower shaft of the furnace was considered. A review of the mass and energy balance calculations was done to confirm that theoretically, there would be no change in the calculations if methane was injected in the lower shaft of the furnace instead of in the wüstite reserve zone.

**Hypothesis 4**: Methane conversion over metallic iron pellets would result in production of carbon monoxide and hydrogen, which would in turn be utilized in the reduction of wüstite. Thus, a furnace can maintain productivity while functioning at higher natural gas rates and lower coke rates.

Review: The experimental work done showed the conversion of methane to carbon monoxide and hydrogen over a bed of metallic iron pellets. Carbon monoxide and hydrogen are known reagents for the reduction of iron ore in the furnace and are expected to reduce the wüstite. Mass and energy balance calculations show that shaft injection of methane would decrease the blast air rates through the tuyères; thereby increasing furnace productivity. Additionally, the coke rate would be lowered.

However, actual furnace trials would be needed to confirm these results.

## 11. Conclusion

This work proposed the injection of natural gas in the furnace shaft as opposed to the current practice of tuyère injection. Mass and energy balance calculations showed a relax in the adiabatic flame temperature constraints due to shaft injection of natural gas. The calculations done showed that shaft injection is feasible and presents benefits in the productivity and coke rate of a furnace.

The injection of methane into the furnace shaft was studied in detail, including the practical parameters to be considered. Kintecus was used to estimate the partial combustion of methane to give the actual composition of gas that would be injected in the furnace.

A detailed analysis of the interaction of methane with a bed of metallic iron pellets was done. The reactions expected on shaft injection of methane were narrowed down to the dominant reactions; dry reforming and steam reforming of methane. The rates of these reactions were then tested over a bed of metallic iron pellets under blast furnace conditions. Once the individual rates were measured, the interaction of pellets was tested with a 'blast furnace gas'. It was concluded that the interaction of a methane-rich blast furnace gas with a metallic iron pellet bed would be similar to  $CO_2$  reforming of methane. Under these assumptions, calculations showed approximately 75% conversion of the injected unreacted methane within two meters of furnace height above the point of injection.

Experimental work also showed that methane concentration must be higher than the CO<sub>2</sub> concentration at the point of injection for any reforming to occur.

Further work may be required to analyze the kinetics of these reactions in greater detail. Additionally, testing the effect of the presence of coke along with the metallic iron is required. Conducting plant trials would further confirm the results presented, specifically for quantities such as coke rates and furnace productivity.

## 12. References

- [1] A. Babich, D. Senk, H. W. Gudenau and K. T. Mavrommatis, Ironmaking Textbook, Aachen: RWTH Aachen University, Department of Ferrous Metallurgy, 2008.
- [2] D. H. Wakelin, "Ironmaking Volume," in *The Making Shaping and Treating of Steel, 11th Edition*, Pittsburgh, AISE Steel Foundation, 1999.
- [3] American Iron and Steel Institute, "Technology roadmap research program for the steel industry," American Iron and Steel Institute, Oak Ridge, 2010.
- [4] J. G. Peacey and W. G. Davenport, The iron blast furnace: Theory and practice, Pegamon, 1989.
- [5] World Steel Association, "Steel's contribution to a low carbon future," worldsteel.org, 2014.
- [6] Iron and Steel Society of AIME, "Annual Blast Furnace Roundup," *Iron & Steelmaker*, 1997-2003.
- [7] U.S. Energy Information Administration, "Natural Gas," U.S. Department of Energy, [Online]. Available: http://www.eia.gov/.
- [8] WorldSteel Association, "Statistics Archive," Worldsteel Association, [Online]. Available: https://www.worldsteel.org/statistics/statistics-archive.html.
- [9] Association for Iron & Steel Technology, "North American Blast Furnace Roundup," *Iron & Steel Technology*, 2012.
- [10] M. Geerdes, Reinoud van Laar and R. Vaynshteyn, "Low-cost hot metal: the future of blast furnace ironmaking," *Iron and Steel Technology*, vol. 8, no. 3, p. 51, 2011.
- [11] D. Newsome, "The Water-Gas Shift Reaction," *Catalysis Reviews: Science and Engineering*, vol. 21, no. 2, pp. 275-318, 1980.
- [12] Tenova HYL, Danieli, "HYL ENERGIRON Technology: General Overview," 2012.
- [13] B. Anameric and S. K. Kawatra, "Properties and features of direct reduced iron," *Mineral Processing and Extractive Metallurgy*, vol. 28, no. 1, pp. 59-116, 2007.
- [14] D. Escareno and et. al., "Method for producing direct reduced iron with limited CO2 emissions". United States of America Patent US8940076 B2, 27 January 2015.
- [15] World Steel Association, "Fact Sheet: Steel and raw materials," worldsteel.org, 2014.
- [16] Midrex Technologies, Inc., "Midrex DRI Technology," August 2014. [Online]. Available: http://www.midrex.com/assets/user/media/MIDREX\_NG.pdf. [Accessed 15 June 2016].
- [17] M. Atsushi, H. Uemura and T. Sakaguchi, "MIDREX<sup>®</sup> processes," *Kobe Steel Eng. Rep.*, vol. 60, no. 1, pp. 5-11, 2010.
- [18] UNICAT Catalyst Technologies, Inc., "Syngas Reforming," UNICAT Catalyst Technologies, Inc., [Online]. Available: http://www.unicatcatalyst.com/syngas/syngas-reforming/. [Accessed 15 June 2016].
- [19] R. M. Klawonn and R. Kakaley, "Using Oxy+ to make reducing gas in the Midrex direct reduction process," *Direct from Midrex,* pp. 3-6, 4th quarter, 2002.
- [20] B. G. Kelley, "Catalyst The factors which affect performance," *Direct from Midrex*, pp. 8-9, 2nd quarter 1998.
- [21] K. Hou and R. Hughes, "The kinetics of methane steam reforming over a Ni/a-Al2O catalyst," *Chemical Engineering Journal*, vol. 82, pp. 311-328, 2001.

- [22] E. L. Oliveira, C. A. Grande and A. E. Rodrigues, "Methane steam reforming in large pore catalyst," *Chemical Engineering Science*, vol. 65, no. 5, pp. 1539-1550, 2010.
- [23] J. Van der Stel, G. Louwerse, D. Sert, A. Hirsch, N. Eklund and M. Pettersson, "Top gas recycling blast furnace developments for 'green'and sustainable ironmaking," *Ironmaking* & Steelmaking, vol. 40, no. 7, pp. 483-489, 2013.
- [24] European Commission, "ULCOS: Ultra-low carbon dioxide steelmaking," Community Research and Development Information Service, 27 June 2012. [Online]. Available: http://cordis.europa.eu/estep/ulcos\_en.html. [Accessed 20 June 2016].
- [25] European Commission, "New blast furnace process (ULCOS)," RFCS Publications, Brussels, 2013.
- [26] E. T. Turkdogan, "Blast furnace reactions," *Metallurgical and Materials Transactions B*, vol. 9, no. 3, pp. 163-179, 1978.
- [27] N. Z. Muradov, "CO2-free production of hydrogen by catalytic pyrolysis of hydrocarbon fuel," *Energy & Fuels*, vol. 12, no. 1, pp. 41-48, 1998.
- [28] D. Pakhare and J. Spivey, "A review of dry (CO2) reforming of methane over noble metal catalysts," *Chemical Society Reviews*, vol. 43, no. 22, pp. 7813-7837, 2014.
- [29] D. Yamaguchi and et. al., "Hydrogen production through methane-steam cyclic redox processes with iron-based metal oxides," *International Journal of Hydrogen Energy*, vol. 36, no. 11, pp. 6646-6656, 2011.
- [30] J. Li, P. Wang, L. Zhou and M. Cheng, "The reduction of wustite with high oxygen enrichment and high injection of hydrogenous fuel," *ISIJ international*, vol. 47, no. 8, pp. 1097-1101, 2007.
- [31] R. J. Smith, M. Loganathan and M. S. Shantha, "A review of the water gas shift reaction kinetics," *International Journal of Chemical Reactor Engineering*, vol. 8, no. 1, 2010.
- [32] P. J. Meschter and H. J. Grabke, "Kinetics of the water-gas shift reaction on an "FeO" surface," *Metallurgical Transactions B*, vol. 10, no. 3, pp. 323-329, 1979.
- [33] M. Bahgat, K. A. Halim, H. A. El-Kelesh and M. I. Nasr, "Fundamental Study of Water-Gas Shift Reaction in Ironmaking Process," *Journal of Metallurgical Engineering*, vol. 1, no. 3, pp. 63-69, 2012.
- [34] J. Gibson, *On the Use of Pre-reduced Feed in the Blast Furnace Process,* Pittsburgh: Carnegie Mellon University, 2016.
- [35] A. Rist and N. Meysson, "A Dual Graphic Representation of Blast-Furnace Mass and Heat Balances," *Journal of Metals,* vol. 19, no. 4, p. 50, 1967.
- [36] P. C. Pistorius, "Technical and economic evaluation of top gas recycling blast furnace ironmaking," in *Proceedings of the Fray International Symposium*, Cancun, 2011.
- [37] J. C. Agarwal, F. C. Brown, D. L. Chin, A. R. Frydenlund, N. S. Jessiman, A. P. Lingras and S. J. Sikirica, "The use of total thermal-plus-chemical energy above 2700°F as a parameter to describe blast furnace operations," *Ironmaking Conference proceedings*, pp. 473-479, 1991.
- [38] M. J. Wojewodka, J. P. Keith, S. D. Horvath, M. A. Alter and C. C. McGovern, "Natural gas injection maximization on C and D blast furnaces at ArcelorMittal Burns Harbor," in *Proceedings of the AISTech conference*, Indianapolis, 2014.
- [39] M. F. Riley and T. Niehoff, "Iron Production," in *Oxygen-Enhanced Combustion, Second Edition*, Boca Raton, CRC Press, 2013, pp. 517-530.

- [40] U.S. Energy Information Administration, "Natural Gas," U.S. Department of Energy,
  [Online]. Available: http://www.eia.gov/dnav/ng/ng\_cons\_heat\_a\_epg0\_vgth\_btucf\_a.htm. [Accessed 23 June 2016].
- [41] C. Tang, Y. Zhang and Z. Huang, "Progress in combustion investigations of hydrogen enriched hydrocarbons," *Renewable and Sustainable Energy Reviews*, vol. 30, pp. 195-216, 2014.
- [42] H. An, J. Chung, S. Lee and S. Song, "The effects of hydrogen addition on the auto-ignition delay of homogeneous primary reference fuel/air mixtures in a rapid compression machine," *International Journal of Hydrogen Energy*, vol. 40, no. 40, pp. 13994-14005, 2015.
- [43] Y. Zhang, Z. Huang, L. Wei, J. Zhang and C. K. Law, ""Experimental and modeling study on ignition delays of lean mixtures of methane, hydrogen, oxygen, and argon at elevated pressures," *Combustion and Flame*, vol. 159, no. 3, pp. 918-931, 2012.
- [44] N. Chaumeix, S. Pichon, F. Lafosse and C. E. Paillard, "Role of chemical kinetics on the detonation properties of hydrogen/natural gas/air mixtures," *International Journal of Hydrogen Energy*, vol. 32, no. 13, pp. 2216-2226, 2007.
- [45] R. K. Cheng and A. K. Oppenheim, "Autoignition in methane-hydrogen mixtures," *Combustion and Flame*, vol. 58, no. 2, pp. 125-139, 1984.
- [46] Z. Chen, "Effects of hydrogen addition on the propagation of spherical methane/air flames: a computational study," *International journal of hydrogen energy*, vol. 34, no. 15, pp. 6558-6567, 2009.
- [47] D. Bradley, P. H. Gaskell and X. J. Gu, "Burning velocities, Markstein lengths, and flame quenching for spherical methane-air flames: a computational study," *Combustion and Flame*, vol. 104, no. 1, pp. 176-198, 1996.
- [48] X. J. Gu, M. Z. Haq, M. Lawes and R. Woolley, "Laminar burning velocity and Markstein lengths of methane–air mixtures," *Combustion and flame*, vol. 121, no. 1, pp. 41-58, 2000.
- [49] G. Yu, C. K. Law and C. K. Wu, "Laminar flame speeds of hydrocarbon+ air mixtures with hydrogen addition," *Combustion and Flame*, vol. 63, no. 3, pp. 339-347, 1986.
- [50] D. L. Baulch and et. al., "Evaluated kinetic data for combustion modelling," *Journal of Physical and Chemical Reference Data*, vol. 21, no. 3, pp. 411-734, 1992.
- [51] N. Peters and F. A. Williams, "The asymptotic structure of stoichiometric methane-air flames," *Combustion and Flame*, vol. 68, no. 2, pp. 185-207, 1987.
- [52] J. C. Ianni, "Kintecus," Windows Version 2.80, 2002. [Online]. Available: www.kintecus.com.
- [53] J. C. Ianni, "A comparison of the Bader-Deuflhard and the Cash-Karp Runge-Kutta integrators for the GRI-MECH 3.0 model based on the chemical kinetics code Kintecus," *Computational Fluid and Solid Mechanics*, pp. 1368-1372, 2003.
- [54] J. Warnatz, U. Maas and R. W. Dibble, Combustion, Heidelberg: Springer-Verlag, 2006.
- [55] M. F. Riley, *Personal Communication*, Indianapolis: Praxair, Inc., 2016.
- [56] Y. Cheng, C. Tang and Z. Huang, "Kinetic analysis of H2 addition effect on the laminar flame parameters of the C1–C4 n-alkane-air mixtures: From one step overall assumption

to detailed reaction mechanism," *International Journal of Hydrogen Energy,* vol. 40, no. 1, pp. 703-718, 2015.

- [57] K. R. Muske, J. W. Howse, G. A. Hansen and D. J. Cagliostro, "Advanced Control of Operations in the Blast Furnace Project. Phase One Effort Documentation: Optimal Operation and Control of the Blast Furnace Stoves. Technical Report LA-UR-99-5051," Los Alamos National Laboratory, Los Alamos, 1999.
- [58] R. Corbari and R. J. Fruehan, "Reduction of iron oxide fines to wustite with CO/CO2 gas of low reducing potential," *Metallurgical and Materials Transactions B*, vol. 41, no. 2, pp. 318-329, 2010.
- [59] H. J. Song, X. H. Jia and X. Q. Zhang, "Controllable fabrication, growth mechanism, and gas sensing properties of hollow hematite polyhedra," *Journal of Materials Chemistry*, vol. 22, no. 42, pp. 22699-22705, 2012.
- [60] K. S. Go, S. R. Son, S. D. Kim, K. S. Kang and C. S. Park, "Hydrogen production from twostep steam methane reforming in a fluidized bed reactor," *International journal of hydrogen energy*, vol. 34, no. 3, pp. 1301-1309, 2009.
- [61] T. Mattisson, A. Lyngfelt and P. Cho, "The use of iron oxide as an oxygen carrier in chemical-looping combustion of methane with inherent separation of CO2," *Fuel*, vol. 80, no. 13, pp. 1953-1962, 2001.
- [62] J. L. Pinilla, R. Utrilla, M. J. Lazaro, R. Moliner, I. Suelves and A. B. Garcia, "Ni-and Febased catalysts for hydrogen and carbon nanofilament production by catalytic decomposition of methane in a rotary bed reactor," *Fuel processing technology*, vol. 92, no. 8, pp. 1480-1488, 2011.
- [63] L. Tang, D. Yamaguchi, N. Burke, D. Trimm and K. Chiang, "Methane decomposition over ceria modified iron catalysts," *Catalysis Communications*, vol. 11, no. 15, pp. 1215-1219, 2010.
- [64] N. Z. Muradov, "How to produce hydrogen from fossil fuels without CO2 emission," International Journal of Hydrogen Energy, vol. 18, no. 3, pp. 211-215, 1993.
- [65] D. Barrett, "Partial oxidation of methane using iron oxide as donor," *Industrial & Engineering Chemistry Process Design and Development*, vol. 11, no. 3, pp. 415-420, 1972.
- [66] L. A. Haas, J. C. Nigro and R. K. Zahl, "Bureau of Mines Report RI-8997," US Department of Interior, Pittsburgh, 1985.
- [67] W.-I. Park and S.-M. Jung, "Effective use of CH4 gas as a reducing agent in suspension reduction process," *ISIJ International,* vol. 55, no. 1, pp. 166-174, 2015.
- [68] Y. Nomura, H. Nakagawa, T. Maeda, K. Nishioka and M. Shimizu, "Rapid reduction of firne ore transported with CH4 gas," *Tetsu-to-Hagane*, vol. 91, no. 6, p. 521, 2005.
- [69] C. W. Bale, "FactSage thermochemical software and databases," *Calphad*, vol. 26, no. 2, pp. 189-228, 2002.
- [70] P. Munster and H. J. Grabke, "Kinetics of the steam reforming of methane with iron, nickel, and iron-nickel alloys as catalysts," *Journal of Catalysis*, vol. 72, no. 2, pp. 279-287, 1981.
- [71] J. Xu and G. F. Froment, "Methane steam reforming, methanation and water-gas shift: I. Intrinsic kinetics," *AIChE Journal*, vol. 35, no. 1, pp. 88-96, 1989.

- [72] H. S. Bengaard, J. K. Norskov, J. Sehested, B. S. Clausen, L. P. Nielsen, A. M. Molenbroek and J. R. Rostrup-Nielsen, "Steam reforming and graphite formation on Ni catalysts," *Journal of Catalysis*, vol. 209, no. 2, pp. 365-384, 2002.
- [73] D. Chen, R. Lodeng, A. Anundskas, O. Olsvik and A. Holmen, "Deactivation during carbon dioxide reforming of methane over Ni catalyst: microkinetic analysis," *Chemical Engineering Science*, vol. 56, no. 4, pp. 1371-1379, 2001.
- [74] X. Liu, H. Zhang, D. Zhao, D. Tang and T. Zhang, "Effect of annealing temperature on the structure and coke-resistance of nickel–iron bimetallic catalytic layer for in situ methane steam reforming in SOFC operation," *Materials Science and Engineering: B*, vol. 189, pp. 45-50, 2014.
- [75] D. L. Trimm, "Catalysts for the control of coking during steam reforming," *Catalysis Today*, vol. 49, no. 1, pp. 3-10, 1999.
- [76] S. Wang and GQ (Max) Lu, "A comprehensive study on carbon dioxide reforming of methane over Ni/γ-Al2O3 catalysts," *Industrial & engineering chemistry research*, vol. 38, no. 7, pp. 2615-2625, 1999.
- [77] D. L. Trimm, "The steam reforming of natural gas: problems and some solutions," *Studies in Surface Science and Catalysis,* vol. 36, pp. 39-50, 1988.
- [78] O.-S. Joo and K.-D. Jung, "CH4 Dry Reforming on Alumina-Supported Nickel Catalyst," Bulletin-Korean chemical society, vol. 23, no. 8, pp. 1149-1153, 2002.
- [79] M. C. Bradford and M. A. Vannice, "Catalytic reforming of methane with carbon dioxide over nickel catalysts I. Catalyst characterization and activity," *Applied Catalysis A: General*, vol. 142, no. 1, pp. 73-96, 1996.
- [80] H. J. Grabke, "Metal dusting," *Materials and Corrosion*, vol. 54, no. 10, pp. 736-746, 2003.
- [81] R. T. Jones and K. L. Baumert, "Metal dusting-an overview of current literature," in CORROSION 2001, NACE International, Houston, 2001.
- [82] S. A. Theofanidis, R. Batchu, V. V. Galvita, H. Poleman and G. B. Marin, "Carbon gasification from Fe–Ni catalysts after methane dry reforming," *Applied Catalysis B: Environmental*, vol. 185, pp. 42-55, 2016.
- [83] J. R. Rostrup-Nielsen, "Sulfur-passivated nickel catalysts for carbon-free steam reforming of methane," *Journal of Catalysis*, vol. 85, no. 1, pp. 31-43, 1984.
- [84] R. Benrabaa, A. Lofberg, A. Rubbens, E. Bordes-Richard, R. N. Vannier and A. Barama, "Structure, reactivity and catalytic properties of nanoparticles of nickel ferrite in the dry reforming of methane," *Catalysis today*, vol. 203, pp. 188-195, 2013.
- [85] M. C. Bradford and M. A. Vannice, "Catalytic reforming of methane with carbon dioxide over nickel catalysts II. Reaction kinetics," *Applied Catalysis A: General*, vol. 142, no. 1, pp. 97-122, 1996.
- [86] G. Jones and et. al., "First principles calculations and experimental insight into methane steam reforming over transition metal catalysts," *Journal of Catalysis*, vol. 259, no. 1, pp. 147-160, 2008.
- [87] U. Olsbye, T. Wurzel and L. Mleczko, "Kinetic and reaction engineering studies of dry reforming of methane over a Ni/La/Al2O3 catalyst," *Industrial & engineering chemistry research*, vol. 36, no. 12, pp. 5180-5188, 1997.
- [88] C. R. Wilke, "A viscosity equation for gas mixtures," *The Journal of Chemical Physics*, vol. 18, no. 4, pp. 517-519, 1950.

- [89] J. M. Steiler, "Iron-making reactions," in Advanced Physical Chemistry for Process Metallurgy, Academic Press; 1st edition, 1997, pp. 309-345.
- [90] T. R. Dulski, "Other measurements and Techniques," in *A Manual for the Chemical Analysis of Metals*, West Conshohocken: ASTM, 1996, pp. 177-188.
- [91] Y. He and P. C. Pistorius, "Laboratory carburization of direct-reduced iron in CH4-H2-N2 gas mixtures, and comparison with industrial samples," *Metallurgical and Materials Transactions B, In Press.*
- [92] D. Qin, J. Lapszewicz and X. Jiang, "Comparison of partial oxidation and steam-CO2 mixed reformingof CH4 to syngas on MgO-supported metals," *Journal of Catalysis*, vol. 159, no. 1, pp. 140-149, 1996.
- U. Balachandran, J. T. Dusek, R. L. Mieville, R. B. Poeppel, M. S. Kleefisch, S. Pei and et. al., "Dense ceramic membranes for partial oxidation of methane to syngas," *Applied Catalysis A: General*, vol. 133, no. 1, pp. 19-29, 1995.
- [94] J. Wei and E. Iglesia, "Isotopic and kinetic assessment of the mechanism of reactions of CH4 with CO2 or H2O to form synthesis gas and carbon on nickel catalysts," *Journal of Catalysis*, vol. 224, no. 2, pp. 370-383, 2004.
- [95] J. F. Munera, S. Irusta, L. M. Cornaglia, E. A. Lombardo, D. V. Cesar and M. Schmal, "Kinetics and reaction pathway of the CO2 reforming of methane on Rh supported on lanthanum-based solid," *Journal of Catalysis*, vol. 245, no. 1, pp. 25-34, 2007.
- [96] M. Jampani and P. Pistorius, "Increased Use of Natural Gas in Blast Furnace Ironmaking: Methane Reforming," in *AISTech Conference Proceedings*, Pittsburgh, 2016.
- [97] Steelonthenet, "Pig Iron prices dollars per tonne," Metals Consulting International, 9 June 2016. [Online]. Available: http://www.steelonthenet.com/files/pig-iron.html. [Accessed 27 June 2016].
- [98] K. Vakhshouri and M. M. Y. M. Hashemi, "Simulation study of radial heat and mass transfer inside a fixed bed catalytic reactor," *Int. J. Chem. Biol. Eng*, vol. 23, no. 1, pp. 1-8, 2008.
- [99] D. Pakhare and J. Spivey, "A review of dry (CO 2) reforming of methane over noble metal catalysts," *Chemical Society Reviews,* vol. 43, no. 22, pp. 7813-7837, 2014.
- [100] J. P. Birat, F. Hanrot and F. Maizières-lès-Metz, "ULCOS: The European Steel Industry's Effort to Find Breakthrough Technologies to Cut Its CO 2 Emissions Significantly," in Workshop on Clean Production and Nanotechnologies, Seoul, 2007.
- [101] A. A. Lemonidou and I. A. Vasalos, "Carbon dioxide reforming of methane over 5 wt.% Ni/CaO-Al 2 O 3 catalyst," *Applied Catalysis A: General*, vol. 228, no. 1, pp. 227-235, 2002.
- [102] J. R. Rostrup-Nielsen and J. B. Hansen, "CO2-reforming of methane over transition metals," *Journal of Catalysis*, vol. 144, no. 1, pp. 38-49, 1993.
- [103] H. Fjellvag, F. Gronvold, S. Stolen and B. Hauback, "On the crystallographic and magnetic structures of nearly stoichiometric iron monoxide," *Journal of Solid State Chemistry*, vol. 124, no. 1, pp. 52-57, 1996.
- [104] O. Levenspiel, Chemical Reaction Engineering, Third Edition, New York: John Wiley & Sons, 1999.
- [105] J. Szekely and N. J. Themelis, Rate phenomena in process metallurgy, New York: John Wiley & Sons, August 1971.

- [106] R. B. Bird, W. E. Stewart and E. N. Lightfoot, Transport Phenomena, Second Edition, New York: John Wiley & SOns, 2002.
- [107] T. Guerra, Personal communication, Tenova HYL.
- [108] Z. H. U. Li, W. U. Keng, E. H. Zhang, S. H. E. Yuan, W. L. Zhan and Q. H. Liu, "A Modified Model for Calculating Theoretical Flame Temperature in Blast Furnace and Its Application," *Journal of Iron and Steel Research, International,* vol. 22, no. 1, pp. 9-14, 2015.
- [109] Association for Iron & Steel Technology, "North Americal Blast Furnace Roundup," *Iron & Steel Technology*, 2015.