Analysis of fixed bed data for the extraction of a rate mechanism for the reaction of hematite with methane.

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Abstract

Chemical looping combustion is a promising technology for the capture of CO₂ involving redox materials as oxygen carriers. The effects of reduction conditions, namely, temperature and fuel partial pressure on the conversion products are investigated. The experiments were conducted in a laboratory fixed-bed reactor that was operated cyclically with alternating reduction and oxidation periods. Reactions are assumed to occur in the shell surrounding the particle grains with diffusion of oxygen to the surface from the grain core. Activation energies for the shell and core reactions range from 9 to 209 kJ/mol depending on the reaction step.

1. Introduction

Carbon dioxide (CO₂) emissions have been identified as a possible reason for climate changes and to address this issue, the U.S. Department of Energy has set goals for carbon capture systems at 90% carbon dioxide (CO₂) capture with less than a 35% increase in cost of electricity [1]. There are four main categories of CO₂ control technologies that can achieve 90% carbon dioxide (CO₂) capture with less than a 35% increase in cost of electricity. These are pre-combustion, post-combustion, oxy-fuel and chemical looping [2]. The work presented in this paper looks into the performance of a fixed bed chemical looping system.

The term “chemical looping” is a relatively new name to an old concept that was utilized in the early 1900s for the coal gasification technology called the Steam-Iron Process and again in the late 1960s and early 1970s for another gasification technology which was called the CO₂ Acceptor Process [3]. This “chemical looping” terminology was introduced in the 1990s to refer to a cyclic processes in which an oxygen rich solid was contacted with a fuel to reduce the oxygen rich solid forming carbon dioxide and

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water (combustion products). The reduced solid could then be transferred to another vessel and re-oxidized. The cycling of the oxygen carrier between the oxidizer and reducer vessels is now termed chemical looping combustion.

Chemical looping combustion is being investigated around the world for power production because the technology allows for fuel conversion with easy CO₂ separation [4, 5, 6]. The current investigation is aimed at evaluating hematite, a naturally occurring Fe₂O₃ ore, as an oxygen carrier for natural gas fueled applications. Fe₂O₃ has been cited as a potential carrier in numerous research publications [4-26] with many of these focusing on the development of required kinetics from TGA experimental investigations for scale-up of this technology.

Methane reacts with iron oxide (hematite) to ultimately produce a mixture of carbon dioxide, water, carbon monoxide, hydrogen and various reduced states of iron oxide from magnetite to iron. This complex process has been extensively investigated both for the production of steel but most recently for use of the hematite as an oxygen carrier in chemical looping processes [8-26] but even so, questions regarding the rate mechanism still exist. Symbolically, the reaction can be written as the unbalanced expression:

The above expression is the result of many reactions, some of which are identified below:

To further complicate the reaction mechanism, there is the significance that the reactions are all heterogeneous with the solid phase reacting and being consumed with time. This creates a moving reaction front within the solid phase (particle).

Researchers have modeled the processes in the above reactions with first order Arrhenius type reaction rate expressions and with more complicated nucleation and growth expressions, see Abad [8] and Lou [23], respectively. Most recently, Breault and Monazam [27] have analyzed the behavior of hematite in a fixed bed reactor with methane as the reducing gas. They found that the hematite particles reacted as a fixed thickness shell giving up oxygen rapidly and a core diffusing oxygen to the shell surface. They also found that the available oxygen in the fast reacting shell decreased with the cumulative time a particle

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4 spent at high temperature when the fixed bed reactor was cycled between reduction and oxidation. This
5 particular work focuses on a more in depth analysis of the first reduction cycle as the experimental data
6 from all the cyclic fluidized bed experiments mimic the first cycle results from the fixed bed tests.
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9 Numerous researchers are investigating various naturally occurring and manufactured iron oxide based
10 carriers. These are summarized in Tables 1. In Table 1, of particular interest is the work of Abad and
11 colleagues [9], as they have put forward the most advanced and complete model for the reduction of
12 ilmenite. Ilmenite is a naturally occurring iron and titanium mineral in the form of FeTiO_3 . The actual
13 material tests by Abad et al. [9] consisted of 94.3% ilmenite with the balance being rutile (TiO_2) and
14 Hematite (Fe_2O_3). The material had a Fe to Ti ratio of approximately 1. Monazam et al. have been
15 exploring the kinetics of North American iron containing ores, primarily hematite from Canada [20, 23
16 and 24]. Monazam et al. [20] found the reaction of methane with the Canadian hematite to occur with a
17 two reaction mechanism. The other authors [11-19, 21 & 22], work primarily with Fe_2O_3 -support/binder
18 mixtures. Furthermore, most use steam or at least humidified CH_4 to inhibit coke formation due to the
19 CH_4 cracking. In general, the rate improved in these studies as the initial fabricated particle became
20 conditioned after several cycles. This is in the opposite direction with the current study which is discussed
21 below for the naturally occurring Canadian hematite. Also, with regard to Table 1, Go et al. [13] found
22 the reaction with Fe_2O_3 and methane to be diffusion controlled. That work used the smallest sample size
23 reported. Also, Johansson et al. [15] found that materials that had seen high temperatures were diffusion
24 controlled. Lou et al. [23] found that the activation energy ranged between 49 and 184 kJ/mol
25 depending on the whether the Fe_2O_3 was synthetic or iron ore, respectively. Zhang et al [24] looked
26 ultralow CH_4 levels ($< 1\%$) simulating mine vents. Forutan et al. [25] provides a good head to head
27 comparison of different carrier performances with iron oxide showing the greatest resistance to sintering.
28 Ku et al. [26] observed carbon deposition as seen in the gas composition during regeneration at 900C
29 indicative of coke formation from the cracking of the methane.
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Table 1. Summary of iron oxide reduction with methane

Author	Reactor Type	Sample Size (mg)	Particle Size (μm)	BET Surface Area (m^2/g)	Sample Frequency (Hz)	Reduction Gas	Reaction Control	Carrie Form
Abad et al. (2007) [8]	Circulating bed	110,000	90 to 212	-	-	Natural gas (88% CH_4)	-	60% Fe_2O_3 and Al_2O_3
Abad et al. (2011) [9]	TGA	50	150 to 300	.8	-	CH_4 and steam	Shrinking grain	FeTiO_3 (Ilmenite)
Adanez et al. (2005) [10]	Bubbling fluidized bed	2×10^5	100 to 300	-	-	CH_4 saturated with H_2O vapor	-	60% Fe_2O_3 and Al_2O_3
Cho et al. (2002)[11]	Bubbling fluidized bed	15,000 to 60,000	125 to 250	-	-	CH_4	-	Fe_2O_3 and Al_2O_3
Gayán et al. (2012)[12]	Bubbling fluidized bed	2×10^5	100 to 300	9.3	-	CH_4 in N_2	-	Fe_2O_3 on Al_2O_3
Go et al. (2008)[13]	TGA	7 to 8	125	9.055	0.033	CH_4	Diffusion	Fe_2O_3
He et al. (2007)[14]	Fixed Bed	60,000	1500 to 2000	-	-	Humidified CH_4 in Ar	-	80% Fe_2O_3 and Al_2O_3
Johansson et al. (2004) [15]	Bubbling fluidized bed	10,000 and 15,000	125 to 180	-	-	CH_4 and steam	Diffusion for materials that have seen high temperatures	Fe_2O_3 on MgAl_2O_4
Leion et al. (2008) [16]	Bubbling fluidized bed	15,000	125 to 180	-	-	CH_4	-	FeTiO_3 (Ilmenite)
Mattisson et al. (2004) [17]	Bubbling fluidized bed	10,000	125 to 180	-	-	CH_4 and steam	Kinetic to Diffusion	60% Fe_2O_3 and Al_2O_3
Mendiara et al. (2012) [18]	Bubbling fluidized bed	3×10^5	150 to 300	.9	-	CH_4 and steam in N_2	-	71% Fe_2O_3 and Al_2O_3
Moghtaderi et al. (2010) [19]	TGA	28 to 40	30 to 40	3.5	1	CH_4 and steam	-	Fe_2O_3
Monazam et al. (2013) [20]	TGA	60		.1	1	CH_4 in N_2	Kinetic and Diffusion (JMA)	Fe_2O_3
Son et al. (2006) [21]	Circulating bed	6×10^5	106 to 150	-	0.04	CH_4	-	Fe_2O_3 on TiO_2 , Al_2O_3 and bentonite
J. Zhang et al. (2012) [22]	TGA	-	-	4	-	CH_4	-	75% Fe_2O_3 and Al_2O_3
Lou et al. (2014) [23]	TGA	10	100 to 200	0.075	-	CH_4 and CO_2	JMA	Fe_2O_3
Y. Zhang et al. (2014) [24]	TGA	10 to 15	75 to 150	-	-	CH_4 in N_2	-	Fe_2O_3 and Al_2O_3
Forutan et al. (2014) [25]	Fixed bed micro reactor	2100	400 to 841	1.232	-	CH_4	-	40 % Fe_2O_3 on Al_2O_3
Ku et al. (2014) [26]	Fixed bed	2.9×10^6	-	-	-	CH_4 in N_2	-	Fe_2O_3 and Al_2O_3
Current work	Fixed Bed	10^6	230	.1	1	CH_4 in Ar	Discussed below	Fe_2O_3

2. Test Matrix, Experimental Facility and Test Procedure

Experiments were conducted according to the (T,%CH₄) test matrix shown graphically in Figure 1. The matrix produced results at constant temperature and at constant methane feed concentration. These experiments were conducted in NETL's MIR facility, a schematic of which is presented in Figure 2. In the unit, nominally 1.0 kg of hematite carrier was placed in the bed. Methane and argon or oxygen and argon were fed to the bed during the reduction and oxidizing processes, respectively. Reduction was carried out for either 10 minutes or 5 minutes depending on the test and the oxidation process was carried out for 20 min. The material properties are presented in Table 2.

The test facility consists of the MIR unit which is fed from gas tanks (methane, argon, and oxygen) as shown in Figure 2 through the mass flow controllers which allow precise control of the gases. The MIR unit has an overall height 62.3 cm, an internal diameter of 6.0 cm. It is surrounded by heaters to control the reaction temperature. The feed gas reacts with the hematite inside the vessel and the product gases are directed through a mass spectrophotometer gas analyzer before it exits the system. The reactor temperature is measured at three locations, one just above the distributor plate, one near the top of the bed and one above the bed.

The general experimental facility operation is summarized in Figure 3. In this figure the temperature, gas flow rate and gas species mass fractions are shown. The temperature is ramped up to the operating temperature under an argon gas flow. Once the reactor temperature has stabilized at the set condition (800 °C), the fuel (reduction) gas flow is initiated and maintained for 10 minutes. This can be seen in Figure 4 by the dip in the argon mass fraction and an increase in the CO₂ and CH₄ mass fraction values. At this time, the fuel gas is switched off and the argon flow increased to purge the reactor of combustible gas for approximately 25 minutes prior to regenerating the hematite with air. The carrier is regenerated for 20 minutes after which the air flow is stopped and the reactor purged of oxygen prior to starting the next reduction cycle. The temperature for the process is essentially constant at 800 °C as see by the temperature trace with the exception of a small rise (15 °C) in the gas temperature when air is introduced during regeneration. This temperature rise will be shown to affect the cyclic stability of the carrier in batch operation.

Table 2. Material properties.

Composition		<u>Units</u>	<u>Value</u>
	Fe ₂ O ₃	%	95
	Inert	%	5
Particle Size		um	230
Particle Density		kg/m ³	4770
Langmuir Surface Area			
	800 °C	m ² /g	0.41
	900 °C	m ² /g	0.09

3. Results

Due to the configuration of the reactor, there is a large recirculation zone located at the top. This can be modeled as a first order decay with a time constant of 40 seconds based upon an argon step change at the flow rates used in the tests. That is, using this time constant, the argon exit trace was converted to a step function, mirroring the input. The exit gas concentrations were corrected using this time constant according to the relation by dividing the measured values by $(1 - e^{-(t/40)})$ for $t > 0$. The exit gas concentration profiles, corrected for the reactor time constant of the reactor assembly pictured in Figure 2, are shown in Figures 4 to remove diffusion and mixing confounding behavior. The graphs in Figure 4 are placed according to the test matrix (Figure 1). That is, the plots across the top are at a constant concentration (~ 8.5%) and vary in temperature from 740 °C on the left to 833 °C on the right. The plots on the vertical axis are at a constant temperature of 800 °C and vary in CH₄ concentration from 5% at the bottom to ~ 8.5% at the top.

In general, it can be observed that the curves for the CO₂ mass fractions rise rapidly for about the first 50 to 150 seconds – creating a “bubble of CO₂” and then reduce to a gradual decay as the hematite is consumed. The CO curves have a similar shape – albeit about 20 times lower in magnitude. Breault and Monazam [27] report the “CO₂ bubble” observance in other’s work and contribute it being the product of a quickly consumed surface reaction. The data at 800 °C and 8.5% CH₄ deviate from this general shape. More specifically, with all parameters constant the peak CO₂ mass fraction is expected to be about 0.01 from the comparison of the 740 °C and 830 °C data. The lack of the “bubble” and the maximum of only about 0.06 for the mass fraction require a deeper investigation of the data.

Breault and Monazam [27] report a reduced CO₂ peak value and the disappearance in the “bubble” between cycles 1 and 2 for material that was overheated during the first oxidation cycle causing morphological changes to the carrier. Since this behavior is similar, it is possible that the carrier was overheated. This is in fact true as seen in Figure 5 where the first reduction cycle for each test condition is identified by the small circles. The carrier for the 800 °C, 8.5% CH₄ test was heated nearly 850 °C prior to it undergoing the first reduction cycle.

The solids in the 800 °C, 8.5 % CH₄ test were over heated for a period greater than 20 minutes prior to initiation of the first cycle. High temperature promotes grain growth with loss of what little surface reactant there is for the carrier [28 – 30]. Callister [28] presents a plot showing the general effect of grains growing with time and temperature where grains can grow in diameter by 2 orders of magnitude when heated from 550 °C to 850 °C for 10 minutes – times and conditions comparable to this work. Bradshaw and Matas [29] credit this grain growth to decreases in the reduction rate of hematite with CO. Bora et al. [30] show a 30% increase in grain size when hematite is heated from 800 °C to 900 °C. In the current work, surface area measurements were taken for the raw material after being held at 800 °C and at 900 °C. The surface area at 900 °C was only 22 % of the surface area at 800 °C. (Table 2). If the loss in surface area is linear with the peak temperature, the material overheated will only have about 70% of the surface area at 800 °C. This is contrasted with the test at 827 °C, which will have a surface area of about 90% of that at 800 °C, a level which is well within the experimental controls. The effect of overheating can be seen in the test data presented in Figure 6 for the first and second cycles of the 7.2%, 800 °C test (extracted from [27]). Note the similarity of the cycle 2 curve with that shown in Figure 4 for the CO₂ curve at 8.5%, 800 °C. In this data (Figure 6), the lack of substantial heat transfer during the fixed bed

oxidation of the carrier caused overheating by as much as 100 °C causing a substantial reduction in the carrier's surface area for the second and subsequent cycles [27].

Breault and Monazam [27] noted the importance of only looking at the first cycle of the reduction in determination of the kinetics to other reactor configurations, specifically bubbling fluidized beds where there is sufficient heat transfer to maintain the particle temperature at a low enough level to inhibit grain growth. This importance can be seen by comparing the CO₂ production data from a fluidized reduction cycle in a similarly sized reactor (Figure 7) to any of the non-overheated CO₂ production data presented in Figure 4. The data in Figure 7 was taken at 850 °C but since the unit was fluidized, none of the carrier particles were overheated for an extended period of time. And so, the CO₂ "bubble" from the surface reaction was maintained without significant degradation as compared to the fixed bed case discussed more thoroughly in this paper. Therefore, the data at 800 °C and 8.5% CH₄ is omitted from the analysis below.

Another point that needs to be made with respect to developing reactor kinetics is the potential that reduction is not constant across experimental test reactors as has been proposed by Hayes and colleagues [31-34]. At NETL and elsewhere, there has been significant research efforts focused on getting kinetics from the TGA (see Table 1). Hayes et al. [31-34] have looked at the hematite reduction under various chemical potentials that might be seen in different reactors. He has reported that hematite reduces differently depending on the gas phase concentrations above it and that these result in different morphologies for the particles. At NETL, we have seen some morphological changes [27], these were attributed to thermal effects during the oxidation cycle but may also be caused by the mechanism that Hayes et al. presents. The difference between TGA experimental facilities and flow reactor like the MIR are shown in Figure 8. In this figure, the solids inventory volume is plotted against the reactor stoichiometry (g CH₄/g Fe₂O₃) where the mass of the gas is the cumulative quantity for the test in the TGA and MIR experiments. As can be seen, the flow reactors and the TGAs are separated by three orders of magnitude with regard to stoichiometry and 6 or more orders of magnitude with respect to reactor volume. According to Hayes [31-34], it is the significantly different stoichiometry (chemical potential) that can lead to different kinetics at the different scales, making it very important to look at the reaction rates of hematite at large scales under similar chemical potentials. Whether or not this holds will be discussed below when activation energies are discussed across the various reactor scales.

4. Analysis

Since the hematite is dense with very little surface area or porosity, it is hypothesized that the reaction between the oxygen in the hematite and the CH₄ occurs at or very near the surface. Therefore, the weight loss was attributed to occur in a shell surrounding the particle grains. Furthermore, it is assumed that the reaction of the Fe₂O₃ and the CH₄ utilizes most of the oxygen at the grain surface. Conceptually, this is shown in Figure 9. In this figure, a slice of a small section of the particle surface is shown consisting of 3 unit cells (note fine dashed line surrounding unit cell [35]) in length and 2 deep (into particle/grain). In the sketch on the left, the surface (left edge) is fully oxidized. In the right side of the sketch, the same section of the particle is shown partially reduced to FeO at the surface (left edge). According to Chatterjee [36], the reduction of dense iron ore occurs by oxygen diffusing to the surface by a lattice vacancy mechanism.

Based upon the earlier work of Breault and Monazam [27], the reaction of methane with hematite takes place according to the process defined below. Methane migrates to the particle surface region (outer shell of particles/grains) and reacts within a shallow layer on the order of 70 °A associated with the shell to produce carbon monoxide and hydrogen gaseous species and likely solids species FeO. This is shown in the sketch presented in Figure 10. The carbon monoxide either reacts very rapidly with hematite in in this shell or escapes the particle though the large pores to react downstream. The hydrogen undergoes the same process. Reported literature [37-38] reaction kinetics for hematite and hydrogen are so fast that the observed free hydrogen as noted above in the results section are at the detection limit except when the methane undergoes cracking late into the particle reduction stage. Once a reasonable large share of the surface available oxygen has been consumed, oxygen diffuses from the core (particle/grain) to the surface region where it reacts with the migrating methane in the same chemical reactions although the rate is controlled by the speed at which oxygen can diffuse from the core hematite lattice to the attached methane. Therefore, the following reactions are proposed

Since no H₂ was measured, its rate of reaction is not explored. Therefore, the reaction rates for the Equations 10-13 are given below in Equations 16 to 19.

$$R_{1,\text{CH}_4} = R_{1,\text{Fe}_2\text{O}_3\|_s} = -R_{1,\text{CO}} = -\frac{R_{1,\text{H}_2}}{2} = -\frac{R_{1,\text{FeO}}}{2} \quad (16)$$

$$R_{2,\text{CH}_4} = R_{2,\text{Fe}_2\text{O}_3\|_c} = -R_{2,\text{CO}} = -\frac{R_{2,\text{H}_2}}{2} = -\frac{R_{2,\text{FeO}}}{2} \quad (17)$$

$$R_{3,\text{CO}} = R_{3,\text{Fe}_2\text{O}_3\|_s} = -R_{3,\text{CO}_2} = -\frac{R_{3,\text{FeO}}}{2} \quad (18)$$

$$R_{4,\text{CO}} = R_{4,\text{Fe}_2\text{O}_3\|_c} = -R_{4,\text{CO}_2} = -\frac{R_{4,\text{FeO}}}{2} \quad (19)$$

The overall rate of reaction for CH₄, CO₂ and CO is given by Equations 20 through 22.

$$R_{\text{CH}_4} = R_{1,\text{CH}_4} + R_{2,\text{CH}_4} \quad (20)$$

$$R_{\text{CO}_2} = R_{3,\text{CO}_2} + R_{4,\text{CO}_2} \quad (21)$$

$$R_{4,CO} = R_{1,CO} + R_{2,CO} - R_{3,CO} - R_{4,CO} = -R_{1,CH_4} - R_{2,CH_4} + R_{3,CO_2} + R_{4,CO_2} \quad (22)$$

The concentration profiles for the methane breakthrough are analyzed according to the following rate model and the closed form solution for a parallel process as identified by Monazam et al. [24, 37, 40].

$$R_{CH_4} = \frac{d(m'_{CH_4}(t))}{dt} \quad (23)$$

The closed form solution for methane going to products in parallel paths is presented in the following equation.

$$m'_{CH_4}(t) = w_{sur}(1 - e^{-a_{sur}t^{n_{sur}}}) + w_{cor}(1 - e^{-a_{cor}t^{n_{cor}}}) \quad (24)$$

Where $m'_{CH_4}(t)$ is the mass of methane leaving the reactor at time, t , and $m'_{CH_4}(0)$ is the mass of methane entering the reactor. The relative weights of the two reactions are w_{sur} and w_{cor} , where

$$\frac{w_{sur}+w_{cor}}{m'_{CH_4}(0)} = 1 \quad (25)$$

The nucleation rate constants for the two reactions are a_{sur} and a_{cor} and the corresponding nucleation shape parameters are n_{sur} and n_{cor} .

The above equation was fitted to the data for the experiments with the fit parameter, R^2 , ranging from 0.99 to 0.999. An example plot is shown in Figure 11 for the test condition $T=800^\circ\text{C}$ and $X_{CH_4, in} = 7.23\%$. The R^2 value for this example is 0.999 and the absolute average percent deviation (AAPD) is 0.001%. The results for the relative reaction weights, the nucleation rate constants and the nucleation shape factors are presented in Table 3.

Table 3. CH₄ Model Parameter Fit Values

T, °C	750	825	800	800
CH ₄ , %	8.59	8.63	5.05	7.24
w_{cor,CH_4}	0.00097	0.00127	0.00261	0.00139
w_{sur,CH_4}	0.000725	0.00043	0.00052	0.00055
n_{cor,CH_4}	1.41	1.00	0.55	0.64
n_{sur,CH_4}	2.47	1.90	1.75	1.77
a_{cor,CH_4} , g/s	1.69E-04	2.52E-03	2.25E-02	1.22E-02
a_{sur,CH_4} , g/s	3.22E-06	9.99E-05	5.33E-04	1.86E-04

The results from the fit analysis show that the average value of n_{sur,CH_4} is equal to 2 and n_{cor,CH_4} is equal to 1 for all cases as was obtained by Monazam et al for the TGA [20]. The functionality is show below.

This average value of n_{cor,CH_4} equal to 1 is the result that most often shows up in reviewed literature.

The early time results are neglected and then bulk of the long reduction time data fits a conventional Arrhenius rate expression quite well. The problem with that analysis is that the conversion predictions are

completely wrong when short reactor reduction times are applied. Using only the Arrhenius fit can miss the conversion by 50% for times on the order of 5 min as the conversion associated with the nucleation in the grain shell counts for a significant part of the conversion.

The functionality of w_{cor,CH_4} , n_{sur,CH_4} , n_{cor,CH_4} , a_{sur,CH_4} , and a_{cor,CH_4} are provided below with respect to temperature and inlet concentration (mass fraction). The average R^2 for the five curve fits was 0.953 for the expressions below:

$$w_{cor,CH_4} = 4.224 \times 10^4 \times T(^{\circ}C)^{-2} \times X_{CH_4}^{-2} \quad (R^2 = 96.4\%) \quad (26)$$

$$n_{cor,CH_4} = 1.041 \times 10^4 \times T(^{\circ}C)^{-2} \times X_{CH_4}^2 \quad (R^2 = 90.0\%) \quad (27)$$

$$n_{sur,CH_4} = 5.034 \times 10^8 \times T(^{\circ}C)^{-3} \times X_{CH_4}^{0.33} \quad (R^2 = 95.6\%) \quad (28)$$

$$a_{sur,CH_4}^{\left(\frac{1}{n_{sur,CH_4}}\right)} = AX_{CH_4}^n e^{-E/RT} = 7.443 X(\%)_{CH_4}^1 e^{-5124/T} \quad (R^2 = 95.1\%) \quad (29)$$

$$a_{cor,CH_4}^{\left(\frac{1}{n_{cor,CH_4}}\right)} = AX_{CH_4}^n e^{-E/RT} = 0.059 X(\%)_{CH_4}^2 e^{-8100\left(\frac{300}{t_R}\right)^{.7}} \quad (R^2 = 99.4\%) \quad (30)$$

The corresponding Activation energy is 41.7 kJ/mol and 65.9 kJ/mol for the surface and core, respectively. This corresponds to 36.3 kJ/mol and 34.4 kJ/mol obtained by Monazam et al. [20] in their analysis of TGA data for the same temperature range.

Looking next at the CO_2 production (see Figures 4), it can be seen that the CO_2 first rises rapidly – the likely product of the CO produced from reaction 1 reacting in reaction 3. Since the production of CO_2 is dependent upon the solid reaction present, equation (methane breakthrough) needs to be modified to account for the disappearance of the solid reactant. The solid species present at any time is proportional to $(e^{-a_{sur}t^{n_{sur}}})_{CH_4}$ and $(e^{-a_{cor}t^{n_{cor}}})_{CH_4}$ for the surface and core species, respectively. Therefore, including these terms in the expression for the CO_2 reactor exit gas gives

$$R_{CO_2} = \frac{d(m'_{CO_2}(t))}{dt} \quad (31)$$

$$\begin{aligned} m'_{CO_2}(t) = & w_{sur,CO_2} \left(1 - e^{-a_{sur,CO_2}t^{n_{sur,CO_2}}}\right) (e^{-a_{sur}t^{n_{sur}}})_{CH_4} \\ & + w_{cor,CO_2} \left(1 - e^{-a_{cor,CO_2}t^{n_{cor,CO_2}}}\right) (e^{-a_{cor}t^{n_{cor}}})_{CH_4} \end{aligned} \quad (32)$$

Table 4. CO₂ Model Parameter Fit Values

T, °C	750	825	800	800
CH ₄ , %	8.59	8.63	5	7.23
w_{sur,CO_2}	0.00490	0.00431	0.00485	0.00217
w_{cor,CO_2}	0.01266	0.01149	0.00561	0.00358
n_{sur,CO_2}	1.56791	1.29299	1.53959	1.58423
n_{cor,CO_2}	0.75465	0.78760	0.72912	0.71209
a_{sur,CO_2} , g/s	0.00359	0.00481	0.00447	0.00195
a_{cor,CO_2} , g/s	0.00553	0.01699	0.11444	0.05825

The results for the example (T=800°C and $X_{CH_4, in} = 7.23\%$), are presented in Figure 12. The combined surface and core models give an R² value greater than 99.5 for this example and greater than 99.4 for all the test points.

The functionality of w_{sur,CO_2} , w_{cor,CO_2} , n_{sur,CO_2} , n_{cor,CO_2} , a_{sur,CO_2} , and a_{cor,CO_2} are provided below with respect to temperature and inlet concentration (mass fraction). The average R² for the four fits was 0.935 for the expressions below:

$$w_{sur,CO_2} = 1.01 \times 10^{10} \times T(^{\circ}C)^{-4} \times X_{CH_4}^{-1} \times \left(\frac{300}{t_R}\right) \quad (33)$$

$$w_{cor,CO_2} = 0.371 \times T(^{\circ}C)^{-1} \times X_{CH_4}^{1.5} \times \left(\frac{300}{t_R}\right)^{1.5} \quad (34)$$

$$n_{sur,CO_2} = 53081 \times T(^{\circ}C)^{-1.5} \times X_{CH_4}^{-0.25} \times \left(\frac{300}{t_R}\right)^{-0.15} \quad (35)$$

$$n_{cor,CO_2} = 0.7459 \quad (36)$$

$$a_{sur,CO_2}^{(1)} = AX_{CH_4}^n e^{-E/RT} = 0.1798(X(\%)_{CH_4}^{-0.5})\left(\frac{300}{t_R}\right)^{0.25} e^{-1100/T} \quad (37)$$

$$a_{cor,CO_2}^{(1)} = AX_{CH_4}^n e^{-E/RT} = 6.61 \times 10^{11} \times (X(\%)_{CH_4}^{-4})\left(\frac{300}{t_R}\right)^{-1} e^{-25509/T} \quad (38)$$

This provides an activation energy of 9.0 kJ/mol for the surface reaction and is comparable to that found by Monazam et al. [40] in their analysis of TGA data of 19kJ/mol. The functionality for the core is shown in Equation (38). It gives an activation energy of 208.7 kJ/mol. This level is significantly greater than that found by Monazam et al. [40]. It is however consistent with the activation energy levels associated for oxygen vacancy diffusion in hematite (154 to 203 [41] and 160 [42]). It is also consistent with the value of 184 kJ/mol obtained for iron ore by Lou et al. [23].

The applicability of the rates presented here can be evaluated by comparing the post-fit predictions for the exit CH₄ and CO₂ data for each case and comparing those values with the experimental data to evaluate the error in the predictions. Equations 25 through 30 were used to develop kinetic parameters for the methane conversion. These values were then used to calculate the exiting methane flow rate as a function

of time from Equation 24. The results of the model are shown in Figure 13 and 14. Figure 13 presents an example model prediction curve for the CH₄ leaving the reactor and compares that to the data for the same case (Case 5, 800 °C, 7.23 % CH₄). The R² value between the model and the data for this case is 99.5 %. The R² for all the test cases ranged for from 98.7 to 99.9%. Figure 14 presents the reacted methane for all the cases and compares it to the model predictions. The error ranged from 1% to 9% with the average being 5.1% excluding Case 3.

A comparison between the model (Equations 33 through 38) and the data is presented in Figures 15 and 16. Figure 15 provides an illustration of the typical fit between the data and the model with the R² for this case being 97.8% The R² for all the cases (excluding Case 3) ranged from 92% to 98%. Figure 15 presents the CO₂ produced for all the cases. The average error is 8.0% with the range being 1 to 12%, excluding Case 3.

5. Conclusion

Methane combustion using hematite as the oxygen carrier was investigated in a fixed bed reactor with application for chemical looping combustion process. Hematite is identified as an important potential oxygen carrier and has emerged as one of the candidates for use as oxygen carrier for CLC and is analyzed in this paper work as it is a relatively inexpensive carrier. During this study, the hematite did not agglomerate. It maintained reasonable reactivity and demonstrated durability through multiple cycles even though it was over heated during the oxidation portion of the cycle which caused some of the reduction in its reactivity due to morphological changes (grain growth and subsequent surface area reduction).

The obtained conversion data in the reduction condition can be represented by a two-step process for the reaction of the ore with methane to form CO and H₂ and then the reaction of the CO to form CO₂. The hydrogen was at the detection limit of the analyzer and was assumed to convert completely and instantly to H₂O. The surface reaction have activation energies of 41.7 kJ/mol for the CH₄ reaction and 9.0 kJ/mol for CO₂ formation reaction which are both comparable to those found by Monazam et al. [20, 40]. The activation energies for the two reactions involving core oxygen are much higher; 65.9 kJ/mol for the CH₄ reaction and 208.7 kJ/mol for the CO₂ formation reaction. These values are comparable to those associated with oxygen vacancy diffusion [41,42], especially the latter for CO₂ formation. Additionally, it is found that CO emissions from the fuel reactor are very small and that H₂ produced by partial oxidation of CH₄ contributes to the reduction of the bed material.

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7. Disclaimer

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Figure

Figure 1. Test Matrix with Case Numbers Shown

Figure 2. Experimental Test Facility

Figure 3. Typical operating cycle for experiments

Figure 4 Test Results

Figure 5. Temperature conditions leading to cycle 1 test – denoted with circle.

Figure 6. Comparison of Cycle 1 and Cycle 2 CO₂ production data

Figure 7 FSB_CO2 multiple cycles

Figure 8 Test Reactor scales

Figure 9. Fe_2O_3 surface prior to reduction and after partial reduction of the surface (adapted from[35]).

Figure 10 Particle model concept.

Figure 11. Example plot of $CH_{4,out}/CH_{4,in}$ comparing data and model fit for Case 5

Figure 12. Example data showing CO2 exit gas and model fit data for Case 5

Figure 13. Comparison between model and data for CH₄ leaving reactor for Case 5

Figure 14. Comparison of CH₄ reacted for model versus data

Figure 15. Rate of CO₂ leaving reactor for Case 5

Figure 16. CO₂ Produced during experiment