

Opportunities for Low-Grade Coals and Biomass for Producing Hydrogen Using Iron Oxide-Based Direct Chemical Looping Combustion with Effective CO₂ Separation

N.V. Gnanapragasam, B.V. Reddy and M.A. Rosen*

Faculty of Engineering and Applied Science, University of Ontario Institute of Technology, Oshawa, Ontario, L1H 7K4, Canada

Abstract: Coal and biomass are abundant in supply but contain carbon which, to avoid greenhouse gas emissions, needs to be sequestered after the primary energy conversion. A comparison is reported here of the performance of four different coals and biomass in an iron oxide-based direct chemical looping combustion system. The principal aim is to identify the coal and biomass with the highest H₂ to CO₂ ratio for a given amount of fuel, based on the resources (air and iron oxide) used. The impact of fuel blend (mix of coal and biomass) on hydrogen production is compared, and the effect of moisture content of the source fuel on hydrogen production is investigated. Simulation results suggest that low-grade coal can also produce the same amount of hydrogen as high grade coal, but with additional energy requirements. In achieving maximum hydrogen production, the final 20 to 30% of hydrogen production consumes the same amount of energy required by the initial 70% of production. When biomass is blended with 20% coal by mass, 10% additional hydrogen is produced. A 10% moisture content in the source fuel reduces the hydrogen production by 10% for high-grade coal while it eliminates the possibility for low-grade biomass to produce hydrogen within the available energy region. Potential improvements of the energy requirement to achieve maximum hydrogen production from low-grade solid fuels are also reported.

Keywords: Chemical looping combustion, hydrogen, coal, biomass, iron oxide, hydrogen energy system, CO₂ separation, energy, fuel reactor simulation.

1. INTRODUCTION

In current industrial markets, hydrogen is mainly used as a commodity for the synthesis of chemicals and clean fuels. However with the move towards a hydrogen economy, which includes hydrogen for the power and transportation sectors, the use of hydrogen as an energy carrier like electricity is becoming more advantageous [1]. The current contribution of solid fuels to hydrogen production is comparable to other sources, with the contribution expected to increase when (i) natural gas price increases due to supply limitations, (ii) losses in production of hydrogen from solid fuels are reduced, (iii) carbon capture becomes economic, and (iv) a hydrogen infrastructure is established and increases demand for hydrogen [2].

Of the total global energy requirement, 80% is supplied by fossil fuels (oil, gas, coal), 13.5% by renewable sources (hydro, solar, wind, geothermal) and 6.5% by nuclear energy [3]. Coal is the most significant contributor among fossil fuels to current global electricity generation, accounting for 40% [4]. The most abundant fossil fuel on the planet, global recoverable coal reserves (evaluated as the reserve-to-production ratio) are estimated to range from 122 years for the world to 216 years for North America and over 500 years

for Brazil at current usage rates [5]. By 2030, it is expected that the US will require over 5 trillion kWh of new electrical generation capacity even without considering replacing old plants [6]. Of this new capacity, the International Energy Agency (IEA) estimates that 80 GW will be met through the construction of coal-fired power plants. Worldwide installed capacity of coal-fired plants is expected to increase by over 40% in the next 20 years, exceeding 1400 GW by 2025 [6]. The supply and utilization of other solid fuels are discussed elsewhere [3,4]. Proximate and ultimate analyses of several coals and types of biomass are compared [7] based on higher heating value (HHV).

Efforts to develop systems to capture CO₂ emissions from carbon-based fuels have increased in recent years. Carbon dioxide is the most significant greenhouse gas and is considered a cause of increasing atmospheric temperatures [8]. One capture approach is based on a chemical looping combustion process developed in the mid 1990s, which uses metallic oxide as an oxygen carrier for combustion [9-11]. The fuel, mostly gases and similar in composition to a typical syngas, reduces the metal oxide to the corresponding metal at low temperature in a reactor. In a second reactor, the metal is oxidized using steam at high temperature to form the metal oxide, which is recycled to the first reactor. Hydrogen is produced from water in the second reactor. During the reaction in the first reactor the oxygen in the metal is transferred to the carbon in the fuel, forming CO₂ and steam [10-12]. The water is condensed, allowing the CO₂ to be separated and sent to storage. This process exhibits greater poten-

*Address correspondence to this author at the Faculty of Engineering and Applied Science, University of Ontario Institute of Technology, Oshawa, Ontario, L1H 7K4, Canada; Tel: 1-905-721-8668, Ext. 3756; Fax: 1-905-721-3370; E-mail: marc.Rosen@uoit.ca

tial for CO₂ separation [12] compared to membrane separation of CO₂ from syngas after gasification [13].

Coal direct chemical looping (CDCL) was proposed recently [11] in which a fuel reactor reduces the metal oxide by directly reacting with coal and some oxygen to produce sequestration-ready CO₂ and a metal stream. Experimentation, process modeling and simulation suggest that a maximum coal-to-hydrogen conversion efficiency of 80% can be achieved using CDCL [11]. Some problems with this process include temperature issues relating to the metal oxide (e.g., very high temperatures destabilize the structure) and sizing the reactor to control reaction rates [11]. A comparison between CDCL and syngas chemical looping (SCL) combustion systems [14] suggests that CDCL produces more hydrogen than SCL for lower air inlet conditions. Similar chemical looping combustion processes were investigated for producing hydrogen and electricity from coal [15] and natural gas [16].

Of the various metal oxides that can be used for the fuel and syngas reduction-oxidation process, iron oxide (Fe₂O₃) was identified as permitting the highest conversion of fuel/syngas to combustion products (CO₂ and water) along with a high conversion of steam to hydrogen [17].

Identifying the most and least advantageous solid fuels (considering coal and biomass) in terms of hydrogen production and effective CO₂ separation remains to be investigated, especially using the direct chemical looping (DCL) combustion system, shown in Fig. (1). Such information is needed to improve the utilization of solid fuels (by producing more specific hydrogen) while reducing the specific CO₂ emission. An ability to use fossil carbon-based solid fuels in an efficient and a clean manner is greatly sought in current energy markets [18]. Direct chemical looping combustion provides an effective solution to manage solid fuels and produce a pure CO₂ stream within a single unit operation. Many of the problems and costs associated with gasification of solid fuels can be avoided with chemical looping combustion [13].

In this study, four coals and four types of biomass (with values of fixed carbon (FC) and volatile matter (VM) as presented in Table 1) are used in the DCL system for producing hydrogen with CO₂ separation. Iron oxide is used as the oxygen carrier apart from oxygen in the air for initial energy supply through partial combustion. The principal aim is to identify the best coal and biomass as well as the potential of low-grade coal and biomass with the highest H₂ to CO₂ ratio for a given mass of fuel. A full range of operating conditions for such parameters as the air and iron oxide flow rates to the fuel reactor, are reported with the corresponding range of energy requirements. The impact of fuel blends (mix of coal and biomass) on hydrogen production is compared, and the effect of fuel moisture content on hydrogen production is investigated to specify the need for dry solid fuels when using the DCL system. The disadvantage of low air consumption and high iron oxide consumption is highlighted through the energy requirement analysis. The potential for coals and biomass in producing hydrogen is discussed. The analysis and results can help in formulating the parameter ranges for an effective design of the fuel reactor within the DCL system.

A process simulation of the DCL system is carried out using ASPEN Plus [19], which facilitates a sensitivity analysis for varying air and iron oxide inlets to the fuel reactor, for a fixed amount of the respective solid fuel. The analysis is focussed on the energy requirements of the fuel reactor (Fig. 1) which constitutes a significant step in reducing the metal oxide by direct interaction with coal or biomass. The other two reactors are for reclaiming metal oxide by oxidation and combustion.

Note that this work does not present a system analysis, though a systemic thermodynamic balance is applied, but instead provides an analysis of components (mainly the fuel reactor) operating as part of the DCL system. This approach is taken to identify regions of interest in the operation of the fuel reactor within the DCL system, in order to focus on the design factors relevant to gas-solid-based fuel reactors. The analysis yields a discrete set of solutions for a continuous set of operating conditions.

2. DIRECT CHEMICAL LOOPING COMBUSTION SYSTEM

The DCL system involves the chemical looping combustion concept without gasification [13]. Solid fuels react directly with oxygen and iron oxide in a fuel reactor (see Fig. 1) in the system. The advantage of using iron oxide (Fe₂O₃) as the oxygen carrier is that it does not involve catalytically dependent reactions [17]. The gaseous products are CO₂ and steam.

The advantages of the DCL system are a reduction in the oxygen consumption thus reducing the energy requirement in the air separation unit [11]. A comparison of chemical looping combustion and chemical looping oxygen uncoupling (CLOU) shows that the conversion rates of solid fuels are a factor of 50 higher when using CLOU [20], which is similar to the DCL system, thus helping to reduce the solids inventory needed and the reactor size.

Recently the minimum requirements for such resources as air, iron oxide and steam for the CDCL system were reported [14] as part of a comparison between direct and syngas-based chemical looping systems. The current work extends the CDCL system from Gnanapragasam *et al.* [14] to the DCL system and identifies the minimum and maximum hydrogen production based on variations in iron oxide consumption for a given air input to the fuel reactor. The corresponding nature of the energy requirements is discussed.

2.1. Fuel Reactor

The fuel reactor is an extended form of a reduction reactor and the series of chemical reactions that occur within this reactor are discussed below. The primary function of the fuel reactor is to reduce iron oxide (Fe₂O₃) to iron using carbon in the fuel and oxygen from air. The fuel reactor is modeled with ASPEN Plus as three separate RGIBBS reactors (rigorous reaction and multiphase equilibrium based on Gibbs free energy minimization) linked together by restricting products from each of the three reactors: partial combustion, fuel reactor top and fuel reactor bottom (Fig. 1). The reactions and conditions in the fuel reactor, following Fan *et al.* [11] and Mattison *et al.* [20], are as follows:

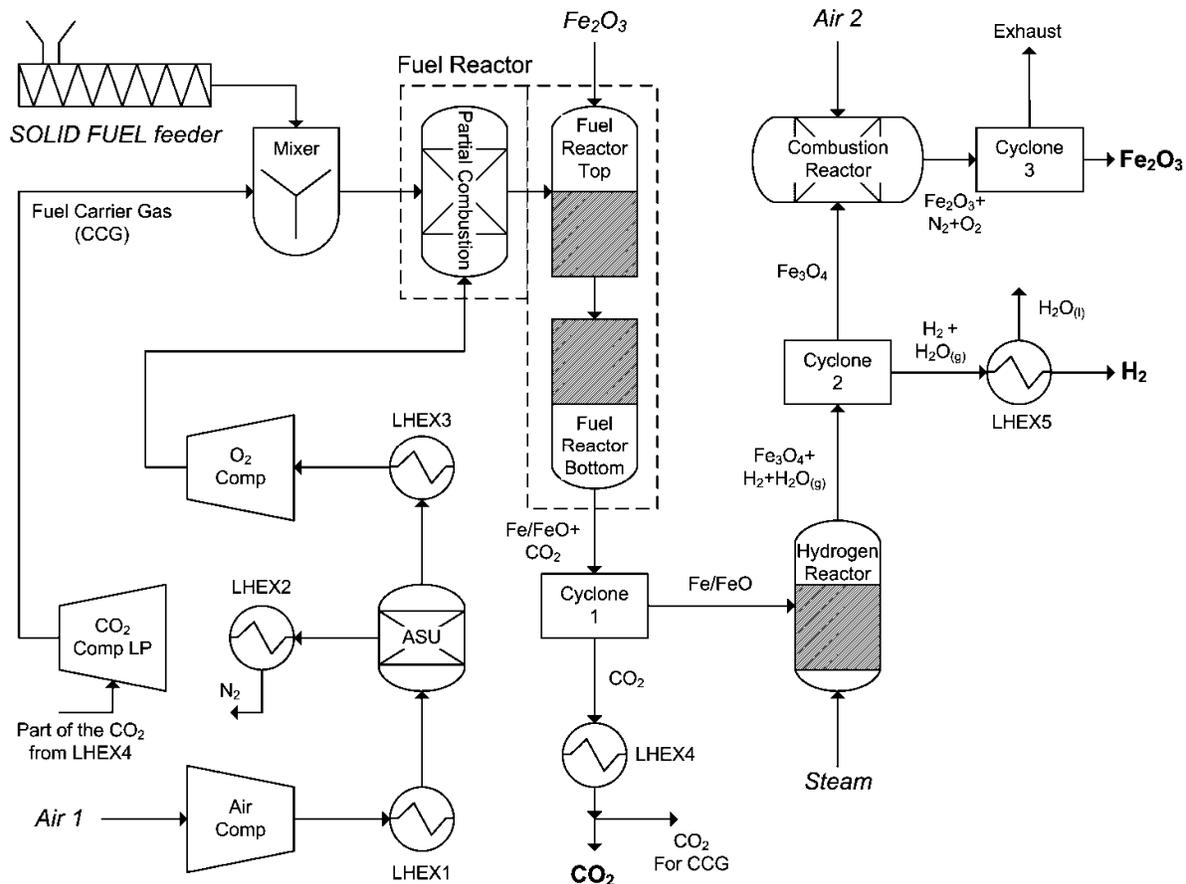
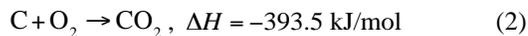


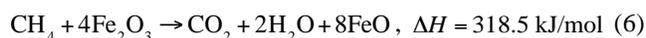
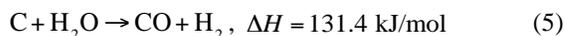
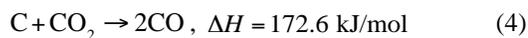
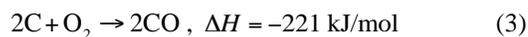
Fig. (1). Schematic of direct chemical looping (DCL) combustion system for H₂ production and CO₂ separation using coal, air, iron oxide and water. This represents operation within one cycle.

- *Partial combustion.* Solid fuel devolatilisation and partial combustion occur as follows:

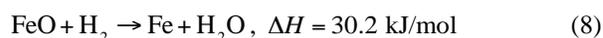


The formula for the solid fuel used here, C₁₁H₁₀O, represents Pittsburgh #8 coal, although a different set of coals and biomass are used in the calculations [11].

- *Fuel reactor top.* Char gasification and iron oxide reduction occur:

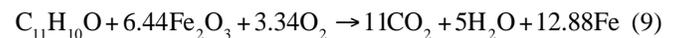


- *Fuel reactor bottom.* Wustite (FeO) reduction occurs:



The overall chemical reaction within the fuel reactor [11]

is

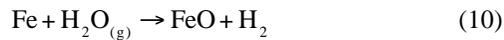


The residence time for the char in the fuel reactor is between 30 and 90 minutes [11], depending on operating temperature (750-900°C) and pressure (1-30 atm). The reaction in Eq. (6) enables the conversion of methane in the gas-solid stream within the fuel reactor to CO₂ and FeO while reducing iron oxide (Fe₂O₃).

In this work, the range of operation of the fuel reactor is extended below and above that previously reported [10,18] to assess the impact of a range of air and iron oxide inlet conditions on reactor energy requirements. This approach enables the identification of possible process integrations for a given range of operating temperatures, within the limits imposed by the stability criterion of iron oxide [21] and the thermal limitation of feedstock materials [13].

2.2. Hydrogen Reactor

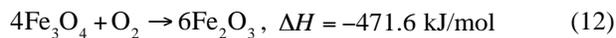
In the DCL system, hydrogen is produced in the hydrogen reactor (in Fig. 1), where oxidation of iron occurs, with the use of iron and steam. To obtain the iron necessary for oxidation, the fuel reactor reduces iron oxide using CO obtained from solid fuels. The oxidation reactor operates at 30 bar (gauge pressure) and 500 to 700°C to oxidize the metal produced in the reduction reactor using steam. The products are 99% pure hydrogen and magnetite (Fe₃O₄). The reactions follow:



Both reactions are slightly exothermic and some of the heat may be used for preheating the feed water to make steam.

2.3. Combustion Reactor

The magnetite formed in the oxidation reactor enters the combustion reactor where it reacts with oxygen to form the more stable form of iron oxide III (Fe_2O_3). A significant amount of heat is produced during the oxidation of Fe_3O_4 to Fe_2O_3 [11]. The reaction is



The gas composition of 'Exhaust' in Fig. (1) is the remaining oxygen after the reaction in Eq. (12) along with the corresponding amount of nitrogen.

2.4. System Details

Design details and explanations of problems associated with the reduction, oxidation and combustion reactors at the laboratory scale have been reported [11,18]. The cyclones remove solids (metal oxide) from the gas stream. In the schematic in Fig. (1), only the solid streams are indicated (Fe/FeO , Fe_3O_4 and Fe_2O_3) after each cyclone. The representation of the DCL system in Fig. (1) is for one cycle of operation. The Fe_2O_3 is not recycled, but the setting for the simulation (through cyclones, heat exchangers and bag filters) is such that all Fe_2O_3 is recovered, thereby representing an ideal or maximum-benefit case.

Since we do not present the energy balance of the overall DCL system in the current work, the thermal energy relationship among the three reactors is not discussed here, but a relevant work in this regard is already published [22]. The current work treats these reactors as independent, although in practice they would be integrated into a unit operation to reduce heat losses [23].

The DCL system is modeled with ASPEN Plus such that all the solids (char and iron oxide) are recovered in each cyclone by adding a bag filter model after cyclone separation. The reason for assuming complete recovery of solids is to focus the analysis on material resource requirements without losses, so the minimum requirement for metal oxide and the corresponding requirements of steam and air are found.

2.5. System Operating Conditions

The pressure in all the reactors is set at 30 bar (gauge pressure). The solid fuel carrier gas (FCG), CO_2 in the current analysis, thus enters the compressor at 15 bar with a 10 kg/s mass flow rate and is compressed to 30 bar before entering a mixer to transport the solid fuel from there to the primary reactor in each of the system. Even though it is also called the 'air' inlet to the fuel reactor, it is actually the oxygen inlet since there is an air separation unit (ASU) in the DCL system as shown in Fig. (1). For all analyses, the simulation performed on the DCL system involves a full range of operating conditions: air inlet to fuel reactor from 1 to 25 kg/s and iron oxide inlet to fuel reactor from 1 to 30 kg/s.

The mass flow rate for coals and biomass is fixed at 5 kg/s for the entire analysis.

One of the objectives of this work is to identify the impact of air versus iron oxide for combustion, and the results are discussed with that focus. When more air is used, more compression work is needed by the ASU for separating oxygen from air. When more air (oxygen) is input to the fuel reactor, more oxy-fuel combustion is induced, thus producing more CO_2 than CO and reducing the overall hydrogen production capability. This measure also increases the temperature of the fuel reactor. If the air (oxygen) input is reduced and the iron oxide input increased, the amount of air separated (and the compression work required) by the ASU becomes very small.

2.6. Thermodynamic Analysis

A thermodynamic assessment is done on the system in Fig. (1) to determine the energy performance of the proposed system. The following simplifications and assumptions are used:

- Chemical and phase equilibrium based on a Gibbs free energy minimization model [24] are used for the fuel, oxidation and combustion reactors.
- Coal is delivered dry, crushed and chlorine free.
- The following components are not included in the thermodynamic analysis: cyclone, bag filter, mixers, gas separators (ASU).
- Only thermodynamically stable components at temperatures above 873 K are considered, including; CO , CO_2 , H_2 , H_2O , CH_4 , $\text{C}_{(s)}$, N_2 , O_2 and H_2S .
- Gas property evaluations are based on the Peng-Robinson equation of state with Boston-Mathias modifications [19], with a reference temperature of 298 K at a pressure of 1 atm.
- The purity of CO_2 and H_2 streams are estimated to be 99.9%, assuming all the water is condensed in each of the streams.

An energy balance for components that involve the mixing of environmental and fuel elements is discussed here for the proposed system. The energy rate balance considering each component in Fig. (1) as a control volume at steady state is

$$\frac{\dot{Q}_{cv}}{\dot{n}_F} - \frac{\dot{W}_{cv}}{\dot{n}_F} = \sum_P n_e \left(\bar{h}_f^o + \Delta \bar{h} \right)_e - \sum_R n_i \left(\bar{h}_f^o + \Delta \bar{h} \right)_i \quad (13)$$

Here, F denotes fuel (coal for the gasifier and syngas for combustors), i the incoming fuel and air/gas streams and e the exiting combustion products. The enthalpies of reactants (R) and products (P) are evaluated by the Aspen Plus code and the energy balance is evaluated with an Excel spreadsheet.

3. HYDROGEN POTENTIAL FOR HIGH- AND LOW-GRADE SOLID FUELS

The four coals and four types of biomass used in this analysis were selected based on having a good variation in fixed carbon, carbon content, oxygen content and HHV.

Table 1. Chemical Composition of Solid Fuels [7] Based on Proximate and Ultimate Analyses with Corresponding Measured Higher Heating Values

No.	Solid Feedstock	Proximate Analysis			Ultimate Analysis					Measured HHV (MJ/kg)
		FC	VM	ASH	C	H	O	N	S	
		% by wt. Dry Basis			% by wt. Dry Basis					
Coal										
1	Northumberland anthracite	84.59	7.09	8.32	83.67	3.56	2.84	0.55	1.05	32.856
2	Coke	91.47	0.92	7.61	89.13	0.43	0.98	0.85	1	31.124
3	German lignite	46.03	49.47	4.5	63.89	4.97	24.54	0.57	0.48	25.1
4	Oak char (438-640°C)	59.3	25.8	14.9	67.7	2.4	14.4	0.4	0.2	24.796
Biomass										
5	Douglas fir	25.8	73	1.2	56.2	5.9	36.7	0	0	22.098
6	Loblolly pine	33.9	65.7	0.4	56.3	5.6	37.7	0	0	21.772
7	Wood chips	23.5	76.4	0.1	48.1	5.99	45.74	0.08	0	19.916
8	Tan oak	9.2	90.6	0.2	48.67	6.03	44.99	0.06	0.04	18.934

Fixed carbon in solid fuels is the carbon remaining after the volatile matter is removed. The data in Table 1 indicate that anthracite has the highest HHV, and has less carbon than coke but more than lignite and oak char. Tan oak has the lowest HHV while loblolly pine has the highest carbon among the four types of biomass. Woodchips have the most oxygen while oak char has the highest ash content.

3.1. Coal and Biomass Profiles

The performance of each coal in the DCL system for hydrogen production is shown in Fig. (2A) and that of each biomass is shown in Fig. (2B). In Figs. (2-12), parts (A) and (B) share the same vertical axis. In Fig. (2) the relative hydrogen produced by the eight solid fuels are compared with the fuel reactor air consumption. Here, 'relative hydrogen' denotes that it is compared with the maximum hydrogen produced among the coals or biomass discussed in a given plot.

The wavy (up and down) profile of the values in Fig. (2) is due to simultaneously varying two parameters in the current model: fuel reactor air consumption and iron oxide consumption. The parameters in Figs. (2) and (3) are plotted for increasing fuel reactor air consumption. The vertical lines in each coal and biomass profile in Fig. (2) are the range of hydrogen produced (as indicated in Fig. (2B) for a corresponding increase in iron oxide mass flow rate at constant air consumption in the fuel reactor.

The wavy profiles also provide minimum and maximum conditions for hydrogen production for each quantity of air used. The magnitude of this range (indicated by the arrow in Fig. (2B) for pine as an example) depends on the oxygen content of the solid fuel. For example, biomass has a larger range compared to the coals, corresponding to the higher oxygen content of biomass, as can be observed in the ultimate analysis in Table 1. Coke has the lowest oxygen content (0.98% in Table 1), and thus exhibits a small vertical

range of hydrogen production (2% in Fig. (2A)), while woodchips have the highest oxygen content (45.74% in Table 1) corresponding with the largest range of hydrogen production (30% in Fig. (2B)), for the same amount of air. This range of hydrogen production is facilitated by a fixed amount of iron oxide consumption as shown in Fig. (3).

3.2. Air and Iron Oxide Consumption

The higher oxygen content of a coal or biomass also reduces the air consumption in the fuel reactor since oxygen is required for partial combustion (Eq. (2)) and char gasification (Eq. (3)). Thus the range of air consumption for each fuel varies in Fig. 2(A) and (B) corresponding to its oxygen content. For example, coke yields no hydrogen below 45,000 kg/h of air while woodchips produce hydrogen above 3600 kg/h of air.

The variation of iron oxide consumed with fuel reactor air consumption is shown in Fig. (3) for the solid fuels. Each vertical line in each of the profiles is the range of iron oxide used to produce the corresponding amount of hydrogen (as indicated in Fig. (3B)). The profiles in Fig. (3A) and (B) are similar to those in Fig. (2A) and (B), suggesting that the amount of hydrogen produced for a given amount of fuel and air is directly proportional to the iron oxide consumed.

For a given iron oxide value (say the horizontal line running across Fig. (3) and for a given air consumption (say 50,000 kg/h), the fuels with low carbon content consume less iron oxide and thus produce less hydrogen (Fig. 2).

3.3. Hydrogen Potential

All the coals produce a maximum hydrogen quantity at least once within the range of air consumption shown in Fig. (2A). For a given air supply above 40,000 kg/h, anthracite produces the most hydrogen followed by coke, with lignite and oak char both producing 20% less hydrogen. Oak char and lignite produce the maximum hydrogen at the lowest air

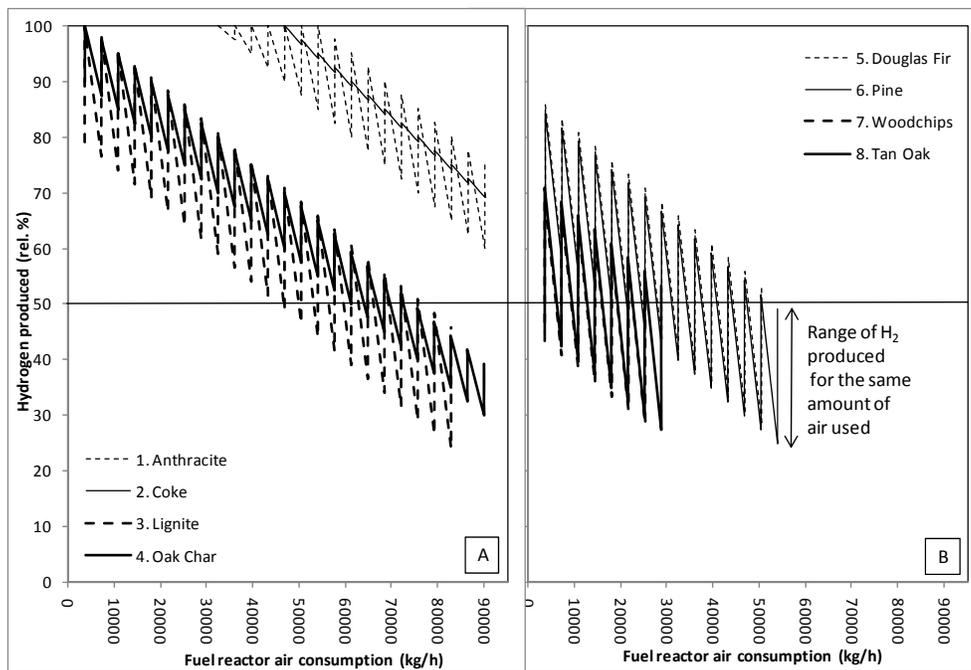


Fig. (2). Variation in hydrogen production with fuel reactor air consumption for four coals (A) and four types of biomass (B).

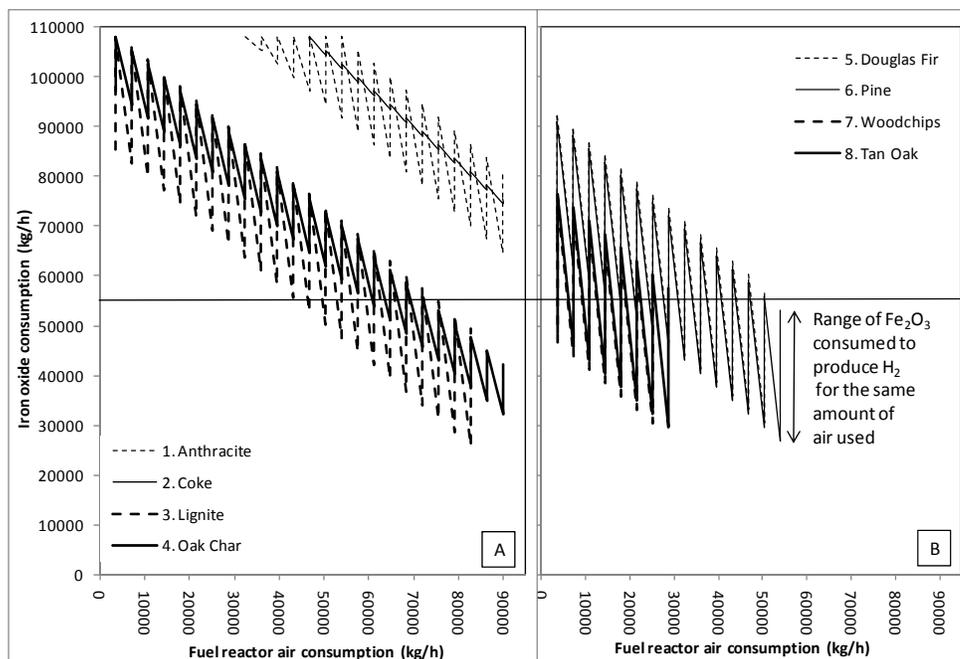


Fig. (3). Variation in iron oxide consumption with fuel reactor air consumption for four coals (A) and four types of biomass (B).

consumption and, from Fig. (3A), at the maximum iron oxide consumption. Also note that both lignite and oak char have higher oxygen contents than anthracite and coke.

Among biomass types, both Douglas fir and pine produce the same amount of hydrogen due to having the same carbon contents (see ultimate analysis in Table 1). Note that in the DCL system, hydrogen production is directly proportional to the carbon (not the fixed carbon) content of the fuel, and the reduction of iron oxide (Eqs. (7) and (8)) is dependent on the amount of CO produced after the first two stages in the fuel reactor (Eqs. (1) to (6)). Woodchips and tan oak similarly

produce the same amount of hydrogen but less than fir and pine. The advantage of having higher oxygen content in biomass is that it enables biomass having higher carbon contents, for example fir and pine, to produce maximum hydrogen at the lowest air and the highest iron oxide consumption (Fig. (3B)).

The comparison of oxygen and carbon contents in solid fuels introduces the limiting factor for high carbon, low oxygen coals. That is, they are able to produce maximum hydrogen only above a certain condition, such as with a considerable amount of air consumption (Fig. (2A)).

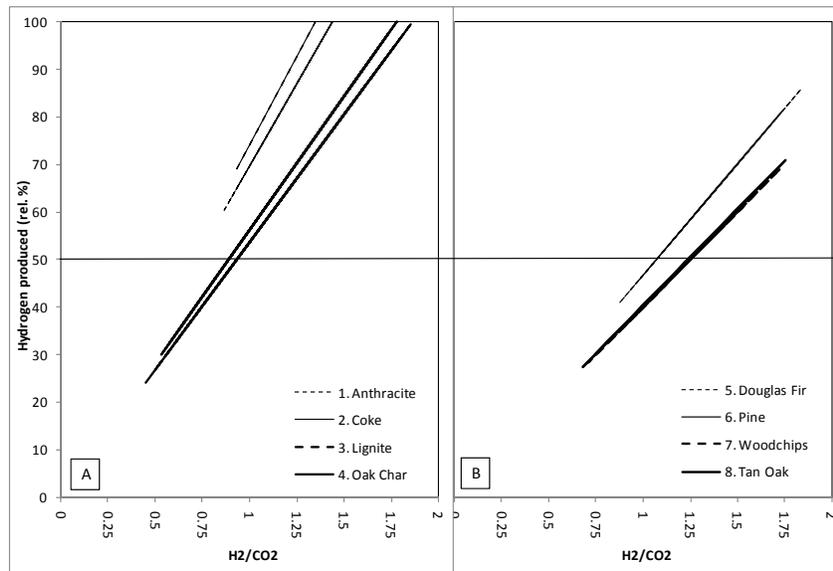


Fig. (4). Variation in hydrogen production with H₂ to CO₂ ratio for four coals (A) and four types of biomass (B).

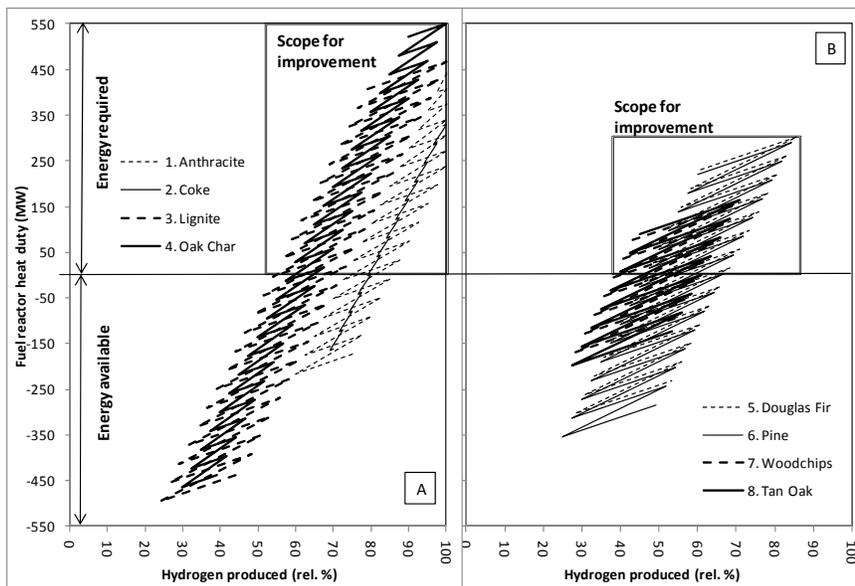


Fig. (5). Variation in fuel reactor heat duty with hydrogen production for four coals (A) and four types of biomass (B).

3.4. CO₂ Emission

The CO₂ emission for each solid fuel is proportional to its carbon content. Note that the DCL system does not reduce CO₂ emissions, but helps in simple separation of CO₂ for storage and other uses. In Fig. (4) the variation of relative hydrogen production with H₂ to CO₂ ratio is compared for coals (A) and biomass (B). With the lowest carbon content (ultimate analysis in Table 1), lignite produces more hydrogen per CO₂ emission than other coals while coke produces more CO₂ than all the solid fuels considered.

Although it was pointed out earlier that the amount of hydrogen corresponds to the carbon content of the solid fuel, it is evident from Figs. (2 and 4) that anthracite produces more hydrogen and less CO₂ than coke when coke has more carbon than anthracite. Since anthracite has a higher HHV than coke, the energy available for the reactions is more than

for coke, thus reducing CO₂ production, in line with the reactions in Eqs. (1) and (6).

Biomass has a better CO₂ profile than the coals and the difference induced by the carbon content is readily visible from the profiles in Fig. (4B).

4. ENERGY REQUIREMENT IN MAXIMIZING HYDROGEN POTENTIAL

The more iron oxide used, the less air is consumed (Fig. 3), since iron oxide replaces air as the oxygen carrier, creating an 'energy requirement' zone as shown in Fig. (5). Because the iron oxide reactions in Eqs. (1) to (8) tend to consume considerable energy and with a consumption profile of air and iron oxide as shown in Fig. (3), the energy requirement increases towards lower air consumption.

In Fig. (5), the energy requirements for all coals and biomass are shown with the corresponding hydrogen pro-

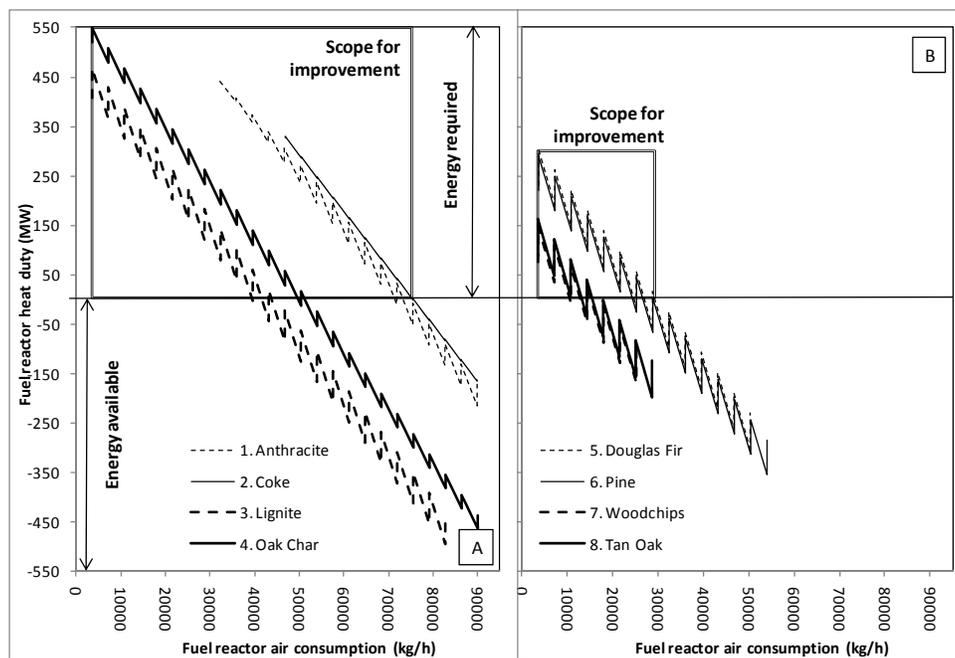


Fig. (6). Variation in fuel reactor heat duty with fuel reactor air consumption for four coals (A) and four types of biomass (B).

duced. The fuel reactor heat duty is the combination of the heat available via partial combustion, and the heat required in the top and bottom of the fuel reactor. The negative region represents the ‘energy available’ and the positive region is the ‘energy required’ as specified in Fig. (5A). The box with the label ‘Scope for improvement’ suggests that the coal and biomass profiles require additional energy to achieve the corresponding hydrogen production. The influence of HHV is distinct in the hydrogen profiles in Fig. (5).

4.1. Hydrogen Capability Based on Available Energy

The hydrogen profile for each coal or biomass below the ‘0’ line of the fuel reactor heat duty in Fig. (5) is the hydrogen produced that is under the capability of each of the fuels. The maximum hydrogen produced without requiring additional energy is examined. For coals, anthracite produces more than 83% of the maximum hydrogen without requiring additional energy, while coke, lignite and oak char produce about 80%, 70% and 65%, respectively. For biomass, the maximum hydrogen produced within the available energy is 65% for fir and pine and 60% for woodchips and tan oak.

Considering the coals in Fig. (5), to achieve more than 90% hydrogen production, both lignite and oak char have to provide a quantity of energy almost equal to that required to get to 70 and 65%, respectively. In practice, this means that almost twice the lignite or oak char is needed to produce the same amount of hydrogen as anthracite. It is impossible to attain 90% of the hydrogen production for biomass without blending or using three to four times the mass of anthracite.

4.2. Influence of Air Consumption on Fuel Reactor Heat Duty

The impact of air consumption on fuel reactor heat duty is shown in Fig. (6A) for coals and Fig. (6B) for biomass. The energy availability increases as the air increases for all fuels due to the partial combustion stage of the fuel reactor.

The temperature after the partial combustion reactions (Eqs. (1) and (2)) when using the coals and biomass is shown in Figs. (7A) and (7B), respectively. The 0 to 2700°C range in Fig. (7) is not the operating temperature range of the fuel reactor, but rather the corresponding temperature after the *partial combustion* step for the range of air inputs to the fuel reactor considered. Thus, this is the local temperature of material in several smaller regions within the partial combustion stage of the fuel reactor. The actual operating range for the fuel reactor is between 700 and 950°C as mentioned earlier.

The energy required is highest when there is less air in the fuel reactor (Fig. 6), a result also suggested by the temperature profiles in Fig. (7), where a lower temperature reflects a lower degree of partial combustion and thus low energy availability. For both lignite and oak char, the maximum hydrogen at low air consumption (Fig. (2A)) is practically not possible with the given temperature profile in Fig. (7). As discussed using Fig. (5), the practical possibility for hydrogen production is below the ‘0’ line. Hence the temperature after partial combustion exceeds 1500°C for coals and 600°C for biomass. The corresponding air consumption exceeds about 40,000 kg/h (11 kg/s) for coals and 15,000 kg/h (4 kg/s) for biomass.

There is also the concern of iron oxide stability, which beyond 1500°C approaches its melting point [7]. It is thus required that the temperature after partial combustion is controlled such that the iron oxide reactions (Eqs. (6) to (8)) use the thermal energy from partial combustion immediately so the temperature of the zone is stabilized below 1500°C.

4.3. Influence of Iron Oxide Consumption on Fuel Reactor Heat Duty

When iron oxide is used almost completely, in such cases as lignite and oak char (Fig. (8A)), so as to maximize hydrogen production, the energy required for the reactions is large. The iron oxide transport in such cases consumes as much or

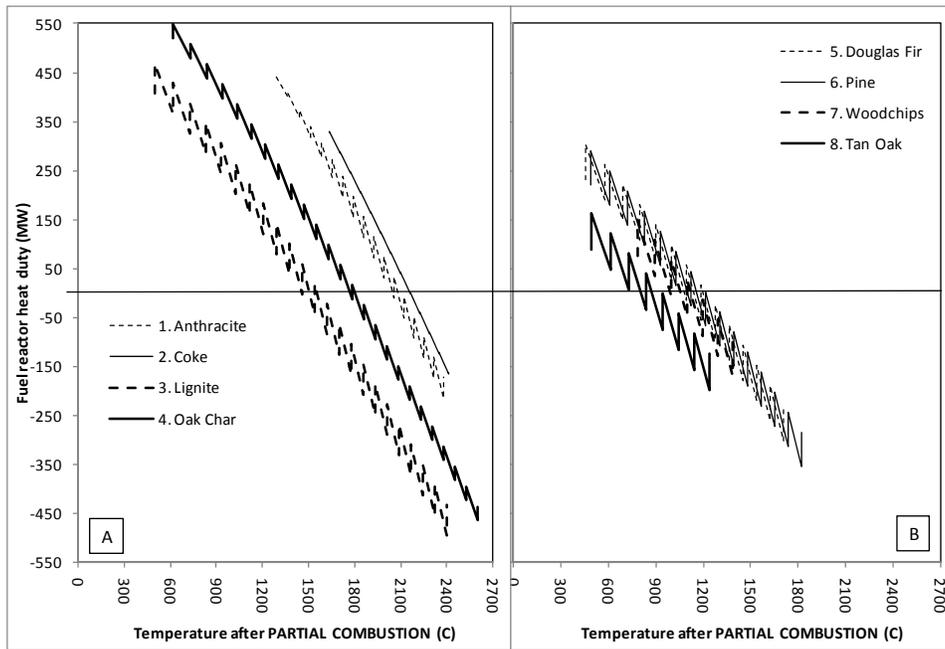


Fig. (7). Variation in heat duty with temperature available after partial combustion reactions in the fuel reactor for four coals (A) and four types of biomass (B).

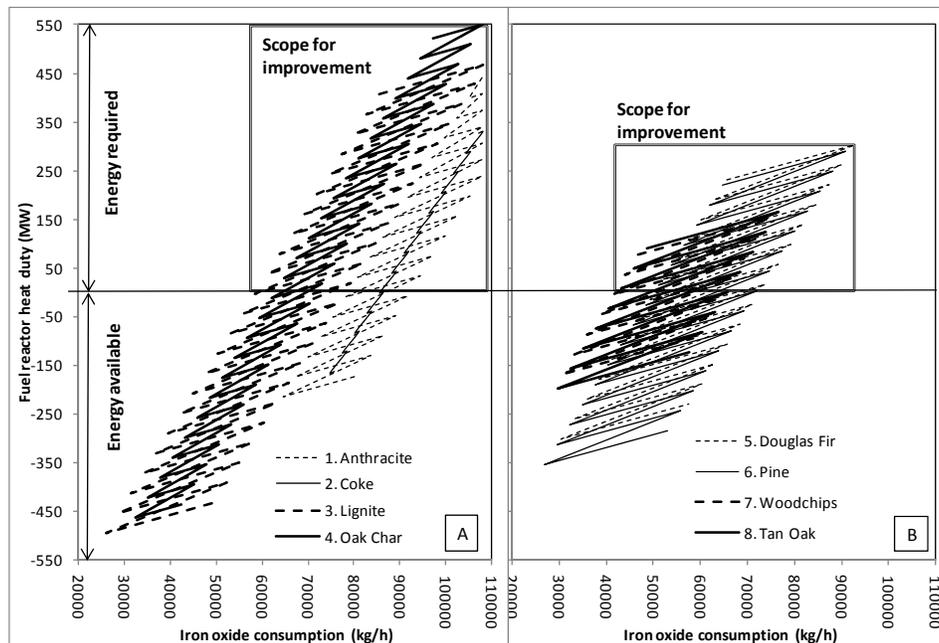


Fig. (8). Variation in fuel reactor heat duty with iron oxide consumption for four coals (A) and four types of biomass (B).

more energy than that of the air supply. Thus there are two energy penalties for increasing iron oxide consumption in the fuel reactor so as to separate CO₂ while reducing iron oxide to iron.

The iron oxide profile is proportional to the hydrogen profile. Fig. (8A) indicates that, for higher hydrogen production, more iron oxide needs to be reduced in the fuel reactor. This leaves low grade coals such lignite and oak char with two options: (i) to accept the hydrogen produced from the available energy at 70% and 65%, respectively, or (ii) to find means to supply the energy requirement for the additional 20

to 30% hydrogen. It is unclear if the latter option is worthwhile, since the energy requirement for the additional 20 to 30% hydrogen output is almost equal to the energy used in producing 70% hydrogen (say for lignite). This is due to the corresponding decrease in the air consumption when iron oxide consumption is increased, thus reducing the energy available through partial combustion.

The material temperature after the fuel reactor top stage is shown in Fig. (9) for solid fuels. This is the temperature available after the iron oxide reaction (Eq. (6)), which uses energy from the partial combustion stage. A negative tem-

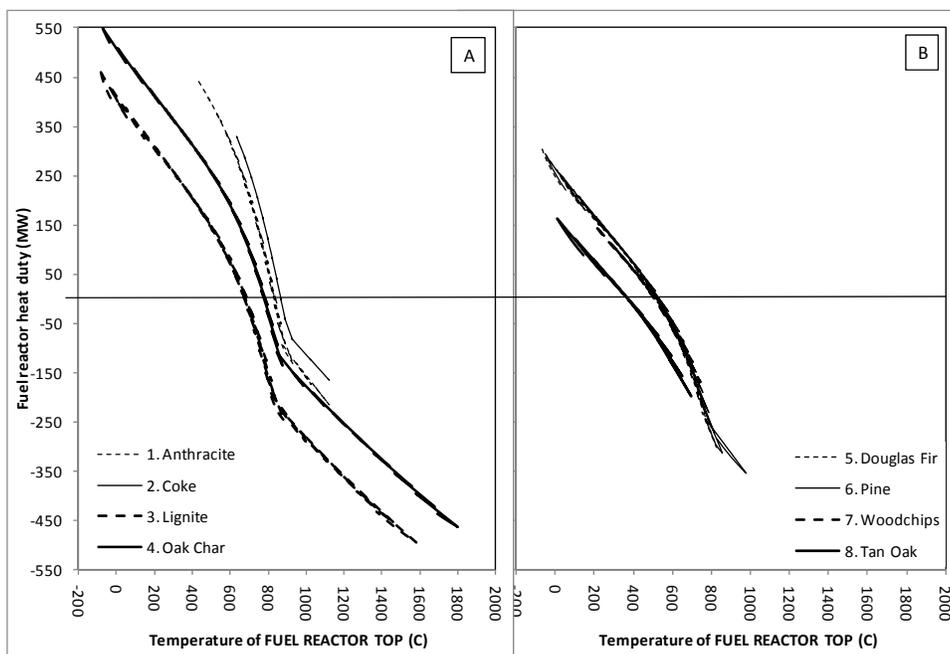


Fig. (9). Variation in heat duty with reactor temperature of FUEL REACTOR TOP (in Fig. 1) for four coals (A) and four types of biomass (B).

perature in Fig. (9) corresponds to the low-temperature region in Fig. (7) (300 to 600°C) where partial combustion has insufficient air to obtain more energy. The ideal range for the temperature from Fig. (9) varies from below the ‘0’ line up to the iron oxide stability level, corresponding to 600 to 1500°C.

Above 1100°C, iron oxide particles start agglomerating, thereby reducing the surface area for reactivity [25]. Although the temperature range between 750°C and 900°C is practically useful for this type of process where a metal oxide is the primary oxygen carrier, the use of more iron oxide and less air yields more hydrogen. This work analyses the energy requirements in such extremes; the stability of reactants and products in such conditions can be found elsewhere [18,26,27]. The availability of such extreme temperatures in the fuel reactor provides opportunities for process integration in generating steam and the option of thermal transport to other systems if the DCL system operates as part of an existing energy conversion system.

5. SCOPE FOR IMPROVEMENT

The energy requirement for maximizing hydrogen output to obtain the additional 20 to 30% for coals and 30 to 40% for biomass can be derived from several sources and options. One option is to increase the specific amount of respective fuel used, but again that would also increase the CO₂ emissions except for biomass. When considering the specific increase in fuel use as an option, it is advantageous to have two units (with 70% hydrogen in each when using say lignite) and produce at least 40% more hydrogen for the same amount of available energy than trying to achieve 100% hydrogen (only 30% more on top of 70% with the same amount of fuel) in a single unit.

Another option is to remain close to the ‘0’ line of the energy spectrum (above the line if additional energy is available) so that losses can be avoided and maintaining the appropriate amount of hydrogen produced from each fuel.

Some of the other options such as blends of low- and high-grade solid fuels, avoiding moisture in the feedstock and using external heat sources are discussed here.

5.1. Blend of Coal and Biomass

It is assumed that the blending of coal and biomass is performed outside the DCL system and the mixed substance is conveyed to the fuel reactor as a single feedstock. The procedures for pre-treating of feedstock such as drying, crushing and blending are not treated as part of the system in this work, but are assumed done prior to the process simulation. Four blends of anthracite and tan oak (the coal with highest HHV and the biomass with lowest HHV) with different combinations are examined. The quantities of hydrogen produced by blends of anthracite and tan oak (20-80, 50-50, 60-40 and 80-20, on a weight percentage basis) are shown in Fig. (10A), as a function of fuel reactor air consumption. When an increased mass of anthracite is used, more hydrogen is produced at higher fuel reactor air consumptions, because of increased energy availability owing to the higher HHV of anthracite. When comparing the 20% anthracite and 80% tan oak blend in Fig. (10A) with 100% tan oak in Fig. (2B), an increase in hydrogen production of about 10% is realized.

For a blend with 80% tan oak, the tan oak contributes to the oxygen demand by producing more hydrogen than at 50% tan oak with less air consumption. The total range of 80% tan oak profile is the only one that shows little influence of anthracite.

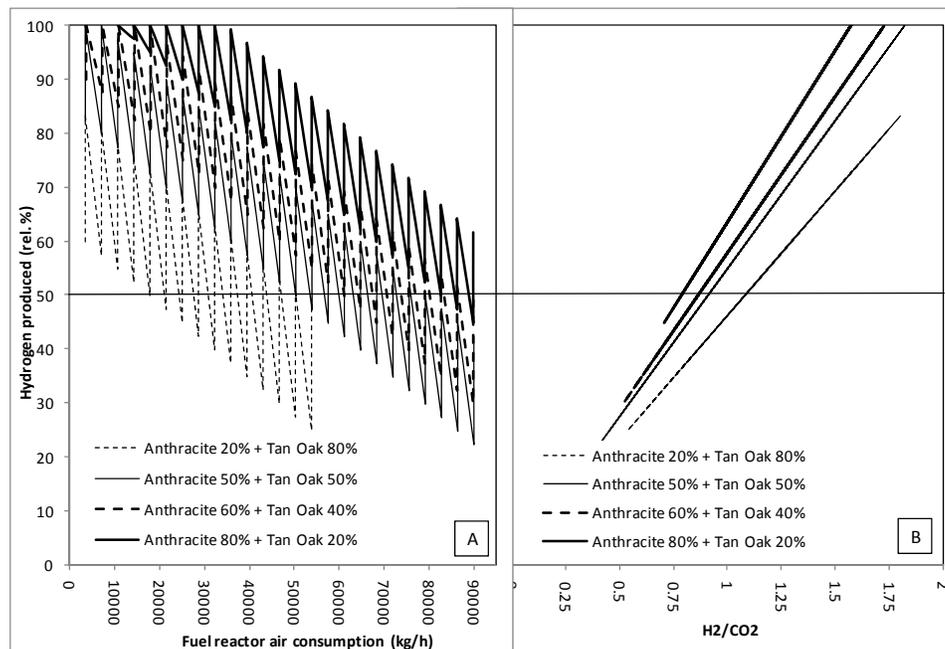


Fig. (10). Variation of hydrogen production, for four blends of anthracite and tan oak, with fuel reactor air consumption (A) and H₂ to CO₂ ratio (B).

The energy spectrum for the blend of anthracite and tan oak is shown in Fig. (11A) with respect to hydrogen production. Based on the energy availability zone (below the '0' line) from Fig. (5B) and Fig. (11A), a comparison of tan oak and 80% tan oak indicates that only 5% more hydrogen is produced by adding 20% anthracite to tan oak. For 50% tan oak with 50% anthracite, the increase in hydrogen production is by 15%, within the energy availability zone. There are three benefits to the 50% blend: (i) the opportunity for using low-grade tan oak, (ii) the opportunity to reduce usage of high-grade anthracite, and (iii) the opportunity to reduce the CO₂ emission of anthracite.

The CO₂ emissions for the four blends are shown as a function of H₂/CO₂ ratio with respect to hydrogen production in Fig. (10B). The CO₂ emission decreases with increasing tan oak contribution to the blend. A comparison of 80% tan oak and 50% tan oak blends indicates that the amount CO₂ produced at maximum hydrogen output for both are the same while the 50% blend produces 15% more hydrogen, which is consistent with the energy availability comparison in Fig. (11A).

Using 50% high-grade coal with 50% of low-grade biomass is one of the better options for increasing the combined energy availability and the corresponding hydrogen production.

5.2. Moisture in the Feedstock

Both coal and biomass contain moisture. The analysis in this work considers all solid fuels on a dry mass basis. The energy spent in drying was not included in the analysis until now. For a 10% fuel moisture content, the corresponding change in hydrogen production is shown Fig. (12A) with fuel reactor air consumption. The moisture reduces the HHV of the fuel and the formulation is available in literature [7]. A

calculator block is added in the Aspen model to update the moisture information.

With 10% moisture in anthracite, the hydrogen production decreases by 15% as shown in Fig. (12A). For tan oak the 10% moisture reduces hydrogen production only by 6%. The corresponding energy profiles are shown in Fig. (11B). With 10% moisture in tan oak, there is no energy available for hydrogen production. If tan oak is delivered wet, the potential for hydrogen production is severely limited unless blended with dry coal or another fuel with a better HHV. For anthracite, 10% moisture reduces the energy availability by 10%.

Since the moisture reduces hydrogen production, the H₂/CO₂ ratio is increased as shown in Fig. (12B) for both anthracite and tan oak. The CO₂ produced is directly proportional to the carbon content (ultimate analysis) in the fuel and thus moisture does not change the CO₂ production unless more fuel is used to meet the hydrogen production criteria.

The advantage of dry solid fuel is realized with higher hydrogen production. Means to dry the fuel may be coupled with waste heat from within the DCL system with proper planning to save resources.

5.3. External Thermal Sources Through Process Integration

The energy availability in the current analysis is discussed only for the fuel reactor. The oxidation reactor (Eqs. (10) and (11)) requires high-pressure and temperature steam which requires additional energy. The combustion reactor with its exothermic reaction (Eq. (12)) generates some thermal energy which can be used for producing steam. Other energy intensive processes within the DCL system include solid fuel and iron oxide transport, air separation, cyclone separation and heat losses from all relevant processes.

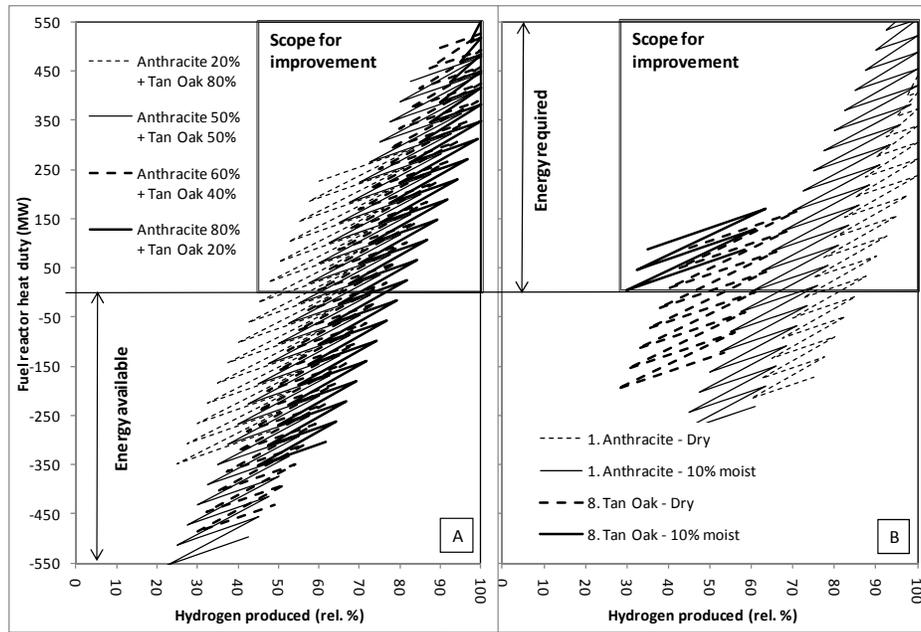


Fig. (11). Variation in fuel reactor heat duty with hydrogen production for four blends of anthracite and tan oak (A) and dry and 10% moist anthracite and tan oak (B).

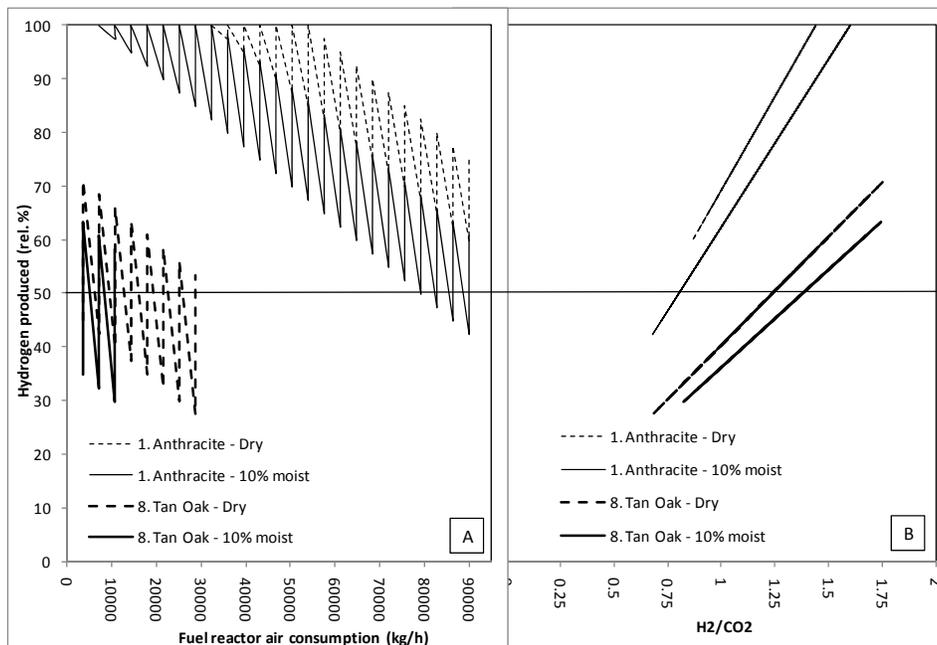


Fig. (12). Variation of hydrogen production, for dry and 10% moist anthracite and tan oak, with fuel reactor air consumption (A) and H₂ to CO₂ ratio (B).

The regions of ‘scope for improvement’ in the figures discussing energy may be optimized by starting from the ‘0’ line and moving up to a certain level where the percentage of hydrogen produced requires the energy that may be available from say the combustion reactor.

Another possibility is when a DCL system is part of larger energy conversion facilities such as natural gas combined-cycle power plants, nuclear power generating stations, steel manufacturing plants, oil refineries, etc. The heat from

other processes in the larger system may be used for increasing the hydrogen production through the DCL system by externally heating the fuel reactor to maintain higher operating temperature.

5.4. System Efficiency

A comparison of energy (thermal) efficiencies (based on the LHV of fuel) of CO₂ capture systems such as the DCL system, membrane based CO₂ separation with water-gas shift reactor, and conventional gas-liquid absorption system, can

highlight the significance of the DCL system. The DCL system has an overall energy efficiency of about 52% at maximum hydrogen production. When a ceramic membrane based is used within a coal gasification system to produce hydrogen from the water-gas shift, the process has an energy efficiency of about 48% [28]. When ceramic membranes are used within an integrated gasification combined cycle system for CO₂ separation [29], the system's energy efficiency is about 37% (when multistage membranes are used) while the polymer membranes attain an energy efficiency of up to 38%. The effectiveness of CO₂ separation (purity) exceeds 80% in all these cases. Amine absorption from a natural gas-based power system [30] is reported to have a total thermal efficiency of 58% without CO₂ removal. The efficiency is reduced to about 50% with CO₂ removal. Although the DCL system's energy efficiency is based on simulation, the real time efficiency would still be higher than that for other conventional CO₂ capture processes, due to it being a cyclic process and expected improvements in reactor design in the near future.

CONCLUSIONS

The direct chemical looping (DCL) system proposed in this work enables the use of various types of coal and biomass ranging from low to high energy contents to produce hydrogen without gasification. The following are some of conclusions drawn from the current investigation:

- The opportunity for low-grade (low-energy) coals to produce maximum hydrogen as high-grade coals providing additional energy is identified.
- When air consumption is reduced, the iron oxide consumption increases which also increases the demand for energy to sustain the iron oxide reactions in converting the CO to a CO₂ only stream.
- The minimum air requirement for maximum hydrogen production from anthracite and coke is about 30% more than that required for lignite and oak char (low-grade coals). But this places the low-grade coals in the energy requirement zone.
- Producing more iron by reducing more iron oxide yields more hydrogen through oxidation by steam.
- In a combustion system involving both oxygen (air) and iron oxide such as the DCL system, it is beneficial to have a solid fuel with higher oxygen content, since it reduces the air intake but increases the iron oxide use, thus providing a greater range for hydrogen production for the same air consumption.
- Anthracite produced the maximum hydrogen output of which 90% was produced within the energy availability of the fuel reactor.
- Lignite produced about 70% of the maximum capacity within the energy availability zone. To achieve the remaining 30% hydrogen, an equal amount of additional energy is required. Also, two units with 70% each can produce 40% more hydrogen than trying to achieve 100% within the same unit for the amount of available energy.

- Blending 20% high-grade coal (anthracite) with 80% low-grade biomass (tan oak) increases the production of hydrogen from tan oak by 10%. The 50-50 blend is economic in terms of the energy availability and H₂/CO₂ ratio.
- A 10% moisture content in the anthracite reduces 10% of the hydrogen production. For tan oak, a 10% moisture content places the hydrogen production out of the energy availability zone.
- Potential improvements through external heat sources can increase the contribution of low-grade solid fuels.

The results from this work will help in designing the fuel reactor with appropriate control measures when operating under variable conditions.

ACKNOWLEDGEMENTS

The authors kindly acknowledge the financial support provided by the Natural Sciences and Engineering Research Council of Canada.

REFERENCES

- [1] Collot, A-G. Matching gasification technologies to coal properties. *Int. J. Coal Geol.* **2006**, *65*, 191-212.
- [2] Collot, A-G. *Prospects for Hydrogen from Coal. Report CCC/78.* Clean Coal Centre: International Energy Agency, **2003**.
- [3] Asif, M., Muneer, T. Energy supply, its demand and security issues for developed and emerging economies. *Renewable Sustain. Energy Rev.* **2007**, *11*, 1388-1413.
- [4] (IEA). International Energy Agency, World Energy Outlook. **2008**.
- [5] British Petroleum. BP Statistical Review of World Energy, **2009**.
- [6] DOE. *Energy Information Agency.* International Energy Outlook. U.S. Department of Energy, **2009**. Accessible at www.eia.doe.gov/oiaf/ieo/index.html
- [7] Parikh, J., Channiwala, S.A., Ghosal, G.K. A correlation for calculating HHV from proximate analysis of solid fuels. *Fuel* **2005**, *84*, 487-494.
- [8] USEPA. Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2006. U.S. Environmental Protection Agency, Washington, DC, April 15, **2008**.
- [9] Ishida, M., Jin, H. Chemical-looping combustion power generation plant system. U.S. Patent number 5, 447, 024A, 1995.
- [10] Jin, H., Ishida, M. A new type of coal gas fueled chemical-looping combustion. *Fuel* **2004**, *83*, 2411-2417.
- [11] Fan, L-S., Li, F., Ramkumar, S. Utilization of chemical looping strategy in coal gasification processes. *Particucology* **2008**, *6*, 131-142.
- [12] Yu, J., Corripio, A.B., Harrison, D.P., Copeland, R.J. Analysis of the sorbent energy transfer system (SETS) for power generation and CO₂ capture. *Adv. Environ. Res.* **2003**, *7*, 335-345.
- [13] Rezaian, J., Cheremisinoff, N.P. *Gasification Technologies: A Primer for Engineers and Scientists.* Taylor and Francis: London, **2005**.
- [14] Gnanapragasam, N.V., Reddy, B.V. Rosen, M.A. Hydrogen production from coal using coal direct chemical looping and syngas chemical looping combustion systems: Assessment of system operation and resource requirements. *Int. J. Hydrogen Energy*, **2009**, *34*, 2606-2615.
- [15] Cleeton, J.P.E., Bohn, C.D., Müller, C.R., Dennis, J.S., Scott, S.A. Clean hydrogen production and electricity from coal via chemical looping: Identifying a suitable operating regime. *Int. J. Hydrogen Energy* **2009**, *34*(1), 1-12.
- [16] Rydén, M., Lyngfelt, A. Using steam reforming to produce hydrogen with carbon dioxide capture by chemical-looping combustion. *Int. J. Hydrogen Energy* **2006**, *31*(10), 1271-1283.
- [17] Gupta, P., Velazquez-Vargas, L.G., Fan, L-S. Syngas redox (SGR) process to produce hydrogen from coal derived syngas. *Energy Fuels* **2007**, *2*, 2900-2908.

- [18] DOE. *Hydrogen from Coal Program: Research, Development and Demonstration Plan for the Period 2007 through 2016*. National Energy Technology Laboratory, Office of Fossil Energy, US Department of Energy, September 2007. Accessible at http://www.netl.doe.gov/technologies/hydrogen_clean_fuels/refsheLf/pubs/External_H2_from_Coal_RDD_Plan_September_13.pdf
- [19] Aspen Technology Inc. ASPEN Plus 12.1 User Guide. <http://www.aspentech.com>, 2006.
- [20] Mattisson, T., Lyngfelt, A., Leion, H. Chemical-looping with oxygen uncoupling for combustion of solid fuels. *Int. J. Greenhouse Gas Control* 2009, 3(1), 11-19.
- [21] Thurnhofer, A., Schachinger, M., Winter, F., Mali, H., Schenk, J.L. Iron ore reduction in a laboratory-scale fluidized bed reactor – effect of pre-reduction on final reduction degree. *ISIJ Int.* 2005, 45(2), 151-158.
- [22] Jin, H., Ishida, M. Reactivity study on a novel hydrogen fueled chemical-looping combustion. *Int. J. Hydrogen Energy* 2001, 26, 889-894.
- [23] Johansson, E., Mattisson, T., Lyngfelt, A., Thunman, H. Combustion of syngas and natural gas in a 300 W chemical-looping combustor. *Trans. Inst. Chem. Eng., Part A. Chem. Eng. Res. Des.* 2006, 84(A9), 819-827.
- [24] Li, X., Grace, J.R., Watkinson, A.P., Lim, C.J., Edenler, A.E. Equilibrium modeling of gasification: A free energy minimization approach and its application to a circulating fluidized bed coal gasifier. *Fuel* 2001, 80, 195-207.
- [25] Fraser, S., Hacker, V., Besenhard, J.O. *Sponge Iron Process for Manned Space Exploration*. Advanced Concepts Team, European Space Agency, Ariadna, Final Report 04-2302, 2005. Available at <http://www.esa.int/act>
- [26] Garcia-Labiano, F., de Diego, L.F., Adanez, J., Abad, J., Gayan, P. Temperature variations in the oxygen carrier particles during their reduction and oxidation in a chemical-looping combustion system. *Chem. Eng. Sci.* 2005, 60, 851-862.
- [27] Jerndal, E., Mattisson, T., Lyngfelt, A. Thermal analysis of chemical-looping combustion. *Trans. Inst. Chem. Eng., Part A, Chem. Eng. Res. Des.* 2006, 84(A9), 795-806.
- [28] Gnanapragasam, N.V., Reddy, B.V., Rosen, M.A. Hydrogen production from coal gasification for effective downstream CO₂ capture. *Int. J. Hydrogen Energy*, 2010, 35(Suppl. 10), 4933-4943.
- [29] Kaldis., S.P., Skodras, G., Sakellaropoulos, G.P. Energy and capital cost analysis of CO₂ capture in coal IGCC processes via gas separation membranes. *Fuel Process. Technol.*, 2004, 85, 337-346.
- [30] Oi, L.E. *Aspen HYSYS Simulation of CO₂ Removal by Amine Absorption from a Gas Based Power Plant*. SIMS2007 Conference, Göteborg, October 30-31 2007.

Received: January 02, 2010

Revised: January 18, 2010

Accepted: February 12, 2010

© Gnanapragasam *et al.*; Licensee Bentham Open.

This is an open access article licensed under the terms of the Creative Commons Attribution Non-Commercial License (<http://creativecommons.org/licenses/by-nc/3.0/>) which permits unrestricted, non-commercial use, distribution and reproduction in any medium, provided the work is properly cited.