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Comparison of Iron and Tungsten Based Oxygen Carriers for Hydrogen Production Using Chemical Looping Reforming

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Abstract. Hydrogen production by using a three reactor chemical looping reforming (TRCLR) technology is an innovative and attractive process. Fossil fuels such as methane are the feedstocks used. This process is similar to a conventional steam-methane reforming but occurs in three steps utilizing an oxygen carrier. As the oxygen carrier plays an important role, its selection should be done carefully. In this study, two oxygen carrier materials of base metal iron (Fe) and tungsten (W) are analysed using a thermodynamic model of a three reactor chemical looping reforming plant in Aspen plus. The results indicate that iron oxide has moderate oxygen carrying capacity and is cheaper since it is abundantly available. In terms of hydrogen production efficiency, tungsten oxide gives 4% better efficiency than iron oxide. While in terms of electrical power efficiency, iron oxide gives 4.6% better results than tungsten oxide. Overall, a TRCLR system with iron oxide is 2.6% more efficient and is cost effective than the TRCLR system with tungsten oxide.

1. Introduction

The interest in hydrogen (H_2) as an energy carrier and decarbonized fuel is growing due to concerns about rising greenhouse gas emissions caused by the use of fossil fuels. A common large scale H_2 production method is steam-methane reforming (SMR). However, CO_2 is also produced during the process. To reduce the environmental impact of this process requires the capturing of CO_2 by using the costly and energy intensive technologies such as pressure-swing adsorption and amine absorption [1]. The use of CO_2 capture method increases the cost of H_2 production. In this regard, chemical looping reforming (CLR) offers a cost effective method of H_2 production with inherent CO_2 capture and no additional air separation unit.

A three reactor chemical looping reforming (TRCLR) process is considered as the most promising CL technology for H_2 production [2]. In this process, an oxygen carrier (OC) is used to transfer oxygen from air to the fuel. This process is economical and the cost of H_2 produced is in parity with other H_2 production technologies [3]. It employs three reactors: fuel reactor, steam reactor and air reactor. In the

Fuel Reactor: $$\mathrm{MeO_x + CH_4 \rightarrow MeO_{x-a} + CO_2 + 2H_2O} \quad (1)$$

Steam Reactor: $$\mathrm{MeO_{x-a} + H_2O \rightarrow MeO_{x-a+1} + H_2} \quad (2)$$

Air Reactor: $$\mathrm{MeO_{x-a+1} + (a-1)O_2 \rightarrow MeO_x} \quad (3)$$

Overall Reaction: $$\mathrm{CH_4 + \tfrac{2}{3}H_2O + \tfrac{2}{3}O_2 \rightarrow CO_2 + \tfrac{8}{3}H_2} \quad (4)$$

fuel reactor (FR), the fuel (e.g., methane (CH_4)) is oxidized to CO_2 and water (H_2O) by taking up the oxygen (O_2) from the OC (eq. (1)). The reduced OC goes into the steam reactor (SR) where it is oxidized by the steam to produce H_2 (eq. (2)). Finally, in the air reactor (AR), the OC is fully oxidized by the air (eq. (3)). The O_2 needed for the reactions is circulated among the three reactors by means of a transition metal OC. The overall reaction is shown in eq. (4).

The selection of OC is very critical task of the TRCLR process. The information about suitable OCs for the CLR process is limited since the range of options for OCs is quite narrow. Zafar et al. [4] investigated different OCs such as CuO, Mn_2O_3, NiO and Fe_2O_3 supported on SiO_2 for H_2 production. They concluded that NiO is the most feasible OC to be used in the process. However, their finding was based on the use of a two reactor CLR system. Kang et al. [5] performed a comprehensive thermal analysis to identify the most suitable OC for the reduction reaction with CH_4 and the oxidation reaction with steam. Oxides of iron (Fe), tungsten (W) and cerium (Ce) were selected for the H_2 production application. Cormos [6] presented the plant concepts and methodology to evaluate the plant performance. Iron based CL systems with different power generation schemes using natural gas and syngas were evaluated. Kathe et al. [7] investigated the thermodynamic limits for full conversion of natural gas through an iron-based CLR system. They reported higher thermal efficiency than that from a conventional SMR process.

In the current study, the best reaction pathways of the OCs of base metal Fe and W are used in a thermodynamic model of a CH_4-fueled TRCLR plant. The model is similar to that used by Khan and Shamim [3] in their techno-economic assessment. All the sub-models and assumptions used are similar. However, in the current study, the plant input fuel capacity is 500 MW as opposed to 350 MW in the aforementioned study. The plant performance based on the electrical, hydrogen and exergetic efficiencies is compared for both OC materials. In addition, the reactor temperatures and the emissions such as CH_4, CO and NO are also compared. It is worth mentioning here that the main objective of the present study is to demonstrate the competitiveness and viability of the CLR technology. This study on TRCLR plant will assist in complying with the urgent need of reduction in CO_2 emissions and transferring the dependence on hydrocarbon fuels to de-carbonized fuels like H_2 to mitigate the threat of climate change.

2. Thermodynamic modeling

The thermodynamic model was developed by employing conservation of mass and energy for all the cases in Aspen plus. The model specifications and the assumptions used can be found in Khan and Shamim [2]. The process flow diagram of the plant with the components used are shown in Figure 1. RGIBBS reactor was used for FR, SR and AR, which assumes chemical and phase equilibrium based on the Gibbs energy minimization concept. Separation of solids and the product gases were assumed to be perfect and was done by using cyclones. A turbocharger was used for compression of incoming air into the AR to a desired pressure and power production through a gas turbine by the outgoing vitiated air from the AR. The exhaust of the AR was used to generate intermediate pressure (IP) and low pressure (LP) steam in a heat recovery steam generator (HRSG). The exhausts from the FR and the SR were used to produce a high pressure (HP) steam in a parallel HRSG. The HP and IP steam were supplied to the steam turbines (ST) to produce power. Some of the LP steam was compressed to IPs to fulfill the steam requirement of the plant by using a steam compressor (SC). HRSG and ST unit constitute a steam cycle. The AR exhaust was released into the atmosphere while the FR and SR exhausts were compressed to the desired pressures in a two stage intercooled compression system (COMP).

Thermodynamic equilibrium has been assumed for the calculations. The properties were evaluated using the property method Redlich-Kwong-Soave (RKS) equation of state with the Boston-Mathias modifications. For the steam cycle the property method STEAM-TA has been used. The base case model was validated with a good agreement in our previous work [2]. The circulating OCs used in the present study were oxides of iron (Fe_2O_3, FeO, Fe_3O_4) and tungsten (WO_3, WO_2, $WO_{2.72}$) with 70% (by weight) inert material $MgAl_2O_4$ according to the reaction pathways shown in Table 1. The operating conditions and assumptions are given in Table 2. All the cases were performed at the stoichiometric OC mass flow rate based on the fuel flow rate. However, in actual systems, excess OC is supplied to ensure full conversion of fuel in the FR. The excess amount is usually 2% of the total flow rate [8]. Hence, the effect of excess OC is insignificant on the plant performance.

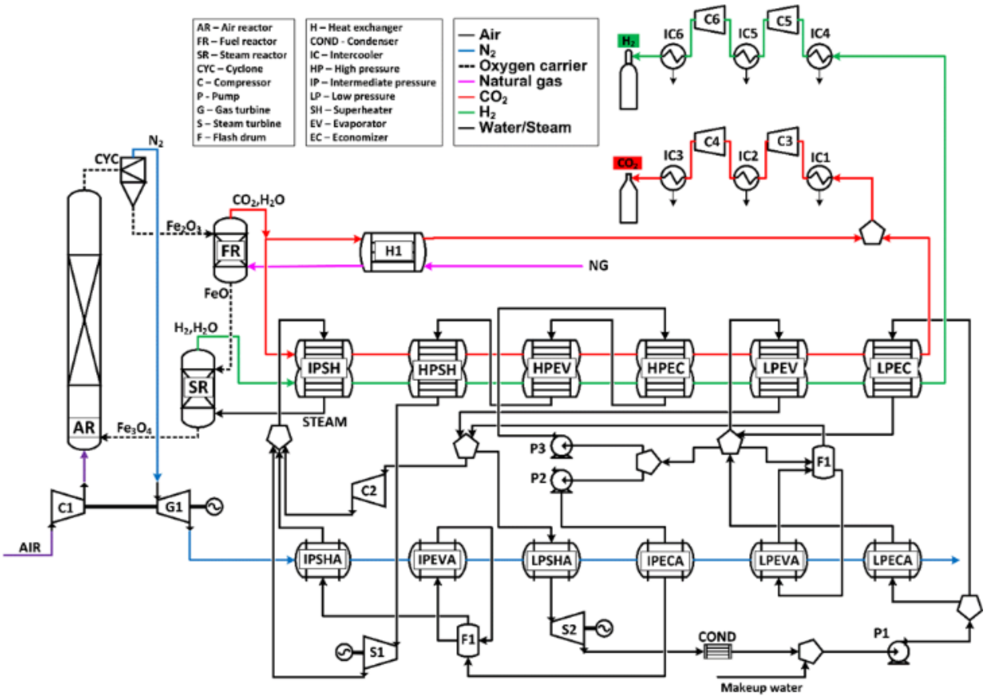

Figure 1. Process flow diagram of TRCLR plant

Table 1. Selected pathway reactions in three reactors

OC	Reaction
	$4\ Fe_2O_3 + CH_4 \rightarrow CO_2 + 2\ H_2O + 8\ FeO$
Iron	$3\ FeO + H_2O \rightarrow H_2 + Fe_3O_4$
	$4\ Fe_3O_4 + O_2 \rightarrow 6\ Fe_2O_3$
	$4\ WO_3 + CH_4 \rightarrow CO_2 + 2\ H_2O + 4\ WO_2$
Tungsten	$1.39\ WO_2 + H_2O \rightarrow H_2 + 1.39\ WO_{2.72}$
	$7.14\ WO_{2.72} + O_2 \rightarrow 7.14\ WO_3$

Table 2. Assumptions and operating conditions

Item	Value
Ambient conditions	15 ℃, 1.013 bar
Natural gas heating value (MJ/kg)	45.467
CL reactors operating pressures (bar)	AR-16, FR-20, SR-18
CL reactors thermal losses	0.2% of thermal input
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Heat exchangers - Pressure loss	2%
GT/TC compressor polytropic efficiency	0.924
GT/TC turbine polytropic efficiency	0.926
Steam cycle pressures (HP, IP, LP, Condensation)	90/22/3/0.04 bar

HRSG pinch, approach temperature	10/25℃
Max. Turbine inlet temperature	500℃
Mechanical efficiency (pumps, compressors, turbines)	98%
Isentropic efficiency (pumps, compressors, turbines)	85%
Liquid CO_2 condition	25 ℃, 120 bar
H_2 condition	25 ℃, 60 bar

For thermodynamic assessment, the technical indicators used are the electrical and H_2 production efficiencies and which are defined as follows

$$\eta_E = \frac{\dot{W}}{Q_{NG}};\ \eta_H = \frac{Q_H}{Q_{NG}} \tag{5}$$

where Q_H and Q_{NG} are thermal power (product of mass flow rate and LHV of the gas) of the H_2 output and natural gas input, respectively, and $\dot{W}$ is the net power output. As the main product of this plant is H_2 and the byproduct is electricity, it is difficult to define a single performance indicator for a co-production plant. However, a single index called global efficiency can be defined which includes both the efficiencies. It can be called as the equivalent H_2 production efficiency as it is calculated based on the fuel used for only H_2 production i.e. the fuel used for electricity production is deducted from the total fuel input.

$$\eta_{GL} = \frac{Q_H}{Q_{NG} - \dot{W}/\eta_{E,REF}} = \frac{\eta_H}{1 - \eta_E/\eta_{E,REF}} \tag{6}$$

where $\eta_{E,\ REF}$ is the reference electrical efficiency of an alternative power generation process. Such a reference efficiency is 50% and is taken from the study on a natural gas fired combined cycle plant. The reference efficiency is used to calculate the equivalent natural gas consumption to produce the same amount of electricity as actually produced by the plant.

The overall exergetic efficiency is defined as the ratio of the exergy of the product obtained from the operation of the components to the exergy of the fuel expended in that operation as shown in equation (7).

$$\varepsilon_{tot} = \frac{\dot{E}_{H_2} + \dot{W}_{net}}{\dot{E}_{Air} + \dot{E}_{Water} + \dot{E}_{Fuel}} \tag{7}$$

3. Results and discussions

As mentioned earlier, the thermodynamic model was validated from the data available in the literature [8]. The results show that the endothermic reaction in the FR forms the products namely CO_2, H_2O, H_2, CO, N_2 and traces of CH_4 while the highly exothermic reaction in the AR gives out argon, CO_2, H_2O, N_2, O_2 and traces of NO. The thermodynamic performance indicators for Fe- and W-based plants are shown in Figure 2. The results show that the H_2 production efficiency, in the case of W-based oxides, is 4 percentage points higher than that of Fe-based oxides while the electrical power efficiency is 4.6 percentage points lower than that of Fe-based oxides. The global efficiency, however, is 2.6 percentage points higher in the case of Fe-based oxide. In terms of exergetic efficiency, W-based plant showed a better performance with 5.3 percentage points higher efficiency than a Fe-based plant. The gross power output obtained in both the scenarios are 59.4 and 31.3 MW, respectively. Of which 65/61 % comes from GT and 35 and 39 % comes from ST, respectively. About 59/68 % and 10/44 % of the gross power output is consumed in air compression and steam compression, respectively. The CO_2 and

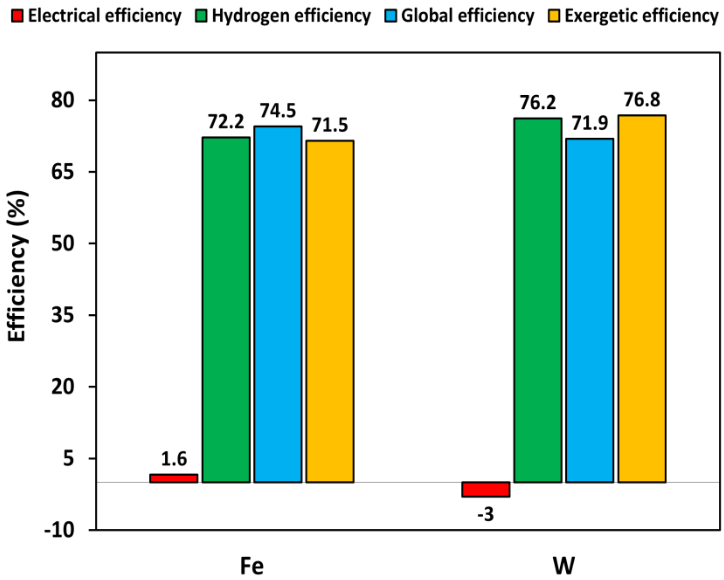

Figure 2. Plant performance with iron and tungsten oxides as oxygen carriers

H_2 compression units consume about 7.7/16 % and 9.3/19 %, respectively. The power output in W-based plant is lower because of the lower reactor temperatures. In the FR, the temperature difference between the Fe-based and W-based plants is about 125 K, whereas, in the SR and the AR, the temperature differences are about 131 K and 156 K, respectively, as shown in Figure 3. Table 3 compares performance data and the emissions of unburnt CH_4, CO and NO. Fe-based plant produces net power whereas there is no net power in W-based plant since extra power is required by the auxiliaries of the plant. The CH_4 emissions from Fe-based plant is very low, about 17 ppm as opposed to 2778 ppm from W-based plant. The CO emissions are similar for both the plants. In terms of NO emissions, W-based plant performs better. This is because of the low reactor temperatures.

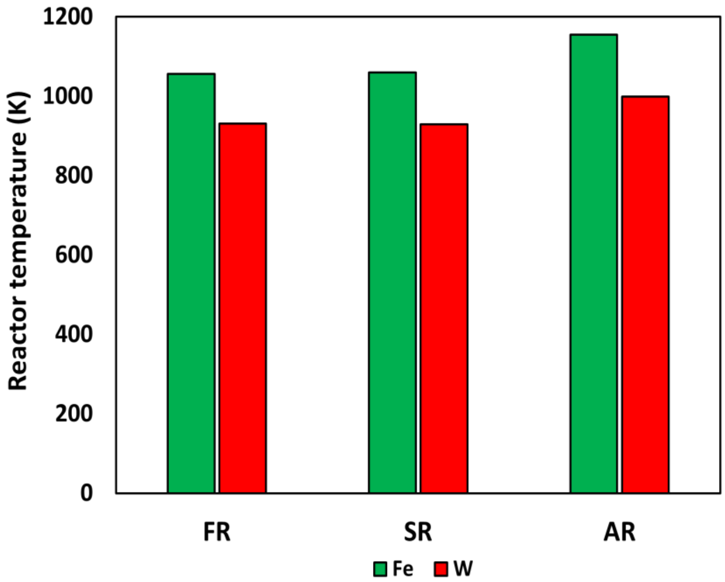

Figure 3. Reactor temperatures with iron and tungsten oxides as oxygen carriers

Table 3. Performance data and emissions from the TRCLR plants

	Fe-based	W-based
Fuel input (kg/s)	11	11
Gross/net output (MW)	59.36/7.9	31.27/-
Auxiliary loads (MW)	16.6	25
OC mass flow rate (kg/s)	1346	1954
Steam mass flow rate (kg/s)	45	48
Air mass flow rate (kg/s)	77	46
Emissions (ppm)		
CH_4	17	2778
CO	25620	26687
NO	87	8E-07

4. Conclusions

The current study investigated the performance of Fe- and W-based OCs in a TRCLR plant. A thermodynamic study has been performed by using these OC materials in an Aspen based model. The results in the form of H_2 and power production efficiencies were compared. The results show that the H_2 production efficiency, is 4 percentage points higher for W-based oxides were than that of Fe-based oxides. The electrical power efficiency is 4.6 percentage points lower for W-based oxides than that of Fe-based oxides. Furthermore, Fe is much cheaper than W. Therefore, an Fe-based plant is the most suitable option for H_2 generation and it has the potential to be used commercially.

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