



Modeling and Analysis of Sorption Enhanced Chemical Looping Biomass Gasification

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Steam biomass gasification has been considered the most favorable option for production of syngas. Nevertheless, the steam biomass gasification is inevitably problematic with undesirable CO₂ and tar formed during the process. Calcium oxide (CaO), when added to the gasification, could play the dual role of tar cracking catalyst and CO₂ sorbent, and thereby producing more hydrogen. The CO₂ capture process is the carbonation reaction of CO₂ and CaO to produce CaCO₃. In general, CaCO₃ can be regenerated at high temperatures and then reused within the cyclic process. Nonetheless, a major disadvantage of the steam biomass gasification with in situ CO₂ capture process is due to high external heat requirement in a regenerator. In this study, the sorption enhanced chemical looping biomass gasification, which is operated without heating and cooling system, for high-purity hydrogen production is investigated. Model of the gasification is developed using ASPEN Plus process simulator and used to analyze its energy efficiency performance. The results show that the maximum energy efficiency performance is 57.67% at the operating conditions of steam to carbon ratio = 2.6, temperature = 636 °C, CaO to carbon ratio = 1 and nickel oxide to carbon ratio = 1.06.

1. Introduction

Hydrogen as an energy carrier has numerous advantages over other conventional energy carriers. It has the highest energy density compared with other fuels (122 kJ per kg, about 2.75 times greater than other hydrocarbon fuel) (Balat and Kirtay, 2010). Hydrogen combustion provides more energy (lower heating value based on mass basis) than that of methane, gasoline and coal. Hydrogen is widely used in the production of pharmaceuticals, fine chemicals and bulk chemicals such as ammonia and methanol. It is also regarded as an energy carrier in the future because it can be produced from renewable sources such as biomass, solar energy, etc., and is efficiently converted to electricity by fuel cells, which provides high efficiency with clean exhaust gas by consuming hydrogen and oxygen. Currently, there are a number of energy sources and technologies to produce hydrogen, but about 99% of hydrogen comes from fossil fuels, mainly by steam reforming of natural gas, which could not address above serious concerns (Mirza et al., 2009). To meet the renewable and sustainable hydrogen production, biomass is considered the ideal primary energy source for gradually replacing the depleting fossil fuels. Biomass can be considered green and renewable sources for sustainable hydrogen production through thermochemical and biological processes. However, the efficiency of the biochemical process makes them less attractive for industries as compared to the thermochemical processes. Among thermochemical processes, gasification is considered as most potential process for hydrogen production. Biomass gasification is the thermochemical conversion of biomass into a combustible or synthesis gas which contains mainly hydrogen, carbon monoxide and methane. Steam biomass gasification has been recommended to be the most favorable option for the production of syngas rich in hydrogen (Florin and Harris, 2008). Nevertheless, steam biomass gasification is inevitably problematic with undesirable CO₂ and tar (high molecular weight hydrocarbon compounds) formed during the process. Calcium oxide (CaO)

when added to the gasification, could play the dual role of tar cracking catalyst and CO₂ sorbent, and thereby produce more hydrogen (Florin and Harris, 2008; Vivanpatarakij et al., 2014). The CO₂ capture process is the carbonation reaction of CO₂ and CaO to produce CaCO₃. In this system, the water gas and water gas shift reactions can be enhanced as the concentration of CO₂ is lowered due to the CO₂ capture by CaO carbonation. As a result, the produced syngas could have very high hydrogen concentration. Nonetheless, the major disadvantage of steam biomass gasification with in situ CO₂ capture process is the requirement of high energy input at a CaCO₃ regenerator. Recently, Rydén and Ramos (2012) proposed the use of a chemical looping process in reforming applications. The basic concept is to implement the few exothermic reactions of a metal oxide (NiO) to its metal (Ni) to supply heat for the regenerator. Chemical looping method is an innovative and potentially promising method for H₂ production with low environmental impacts. In such a method, there is no direct contact between the fuel and oxidizer; oxygen is supplied to the fuel by using an oxygen carrier, which is generally a transition metal such as Ni, Cu, and Mn (Khan and Shamim, 2016). The present work is focused on modelling and analysis of the sorption enhanced chemical looping biomass gasification for high-purity hydrogen production, which is operated without heating and cooling system, using ASPEN Plus process simulator. Two parametric analyses methods are comprehensively applied to investigate the high-purity hydrogen production and used to study the energy efficiency performance of the process.

2. Sorption enhanced chemical looping biomass gasification

2.1 Model description

In this study, wood residue is selected as the feedstock for biomass gasification process (Fremaux et al., 2015). The properties of wood residue such as proximate analysis, ultimate analysis, and higher heating values (HHV) are presented in Table 1.

Table 1: The properties of biomass (wood residue) (Fremaux et al., 2015).

Proximate analysis (dry basis) (wt. %)	
Volatile matter	81.81
Fixed carbon	17.83
ASH	0.36
Ultimate analysis (dry basis) (wt. %)	
C	50.08
H	6.70
O	42.51
N	0.16
S	0.20
ASH	0.36
Moisture content (wt. %)	5.01
Higher heating value (MJ/kg)	19.97

Modeling of the sorption enhanced chemical looping biomass gasification is based on mass balance, energy balance, and chemical equilibrium and developed using ASPEN Plus process simulator. The following main assumptions are made in this study for developing the process model: (1) the process is operated under steady-state and isothermal conditions; (2) all the chemical reactions are assumed to be at equilibrium (Mahishi et al., 2007 and Rydén and Ramos, 2012), (3) pressure drops and heat losses are neglected; (4) char is assumed as graphitic carbon (C) (Kannan et al., 2013); and (5) tar formation is neglected (Kannan et al., 2013). The Peng-Robinson equation of state is used to estimate all thermodynamic properties of the conventional components. Figure 1 shows the simulation flowchart of the system. Initial conditions of feedstock and primary parameters in the model are summarized in Table 2. The biomass gasification process is modelled with two reactors. The first reactor is represented by a conversion reactor, RYield (DECOMP), which converts the non-conventional biomass into conventional components including C, O₂, N₂, H₂, sulfur and ASH by specifying the yield distribution according to the feedstock's proximate and ultimate analyses. The yield distribution is specified by FORTRAN statement in the calculator block in ASPEN Plus. The outlet stream from the DECOMP block together with the mixture of steam and particles consisting of solid oxygen carrier (NiO) and CO₂ sorbent (CaO) are sent to the second reactor, RGibbs (GASIFI), which is used to simulate the biomass gasification. In this block, the chemical and phase equilibrium calculations are based on the Gibbs free energy minimization and the main reactions for biomass gasification are shown by Eq(1)-(6). The solid oxygen carrier (NiO) reacts with steam in Eq(7)-(10) and CaO can absorb CO₂ in form of CaCO₃ in Eq(11). A

separator model (CYCLONE-1) is used to separate solids (SOLID-1) and product gas (PRODGAS). Heat in the product gas (PRODGAS) is used to preheat air stream (FEEDAIR). The mixture of solids is fed into the calcination reactor, represented by the RGibbs reactor (CALCIN), where the calcination reaction in Eq(12) occurs in a regeneration process. The calcination reactor is operated at intermediate temperature (880 °C) and the overall reaction is endothermic. The outlet stream is sent to a separator model (CYCLONE-2) to separate solids (SOLID-2) and a pure of CO₂. The solids from the calcination reactor are divided in three parts: the necessary amount of NiO and CaO along with some Ni is extracted and taken to the gasifier reactor (Rydén and Ramos, 2012); the deactivated CaO was accumulated in the system after several cycles so that it is necessary to remove some of the sorbent from the regeneration process and replace it with a make-up flow of fresh CaCO₃ (Grasa et al., 2008); the large solids are sent to the air reactor because the solids circulation between the air reactor and the calcination reactor needs to be the large heat for the regeneration process. Finally, the solids residue is fed into the air reactor, the RGibbs reactor (AIRRECT), operated at high temperature (1000 °C). In this reactor, the oxygen carrier is re-oxidized with air according to the exothermic reaction in Eq(13). The outlet stream is sent to a separator model (CYCLONE-3) which is employed to separate solids (SOLID-3) and N₂ stream where useful heat is recovered for preheating the water stream (WATER). The total amount of solids is recycled to the calcination reactor. Heat is transferred from the air reactor to the calcination reactor via the solid circulation and then all the three reactors could be operated without heating or cooling.

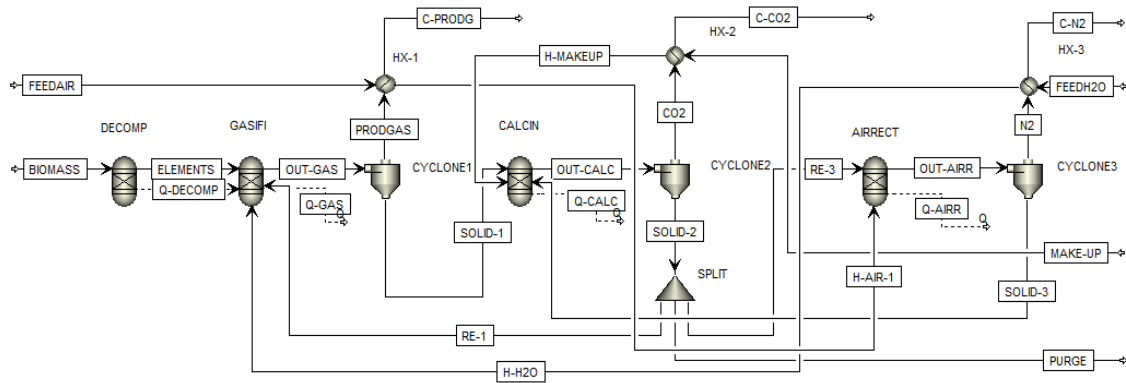
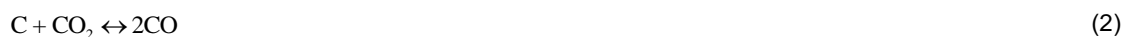


Figure 1 Process flowchart of the sorption enhanced chemical looping biomass gasification for high-purity hydrogen production.

Table 2: Input parameters and operating conditions.

Inlet temperature of feed streams, (°C)	25
Outlet temperature of feed streams, (°C)	35
Operating pressure, (atm)	1
Biomass feed stream, (kg/hr)	1
Gasifier temperature, (°C)	620-750
Calcination temperature, (°C)	880
Air reactor, (°C)	1000
S/C molar ratio, (-)	2.6-4.0
CaO/C molar ratio, (-)	1.0
NiO/C molar ratio, (-)	0.98-1.31
CaCO ₃ make-up ratio, (-)	0.06
Minimum temperature approach, (°C)	10





2.2 Parametric study

In this study, two methods are used to study the effect of the gasifier temperature (T) and steam to carbon molar ratio (S/C) on the energy efficiency (η_{EN}) of the sorption enhanced chemical looping biomass: (1) the intuitive method, which one operating parameter (T or S/C) is varied while keeping the others constant, and (2) the design of the experimental (DOE) method, which two parameters (T and S/C) are changed simultaneously. The energy efficiency is used to evaluate the process performance and can be defined as the ratio of the system energy output to the energy input (Mahishi et al., 2007). The energy input is calculated as the sum of the lower heating values (LHV , kJ/hr) of biomass and energy requirement of the system. The energy output is the LHV of the hydrogen product. The energy efficiency (η_{EN}) is calculated as follows:

$$\eta_{EN} = \frac{m_{\text{H}_2} \times LHV_{\text{H}_2}}{m_{\text{BIOMASS}} \times LHV_{\text{BIOMASS}}} \times 100 \quad (14)$$

The DOE method involves the development of the mathematical model that predicts the relationship between the energy efficiency (η_{EN}) and the operating parameters (T and S/C). Generally, most factorial experiments are developed on the basis of two-level factors with a linear relationship between the parameters for simplicity. However, according to the intuitive method results, the factors appear to have a non-linear relationship with the energy efficiency. Therefore, a central composite design (CCD) of orthogonal type is employed in this study. The corresponding response surface model (RS-model), known as a regression or an empirical equation, represents a second-order polynomial approximation of experimental data and is stated by the following relationship (Eq(15)) (Hajjaji et al., 2014; Meryemoğlu et al., 2014).

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{12} X_1 X_2 \quad (15)$$

where Y is the predicted response (the energy efficiency, η_{EN}), β_i is the regression coefficient, and X_1 and X_2 are the coded variables for T and S/C , respectively. The number of experiments required to establish this model, via the CCD method, is $N = 2k + 2k + 1$. For $k = 2$ (two variables, T and S/C), $N = 9$, and 9 experiments are required.

3. Results and discussion

3.1 The intuitive method

Figure 2a shows the effect of the gasifier temperature (T) on the energy efficiency performance of the sorption enhanced chemical looping biomass gasification. The energy efficiency of the biomass gasification decreases with the increasing temperature. At lower temperatures, the equilibrium of the exothermic carbonation (Eq(7)) and water gas-shift (WGS) (Eq(4)) reactions is shifted forward to increase hydrogen production and thereby, increasing the energy efficiency of the system. The effect of steam to carbon molar ratio (S/C) on the energy efficiency performance of the system is presented in Figure 3. Generally, the addition of steam shifts the equilibrium of the WGS reaction (Eq(4)) toward the hydrogen production. However, it can be seen from Figure 2b that increasing the S/C ratio decreases the amount of H_2 produced and energy efficiency of the system because the excess water causes an increase in the heat requirement for heating and vaporizing the feed stream. High heat required for the gasification reactions leads to an increase in the oxygen carrier or NiO,

compared with the amount of H₂ produced. Thus, a significant decrease in the energy efficiency of the system is observed.

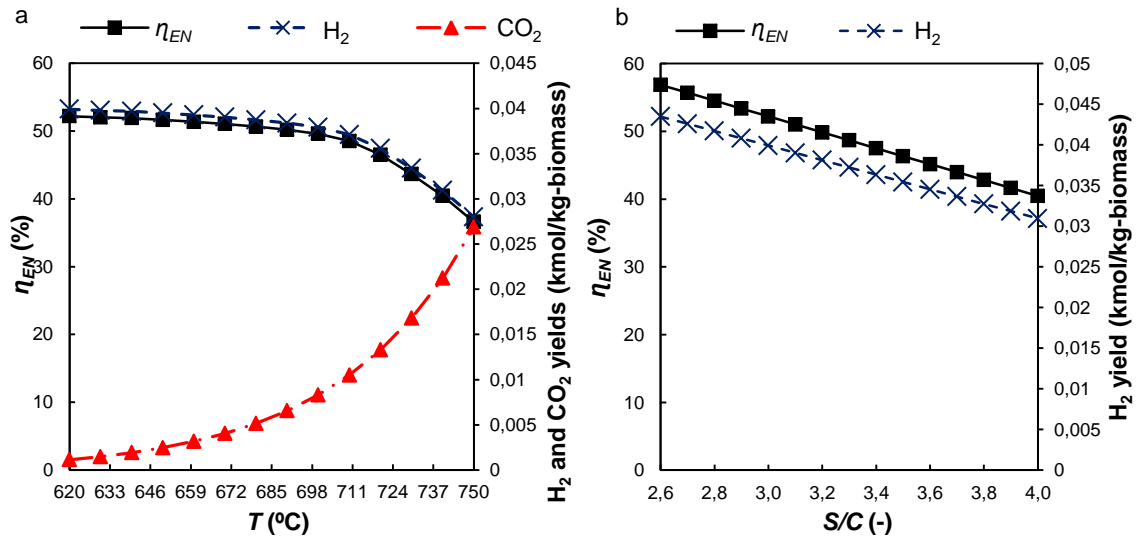


Figure 2 The effect of (a) the gasifier temperature (T) and (b) steam to carbon molar ratio (S/C) on the energy efficiency of the sorption enhanced chemical looping biomass gasification.

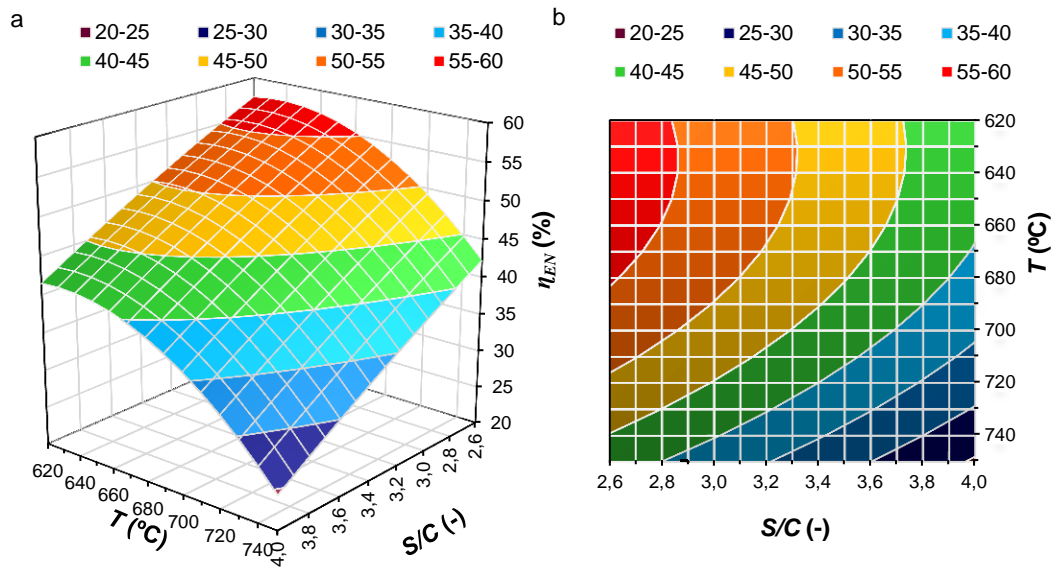


Figure 3 The effects of steam to carbon molar ratio (S/C) and the gasifier temperature (T) on the energy efficiency performance of the sorption enhanced chemical looping biomass gasification for high-purity hydrogen production (a) response surfaces plot and (b) contour-surfaces map.

3.2 The design of the experimental (DOE) method

The operating region and correspondence between the actual and coded values of the design variables are given in Table 3. The second-order RS-model with coded variables obtained for the energy efficiency of the system is given by Eq(16). The results of response surface and contour surface are illustrated in Figure 3. It is noted that the interpretations of the DOE results are similar to the results of the intuitive method. The energy efficiency of the sorption enhanced chemical looping biomass gasification increases with decreasing the gasifier temperature (T) and steam to carbon molar ratio (S/C). In Eq(16), the maximum energy efficiency of the gasification process is 57.67% at the operating condition $S/C = 2.6$ and $T = 636$ °C and the corresponding hydrogen production is 0.044 kmol/kg-biomass.

$$\eta_{EN} = 470.071 - 84.013X_1 - 80.526X_2 - 5.972X_1^2 - 50.341X_2^2 - 4.706X_1X_2 \quad (16)$$

Table 3: Correspondence between the actual and coded values of the design variables.

	S/C	T (°C)
X_i^{-1}	2.6	620
X_i^0	3.3	685
X_i^{+1}	4.0	750
X_i	$(S/C-3.3)/0.7$	$(T-685)/35$

4. Conclusions

Modeling of the sorption enhanced chemical looping biomass gasification for high-purity hydrogen production consisting of gasifier, calcination, and air reactors, is performed using ASPEN Plus process simulator. A mixture of particles consisting of solid oxygen carrier (NiO) and CO₂ sorbent (CaO) is used as bed material. The parametric analyses (using the intuitive and DOE-based methods) indicate that the energy efficiency depends on the steam to carbon molar ratio (S/C) and the gasifier temperature (T). Based on the developed second-order response surface model, the maximum efficiency of the sorption enhanced chemical looping biomass gasification is 57.67% with the hydrogen production of 0.044 kmol/kg-biomass at the operating conditions S/C = 2.6 and T = 636 °C.

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