

Hydrogen Production by Coal Gasification Coupled with *in Situ* CO₂ Capture

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ABSTRACT

CO₂ adsorption enhanced gasification process is a prospective technology to be used in hydrogen production with nearly zero CO₂ emission. In this paper, a gasification kinetics steady state model is developed based on the chemical kinetics mechanism with the condition of fluidization. It is used to predict the parameters of gas phase and solid phase for a continuous flow reactor with steady state. The variation of components distribution with gasification temperature and pressure are determined, from which the optimal operation parameters of gasifier can be obtained.

Keywords: Kinetics Modeling; Gasification Temperature and Pressure; Products Compositions; Conversion Ratio

1. Introduction

 CO_2 adsorption enhanced gasification processes [1,2] apply the concept of one step hydrogen production with in situ CO_2 capture. Coal is gasified with steam and calcium based compounds in the absence of O_2 . The gasification reaction is coupled with carbonation reaction by mass and heat exchange. In these processes, hydrogen molar fraction in syngas can be higher than 80%. The remaining part is mainly methane and the content of CO_2 is very low.

Above benefits enable CO₂ adsorption enhanced gasification processes as one prospective technology to be used in hydrogen production with nearly zero CO₂ emission. One of the key point of its research is how to predict the performance of gasification process. Experiment and unit theoretical model are two important ways to make it. Unit theoretical model is especially necessary in the systematic study of coal to energy process. In references [2-8], chemical equilibrium composition of mixture of C/coal with H₂O and CaO is calculated by theoretical model based on Gibbs free energy minimization. The influence of gasification temperature, pressure, ratio of CaO/C and steam/C is investigated. The thermodynamic equilibrium model offers greater flexibility for complex reaction system with limited given conditions for which the reaction pathways are unclear. Usually some correction factors, such as temperature approach, carbon conversion ratio, are applied to improve predicttion precisions [8-11]. But in realistic condition, product distributions and conversion ratios of carbon and CaO depend on chemical kinetics and hydrokinetics, which is

determined by reaction temperature, pressure and other factors. As a supplement of previous study, it is necessary to investigate gasification performance from the point of view of chemical kinetics and fluid hydrodynamic. Kinetics models have the advantage to directly illustrate the effect of pressure, temperature, reactants compositions and other parameters on product distributions and reactants conversion ratios. A dynamic simulation model of CO2 adsorption enhanced gasification processes is established in reference [12]. It is used to study the influences of reaction conditions on the proportion of the reactants. However, there are some drawbacks of kinetics model. Prediction precision is highly dependent on the kinetics parameters, which are usually measured and deduced from experiments that conducted under some specific conditions (e.g. coal rank, reactor type and operation conditions, etc.). So deviation of simulation assumptions from experiment conditions will lead to prediction errors. Furthermore, more inputs and more detailed feed streams characteristics are required when kinetics models are applied.

Comparing with previous work, some changes about gasifier modeling can be made as follows. 1) Because the variation of solid compositions and flow rate are not taken into account in the dynamic model developed in reference, it is necessary to set up mass and energy conservation equations of solid phase, which is required when analyzing the mass and heat interaction between syngas production section with regenerator and other parts; 2) The results calculated from dynamic model vary with reaction time, which make it difficult to be used in

steady state systematic performance analysis. A steady state gasifier model based on the kinetics mechanism and with the condition of fluidization should be set up.

Summarily, in this paper, a steady state gasifier model is developed based on kinetics mechanism and with the condition of fluidization. It is used to predict parameters of gas phase and solid phase of a continuous flow reactor at steady state. The variations of components distributions with gasification temperature and pressure are determined, from which the optimal operation parameters of gasifier can be obtained.

2. H₂ Rich Syngas Production with CO₂ Sorption Enhanced Coal Gasification

As shown in Figure 1, CO₂ adsorption enhanced coal gasification is divided into two reactors, namely a syngas production reactor (SPR) with CO₂ sorption and a absorbent regeneration reactor (RER). The mass and heat flux are transferred by recycling solid particles. In SPR, carbon contained feedstock reacts with steam and calcium compound. Pyrolysis reaction, gasification reaction and carbonation reaction are integrated into SPR. Carbon is converted to syngas and meanwhile, CO2 released from gasification reactions is absorbed by calcium based absorbent. Syngas is composed of H₂ with 60% - 95% molar fraction and methane with 5% - 40% molar fraction. CO₂ and CO content can be lower than 1%. Calcium carbonate produced together with ash, unconverted carbon and CaO are discharged to the regenerator to be calcined in the atmosphere of H₂O and CO₂. CaO regenerated is recycled to SPR. CO₂ from calcinations is released at nearly pure state, which make its possible to capture with relatively lower cost. In the above process, high temperature particles feeding to SPR are not only act as absorbent, but also as heat carrier to provide heat for endothermal reactions.

The production of syngas in SPR can be explained by the following reactions:

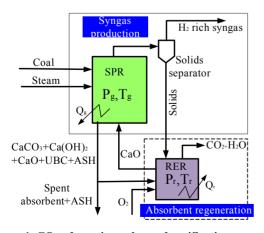


Figure 1. CO₂ adsorption enhanced gasification process.

$$\begin{split} &C(s) + H_2O(g) \leftrightarrow CO(g) + H_2(g) + Q \\ &C(s) + CO_2(g) \leftrightarrow 2CO(g) + Q \\ &C(s) + 2H_2(g) \leftrightarrow CH_4(g) - Q \\ &CO(g) + H_2O(g) \leftrightarrow CO_2(g) + H_2(g) - Q \\ &CH_4(g) + H_2O(g) \leftrightarrow CO(g) + 3H_2(g) + Q \\ &CaO(s) + CO_2(g) \leftrightarrow CaCO_3(s) - Q \\ &CaO(s) + H_2O(g) \leftrightarrow Ca(OH)_2(s) - Q \end{split}$$

3. Performance Prediction Model of CO₂ Adsorption Enhanced Coal Gasifier

3.1. Coal Properties and Model Assumptions

Shen-mu coal is used as the feedstock of systems analyzed in this paper. It contains 65.2% C, 4.63% H (ultimate analysis, daf basis) and 54.8% fixed carbon, 28.15% volatile (proximate analysis, daf basis).

The following are some assumptions and limitations of the model: 1) It is assumed that the coal conversion process can be divided into a pyrolysis zone and a gasification zone. Devolatilization is completed instantaneously and then products from coal pyrolysis including volatile and char react with steam and CaO in gasification section; 2) Solid phase is treated as continuous stirred flow; 3) Solid components including char, ash, calcium compound, are distributed homogenously in the reactor; 4) Gas phase is composed of H₂, CH₄, CO₂, CO, H₂O, H₂S, N₂ and treated as plug flow; 5) Gas components are assumed to be functions of the height of gasification section; 6) Temperature is homogeneous in the syngas production reactor (SPR). Ca(OH)₂ is not included in reaction system; 7) Surplus heat generated in reactor is removed by steam generation.

3.2. Mass Balance of Syngas Production Reactor

During pyrolysis process, coal is converted into volatile and char instantaneously after it is fed to the furnace. Volatiles are assumed to be composed of CH₄, CO, CO₂, H₂, H₂O, N₂ and H₂S. According to the prediction method in reference [13], mass fractions of coal pyrolysis products are calculated.

The input parameters for gasification section include: flow rates, compositions of pyrolysis products, appointed gasification temperature (or Q_{ST} : appointed heat exchanged with cooling agent), appointed gasification pressure, appointed steam parameters (flow rate, inlet temperature and pressure), appointed absorbent parameters (inlet temperature, pressure, compositions and flow rate). Output parameters include: conversion ratios of char (X_{char}) and CaO (X_{CaO}), coal to H₂ efficiency, cold gas efficiency, gases distributions along height of reactor, calculated compositions and flow rates of bed materials and discharged solid, calculated yield and composition of

hydrogen rich syngas, calculated Q_{ST} (or calculated operation temperature).

3.2.1. Mass Balance of Solid Phase in Gasification Zone

$$X_{char} = 1 - \left(G_{slag} + G_{ent}\right) W_{char,bed} / G_{char,in} \tag{1}$$

$$X_{\text{CaO}} = 1 - \left(G_{slag} + G_{ent}\right) W_{\text{CaO},bed} / G_{\text{CaO},in}$$
 (2)

$$G_{char.in} = \left(G_{slag} + G_{ent}\right) W_{char.bed} + R_{s-g} \tag{3}$$

$$G_{\text{CaO},in} = \left(G_{slag} + G_{ent}\right) W_{\text{CaO},bed} + R_{\text{CaO-CO}}, \tag{4}$$

$$G_{\text{CaCO}_3,in} = \left(G_{slag} + G_{ent}\right) W_{\text{CaCO}_3,bed} - \frac{R_{\text{CaO-CO}_2}}{\mu_{\text{CaO}}} \mu_{\text{CaCO}_3}$$
 (5)

$$G_{ash,in} = (G_{slag} + G_{ent})W_{ash,bed}$$
 (6)

$$W_{\text{CaO},bed} + W_{\text{CaCO}_3,bed} + W_{char,bed} + W_{ash,bed} = 1$$
 (7)

Equations about solids phase in gasification section are composed of definitions of conversion ratio of char and CaO, components (char, ash, CaCO₃, CaO) mass balance, mass balance of bed materials. Where, Symbol X_{char} and X_{CaO} means conversion ratio of char and CaO respective. Symbols G means mass flow rate. Symbol $W_{i,j}$ means mass fraction of component i contained in control volume j, j = bed, ent, slag. Symbols bed, ent and slag mean bed material, entrained solid in raw hydrogen rich syngas and slag respectively. Symbol R means chemical reaction rate. It is assumed that compositions of solid entrained in raw syngas stream and discharged as slag are of the same compositions with that of bed material.

3.2.2. Mass Balance of Gas Phase in Gasification Zone

Along the direction of gasification reactor height L, reaction zone is divided into numbers of cells in which mass balance for each gas components is set up. In each cell, the mass balance of component i is expressed as:

$$PY_i = f\left(P, \tilde{Y}_i, \tilde{Y}, R_{\text{CaO}-g_i}, R_{char-g_i}, \sum R_{g_i-g_i}\right)$$

One specific gas flow rate is determined by its flow rate and chemical reaction rates with other gases and solids, where symbols P, T are the total pressure and temperature of SPR section. \tilde{Y} is the molar fraction vector of gases. R_{i-j} means reaction rate of reaction between component j and i. Symbols g and s mean gas phase and solid phase respectively.

3.2.3. Chemical Kinetics Rates in Gasification Zone

$$\begin{split} R_{char-gi} &= \int_{0}^{L} \left[f_{char-g_i} \left(G_{char,in}, G_{bed}, W_{char,bed}, X_{char}, P, \tilde{Y}, T \right) \right. \\ \\ R_{g_j-g_i} &= f_{g_j-g_i} \left(P, \tilde{Y}, T \right) \right] \end{split}$$

$$R_{\text{CaO-CO}_2} = \int_{0}^{L} f_{\text{CaO-CO}_2} \left(G_{\text{CaO},in}, G_{bed}, W_{\text{CaO},bed}, X_{\text{CaO}}, P, \tilde{Y}, T \right)$$

Chemical kinetics rates of gas-solid reactions, gas-gas reactions are determined by reaction temperature, total pressure, molar fractions of gases, solid contents, and hydrodynamic parameters, where *f* is a function of several variables. It stands for reaction rate and the definition can be found in references [14-16].

3.3. Energy Balance of Syngas Production Process (Pyrolysis Zone + Gasification Zone)

Pyrolysis sub-reactor and gasification sub-reactor are put together to model energy balance. At given input parameters (steam and absorbent flow rates, gasification pressure, reactor heat loss, and appointed gasification temperature/or appointed heat Q_{ST} transferred with heating/cooling medium), the result of heat Q_{ST} or gasification temperature can be calculated. Enthalpies of components are defined according to reference [17].

3.4. Model Solution Methodology

Figure 2 shows the simulation procedure of SPR. Its main inputs are coal properties, ratio of CaO to coal, ratio of steam to coal, reaction pressure, reaction temperature (or heat exchanged with medium), reactor parameters (height, superficial velocity, bed materials loading). Outputs include gas compositions and yields, solid phase compositions, discharged solid, solid entrained by gas, heat exchanged with medium (or temperature). Carbon conversion ratio, CaO conversion ratio and gas compositions distributions along height of reactor are estimated and determined by iteration procedure.

3.5. Comparison with Experimental Results

In **Tables 2(a)-(b)**, calculation results based on model described above and data of experiment and demonstration plant are compared. In **Table 1(a)**, running results of commercial Winkler gasifier and U-gas demonstration fluidized bed are collected from reference [10]. In **Table 2(b)**, experimental data are got from a continuous experiment high pressure reactor [18] fed by Taiheiyo coal. Reaction temperature is set at 650°C. The description of test rigs and more detailed experiment results can be found in references.

Table 2(a) shows the percentage deviations of H₂ and CO compositions between computed and experimental gas compositions are less than 20%. In **Table 2(b)**, it can be seen that the variation tendencies of gas molar fraction with temperature are coincident with that of experiment. The maximal prediction error of H₂ molar fraction is 6.6%. But prediction errors of CO₂, CO and CH4 molar fractions are quite high. In **Table 2(b)**, it is found that the

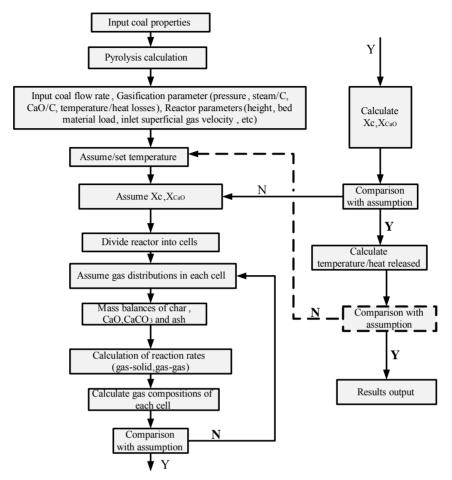


Figure 2. Model solution methodology.

Table 1. Properties of Shen-mu coal.

		(a)				
	Proximate analysis (w%, ad)					
M	A	V	FC	(kJ/kg)		
4.48	12.57	28.15	54.8	27860		
		(b)				
	Ultimate analysis (w%, ad)					
С	Н	О	N	S		
65.2	4.63	12.01	0.89	0.22		

prediction results of H_2 compositions are near to that of experiment. But the methane molar fraction shows different variation trend with pressure. This maybe result by that, in flow type reactor, the product gases leave the bed quickly. The generation rate of methane by reaction C^+ $2H^{2-} \rightarrow CH_4$ is not evident. But in theoretical model, this reaction rate is considered to be direct proportion to pressure. And methane shortcut is not considered in theoretical model.

The comparison results show that the H₂ molar frac-

tion predicted by theoretical model is near to that of experiment and pilot plant. Theoretical model can be applied in system study. But it should be improved to increase prediction precision of CO₂, CO and methane. More factors should be considered to improve the model prediction precision, including the use of improved semi-experiential parameters of devolatilization model, to adopt comprehensive hydrodynamic model, more detailed consideration about residue time and shortcut gas, and to improve semi-experiment parameters of chemical kinetics model, etc.

4. Influence of Temperature and Pressure on Syngas Production Process

4.1. Performance Indicators and Definitions

Coal to hydrogen efficiency $(X_{coal-eg})$, Char conversion ratio (X_{char}) and Caladium conversion ratio (X_{CaO}) are used to evaluate gasification performance. Coal to hydrogen efficiency $(X_{coal-eg})$ is defined as that given in reference [2]. Char conversion ratio (X_{char}) means the char converted to syngas to carbon contained in feedstock. Caladium conversion ratio (X_{CaO}) is the ratio of the

Table 2. (a) Comparison between fluidized gasification [11]; (b) Comparison with experiment results of reference [18].

	(a)	
Molar fraction	7	Winkler-UR lignit	te
(dry basis, %)	Е	С	Error %
H_2	35.3	38.93	10
CO_2	13.3	11.47	14
CO	48.2	42.80	11
$\mathrm{CH_4}$	1.8	5.63	213
N_2	0.9	0.90	0.00
Xc, %	57-88	70.80	

Molar fraction		UGAS-washed	
(dry basis, %)	E	С	Error %
H_2	42.2	43.24	2.5
CO_2	28.6	23.39	18.2
CO	25.6	29.63	15.8
$\mathrm{CH_4}$	2.9	2.28	21.1
N_2	0.6	0.55	8.3
Xc, %	89.7	98.	9.9

 $E\hbox{: Experimental results; C: simulation results; Xc: carbon conversion ratio.}\\$

(b)

	P = 1 MPa		P = 3 MPa	
	Е	C	Е	С
H ₂	58	59	76	75
CO_2	5	5	2	5
CO	7	21	0	4
$\mathrm{CH_4}$	23	14	17	15
$C_2H_6 + C_2H_4$	7		5	

	P = 5 MPa		P = 6 MPa	
_	Е	С	Е	С
H_2	76	78	77	79
CO_2	2	3	2	3
CO	0	1	0	1
$\mathrm{CH_4}$	17	16	16	16
$C_2H_6 + C_2H_4$	5		5	

E: Experimental results; C: simulation results.

amount of caladium in the form of generated calcium carbonate to total amount of CaO input.

With chemical kinetics model proposed in Section 3.2.3, the effect of temperature and pressure on gasifier

performance can be plotted. Results are shown in **Figures 3-5**, where temperature and pressure are appointed and independent. Variable Q_{ST} is calculated from reactor heat balance. It means the ratio of the extra heat needed for heating or cooling to the coal input thermal energy.

4.2. The Variation of Gas Composition with Temperature, Pressure

Variation of H₂ molar fraction shown in **Figure 3(a)** illustrates that the maximal hydrogen molar fraction around 82% - 84% can be obtained in the temperature range of 675°C - 840°C and pressure range of 1 - 4.5 MPa. The variation of H₂ molar fraction is relatively small in the above ranges. In the region of temperature greater than 850°C and pressure lower than 0.5 MPa, the H₂ molar fraction is lowest and only around 54% - 56%. Under this operation condition, CO₂ partial pressure is smaller than CO₂ equilibrium pressure and CO₂ can not be captured by absorbent which result in large amounts of CO₂ in that region. Simulation results show that pressure and temperature are important for hydrogen molar fraction. It can be increased greatly with CO₂ captured by CaO with suitable pressure and temperature.

Figures 3(b) and **(c)** are two sectional figures from X and Y directions of **Figure 3(a)** respectively, in which pressure are set to 2.5 MPa and temperature set to 750°C respectively. Sensitive studies show that evaluated by H₂ molar fractions, the optimal operation range of temperature is 700°C to 750°C with pressure varies from 2 to 3 MPa. Based on this result, pressure is set to 2.5 MPa in **Figure 3(b)** with temperature varies from 600°C - 1050°C.

At a given pressure and evaluated by kinetics, the reaction rates are speed up with the increase of reaction temperature. However, from the point of view of thermodynamic equilibrium, increase temperature is disadvantage to exdothermal reactions, e.g. CO conversion by shift reaction and CO₂ capture by carbonation reaction. Thus there should be a trade-off between these factors. At temperature of 750°C, the maximum H₂ molar fraction can be achieved. At lower temperature, CO₂ partial pressure is higher than its equilibrium pressure and CO₂ can be captured by CaO continuously. CO2 content decreases with temperature increase and at temperature 700°C, the CO₂ content is the lowest. If temperature increases further, the differences between CO₂ partial pressure and equilibrium pressure decline and the ability for CaO to absorb CO₂ declines. With temperature higher than 950°C, carbonation reaction stops because of higher CO₂ equilibrium pressure. As shown in **Figure 3(c)**, similar to the influence of temperature, there is an optimal pressure at which H₂ content is highest. Methane

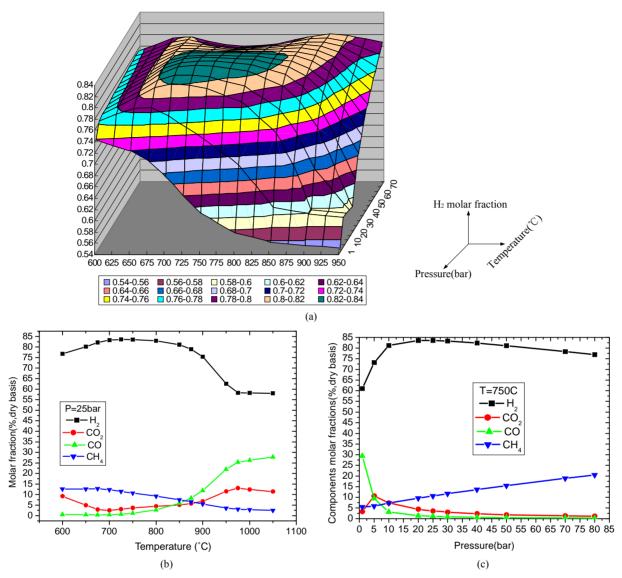


Figure 3. Gas compositions variations with temperature and pressure. (a) Effect of temperature and pressure on H_2 molar fraction; (b) With temperature; (c) With pressure.

molar fraction will increase with pressure. At pressure lower than 0.5 MPa, carbonation reaction can not proceed because of low CO_2 partial pressure. CO_2 content increases with pressure in this range. At pressure higher than 0.5 MPa, carbonation reaction plays an important role on syngas compositions. CO_2 and CO contents decline quickly with pressure. At pressure higher than 5 MPa, the contents of CO_2 and CO are very low and their variations are small.

The influences of CaO activity on syngas compositions are also investigated. Results show that with CaO activity decline from 100% to zero, H_2 molar fraction decreases from 80% to 57% and the CO_2 molar fraction increases from around 1% to 22%. Thus to maintain high CaO activity is important to suppress CO_2 concentration in syngas.

4.3. Influence of Temperature and Pressure on Solid Compositions

Figure 4 gives the solid compositions variation with pressure and temperature. With the given pressure of 2.5 MPa and temperature in the range of 850°C - 875°C, the CaCO₃ weight fraction in solid is the highest as shown in **Figure 4(a)**. Corresponding, the CaO mass fraction is the lowest. With temperature lower than 600°C or higher than 950°C, the rate of carbonation reaction is very slow and nearly closes to zero, there is almost no CaCO₃ in solid. Carbon conversion is speed up with the increase of temperature. At temperature higher than 950°C, almost all carbon is converted to syngas. With the given temperature of 750°C, CaO conversion ratio increases with pressure as shown in **Figure 4(b)**. But at pressure higher

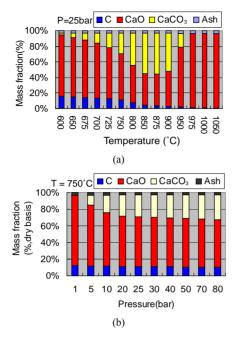


Figure 4. Solid compositions variations with temperature and pressure. (a) With temperature; (b) With pressure.

than 4 MPa, mass fractions of CaO and CaCO $_3$ vary slightly. Comparing to temperature, the effect of pressure on carbon conversion ratio is less important than that of temperature. At ambient pressure, there is no CaCO $_3$ due to no CaO reacts with CO $_2$.

4.4. Coal to H₂ Efficiency and CaO Conversion Ratio Variation with Temperature and Pressure

Figure 5(a) shows the effect of temperature and pressure on coal to H_2 efficiency. It can be seen when the temperature is lower than 850°C, coal to H_2 efficiency can be increased evidently with temperature increase. The optimum operation range for pressure is 1 - 4.5 MPa when temperature is varied from 750°C to 840°C. For a given temperature, there exists a pressure at which coal to H_2 efficiency is the highest.

As plotted in **Figure 5(b)**, the carbonation reaction procedure is benefit with the increase of pressure, especially at higher temperature. With pressure higher than 2 MPa and temperature lower than 800°C, the influence of pressure on CaO conversion ratio is not obvious. For a given pressure, there is an optimal temperature at which the CaO conversion ratio is the highest and the optimal temperature increases with pressure. The simulated results agree well with reference [2].

5. Conclusions

This paper presents a new approach for hydrogen and power co-production. It is based on coal gasification with

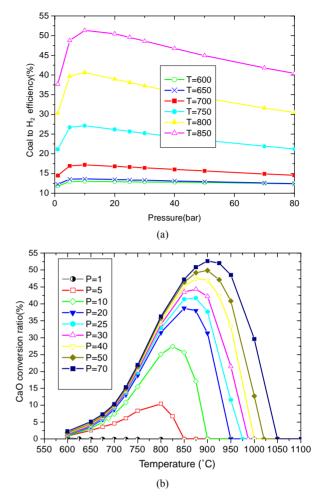


Figure 5. Effect of temperature and pressure on conversion ratio. (a) Coal to H₂ efficiency; (b) CaO conversion ratio.

in situ CO₂ capture. The influences of plant configuration and gasification operation parameters (temperature and pressure) on the performance of SPR process are invest-tigated. From analysis, it shows that:

- With the operation temperature in the range of 675°C to 840°C and pressure in the range of 1 MPa to 4.5 MPa, the highest hydrogen molar fraction, i.e. 82% 84%, can be obtained and the variation of H₂ molar fraction is relatively mild in the process. With the given pressure of 2.5 MPa and temperature in the range of 850°C 875°C, the CaCO₃ weight fraction in solid is the highest.
- For a given temperature, there exists a pressure at which coal to H₂ efficiency is the highest. The optimum operation range for pressure is 1 MPa to 4.5 MPa when temperature is varied from 750°C to 840°C. For a given pressure, there is an optimal temperature at which the CaO conversion ratio is the highest and the optimal temperature increases with pressure.
- More related factors should be included to improve the model precision and to improve the feasibility of

the proposed technique, including more detailed hydrodynamic modeling, consideration of the influence of absorbent cyclic characteristics and eutectic problem of calcium based compounds, etc.

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