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Catalytic Coal Gasification Process Simulation with Alkaline Organic Wastewater in a Fluidized Bed Reactor Using Aspen Plus

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Abstract: A co-gasification process was proposed both for treating alkaline organic wastewater and to promote coal gasification by the alkaline substances in situ. A catalytic gasification model was developed by introducing a catalytic correction factor to describe the catalytic effects quantitatively. An integrated process simulation was carried out using Aspen Plus equipped with FORTRAN subroutines. The model was verified using the root mean square error between the simulation results and experimental data from the literature. Syngas composition, cold gas efficiency, and carbon conversion efficiency were analyzed with respect to different operating conditions (reaction temperature, steam/coal ratio, and equivalence ratio). The optimal conditions are summarized based on a self-sufficient system by using sensitivity analysis: Gasification temperature of 700 °C, steam/coal ratio = 1.0, and equivalence ratio = 0.4.

Keywords: coal; gasification; alkaline organic wastewater; catalytic correction factors; ASPEN PLUS

1. Introduction

The energy crisis and environmental pollution are becoming increasingly serious due to rapid industrialization. In China, large amounts of alkaline organic wastewater are created by the paper-making, chemical, pharmaceutical, and textile industries, as a special source of bioenergy [1], which significantly damages the environment because of the presence of metal ions and complex organic compounds. Hence, how to dispose of this massive volume of wastewater in an environmentally friendly and cost-effective manner is becoming an attractive research issue for scientists.

Some researchers have proposed methods to handle organic wastewater, such as physicochemical, electrical, and biological processes [2]. Incineration is the most common technique for highly toxic organic wastewater with complex compositions, and combustion efficiency is usually 99% [3,4]. Incinerating wastewater containing alkali metal ions and organic compounds leads to agglomeration and coking in the fluidized bed [5,6]. There are two major causes for agglomeration and coking: (i) The alkali metal compounds in wastewater (Na₂CO₃, NaCl, Na₂SO₄, and other sodium-based salts) turn to melted ash because the temperature inside the incinerator is higher than their melting point (melting points of NaCl, Na₂SO₄, and Na₂CO₃ are 801, 884, and 851 °C, respectively). Then, the molten liquid sodium salts flow along with the flue gas, contact the surface of the fluidized bed, and eventually condense to form coke and slag. (ii) The alkali elements in wastewater, particularly Na and K, react with bed materials, and SiO₂ forms sodium silicates, which melt under the high temperature [5].

A process of gasification combined with combustion is proposed in Figure 1 to thoroughly decompose the alkaline organic wastewater and avoid agglomeration. The entire process can be
divided into four stages: (i) Coal and wastewater are mixed to form metal-ion-exchanged coal. (ii) Metal-ion-exchanged coal and wastewater are co-gasified in the fluidized bed, where steam is introduced into the system as a gasifying agent. The gasification temperature must be controlled below the ash melting point. (iii) Separation of the mixed products. (iv) The gaseous products serve as a fuel to undergo further combustion to produce energy and heat, while the fly ash remains static and can be separated and recovered in a solid state.

![Gasification process diagram](image)

**Figure 1.** Gasification combined with combustion process.

Some researchers have established a two-stage system to avoid agglomeration and coking [7,8]. However, they mainly focused on controlling the temperature of the first stage without exploiting the catalytic effects of metal ions in the wastewater.

The catalytic effects of alkali and alkaline earth metallic species on coal gasification have been proved since the 1980s [9–11]. The co-gasification of wastewater and coal has been preliminarily studied, which demonstrated the feasibility of using wastewater as a catalyst for coal gasification. Zhang et al. [12–16] evaluated the performance of black/viscose liquor and organic sodium as the catalyst during anthracite steam gasification at temperatures of 850–950 °C. The experimental results showed the remarkable catalytic effect of alkaline organic wastewater, and the saturation of adding alkali metal compounds is about 8–10 wt%. Wastewater increases surface activity as well as decreases the activation energy of gasification when mixed with coal. Kuang et al. [17,18] investigated the catalytic gasification of a coal black liquor slurry (CBLS) and found that many mesopores and micropores exist on the surface of CBLS coke, which play a crucial role in catalytic gasification. Beyond the catalytic function of alkali metals, the lignin and cellulose contained in the wastewater also enhance the heat value of the syngas. However, previous researches mainly focused on the catalytic effect of alkali metals at temperatures >800 °C, which deviates from the gasification temperature required by our proposed process. Efforts should be made to expand studies of gasification characteristics in a relatively low temperature range.
ASPEN PLUS has been used to simulate the gasification process of different raw materials, such as coal, biomass, and solid waste, in different reactors (fixed bed/fluidized bed/entrained-flow bed) for the past decade [19–24]. There are two ways for the simulation of coal gasification in a fluidized bed to occur, i.e., the equilibrium method and the kinetic method. The equilibrium models mainly use the RYield and RGibbs modules to describe the pyrolysis and gasification process [21], while kinetic models adopt RCSTR to represent the fluidized bed [22]. The equilibrium model is more accurate when applied to complete equilibrium states and is more suitable to describe equilibrium of the gasification reaction, especially when the gasification temperature is relatively high. The kinetic model is much more complex and relies on experimental data, but is more precise and adaptable than the equilibrium model. Jorge et al. [25] and Che et al. [26] simulated biomass and coal co-gasification in a fluidized bed at temperatures of 700–900 °C. The results showed that the simulation results were highly accurate with a maximum deviation of about 7.23%. Accuracy was favored by gasification temperatures >800 °C. In particular, a catalytic coal gasification model was developed by Jang et al. who added catalytic effects of K$_2$CO$_3$ to a fixed bed model, where kinetic values were calculated from the experimental data, and the maximum error of the syngas component was 6% [27]. However, few literature can be found in regard to the simulation of co-gasification of coal and wastewater with catalytic effects in a fluidized bed.

The objective of our study was to develop a catalytic gasification model of coal and alkaline organic wastewater in a fluidized bed using Aspen Plus. We used the model to clarify the effects of operating parameters including gasification temperature, the steam/coal (S/C) ratio, and equivalence ratio (ER) on carbon conversion efficiency, gas yield, and composition. An energy analysis based on sensitivity was conducted to obtain optimal operation conditions.

2. Method Description

2.1. Process Assumptions

The following assumptions were applied to the comprehensive model:

- Gasification temperature remains stable.
- The raw material particles are mixed with the gasifying agents in the furnace quickly and uniformly.
- H, O, N, and S in the coal all changed into the gas phase, and C was assumed to be incompletely transformed according to the reaction.
- The char contains only fixed carbon and ash.
- Ash in coal is inert and does not participate in chemical reactions.
- The syngas consists of H$_2$, CO, CO$_2$, CH$_4$, H$_2$O, N$_2$, and C$_6$H$_6$.
- The fluidized bed was divided into dense and dilute phases.
- The composition of the gas phase under the simulation conditions is regarded as an ideal gas, and it is applicable to the physical properties, methods, and models in the software.
- The catalytic effect was introduced into the gasification model of the fluidized bed using a correction factor.

2.2. Reactions

The following reactions (1)–(7) were considered during the pyrolysis, char gasification, and combustion processes and all the reaction rates are shown in Table 1 [28].

Pyrolysis:

\[
\text{Coal} \rightarrow \text{CO} + \text{H}_2 + \text{CO}_2 + \text{H}_2\text{O} + \text{H}_2\text{S} + \text{N}_2 + \text{CH}_4 + \text{C}_6\text{H}_6 + \text{Char}
\]  

Solid-gas reactions:

\[
\text{C} + \frac{Z + 2}{2Z + 2} \text{O}_2 \rightarrow \frac{Z}{Z + 1} \text{CO} + \frac{1}{Z + 1} \text{CO}_2
\]
C + H₂O → CO + H₂ (3)
C + CO₂ → 2CO (4)
C + 2H₂ → CH₄ (5)
CO + H₂O → CO₂ + H₂ (6)
H₂ + 0.5O₂ → H₂O (7)

Table 1. Reaction rates for reactions (2)–(7) [28].

| Reaction | Reaction Rate | Remarks |
|----------|--------------|---------|
| 2 | \[ \frac{P_{O_2}}{k_{film} + k_{ash}} \] | \[ k_{film} = 0.0292 \times 4.26 \times \left( \frac{T}{1800} \right)^{1.75} \] |
| 3 | \[ 930 \times e^{-\frac{4400}{T_{H_2O}}} \times [C] \times (P_{H_2O} - P'_{H_2O}) \] | \[ k_{ash} = k_{film}^{2.5} \] |
| 4 | \[ 930 \times e^{-\frac{4400}{T_{CO_2}}} \times [C] \times (P_{CO_2} - P'_{CO_2}) \] | \[ P'_{H_2O} = \frac{P_{H_2O}}{P_{CO_2}} \] |
| 5 | \[ e^{-7.087 - \frac{35000}{T_H_2}} \times [C] \times (P_{H_2} - P'_{H_2}) \] | \[ P'_{CO_2} = \frac{P_{CO_2}}{P_{H_2O}} \] |
| 6 | \[ F_w \times 2.877 \times 10^5 \times e^{-\frac{7270}{T_{H_2O}}} \times \left( x_{CO}x_{H_2O} - \frac{x_{CO_2}x_{H_2}}{k_{wgs}} \right) \times P^{0.5} \times e^{-8.91 + \frac{5860}{P}} \] | \[ k_{wgs} = e^{-3.689 + \frac{724}{T_{H_2O}}} \] |
| 7 | \[ 8.83 \times 10^5 \times e^{-\frac{6350}{T_{H_2O}}} \times \sqrt{C_H_2 \times C_{O_2}} \] | \[ P'_{H_2} = \left( \frac{P_{H_2}}{P_{CO_2}} \right)^{0.5} \] |

2.3. Process Modeling

Based on the above hypothesis, a mixed air-stream gasification model was established in the fluidized bed (Figure 2). The model consists of nine unit operation modules and seventeen material streams. A brief introduction to the model is given in Table 2.

![Flowsheet of the gasification process in Aspen Plus.](image-url)
Table 2. Block descriptions.

| Block Name   | Block Description                                      |
|--------------|--------------------------------------------------------|
| DRYER        | RYield Simulate coal drying based on the water content value in proximate analysis of coal |
| PYROLYS      | RYield Simulate coal pyrolysis based on pyrolysis experiment |
| CHAR-DEC     | RStoic Decompose char into C, H₂, O₂, N₂, S, and ash |
| GASIFI-1/2   | RCSTR Simulate char gasification                        |
| MX           | MIXER Mix the feed-in streams                           |
| SEP          | SEP Separate the gas and solid                          |

2.3.1. Component Definitions and Method

In the global setting, we set the streams and defined the component parameters and physical properties. All components involved in the coal gasification process were divided into conventional components and non-conventional components (NC). Conventional components refer to conventional chemical compounds with definite molecular formulas, such as O₂, N₂, H₂, CO, CH₄, and CO₂. The physical properties of the conventional components were specified directly through the physical database of the Aspen Plus system, whereas the non-conventional components, such as coal, could not be defined by the system’s database. The char and ash generated in the reactions were defined as NC components. NC components was never involved in the calculation of phase equilibrium and chemical equilibrium during the simulation, and they worked as inert substances [29]. Thus, it was necessary to use the HCOALGEN and DCOALIGT models to calculate their density and enthalpy based on proximate and ultimate analyses.

The choice of physical properties affects the accuracy of the simulation results. Property methods, such as RKS-BM, RK-SOAVE, or PR-BM, are selected when gasification occurs at high temperature, high pressure, and the components consist mostly of light gas. The IDEAL property method can be considered when the gas components are H₂O, N₂, and O₂ on a low-pressure condition [29]. This study used RK-SOAVE to calculate the physical properties of the components in the simulation.

2.3.2. Process Description

We selected the appropriate blocks and established the process flow (Figure 2). The full-flow reactor (RCSTR) was selected as the key fluidized bed gasification reactor model, as it can handle both equilibrium and kinetic control reactions simultaneously [30]. The entire coal gasification process consisted of drying, pyrolysis, decomposition of the char and gasification.

1. Drying: A stream of coal, with a mass flow, was fed into the DRYER reactor in which the physical moisture bound was released completely into the gas phase. The amount of vaporized water was determined by the proximate analysis of the coal. We assumed that coal drying was instantaneous compared with that of the coal gasification process. Water content for the specific coal we used was set to x%, according to the proximate analysis. As a result the yield of dried coal was set to 1 – x%. The output was separated by a gas–solids separator called SEP-1.

2. Pyrolysis: The output of the drying process was called DRY-COAL, whereafter it entered the PYROLYS block. Pyrolysis is a complex thermochemical process that occurs during coal gasification which is difficult to simulate accurately using the database of Aspen Plus. Two ways are available to simulate coal pyrolysis. One is based on experiments and the other is to use functional group models based on a theoretical method [19]. Using experimental results will be simpler compared with using a functional group. Thus, the pyrolysis experimental data for a specific coal species was used to specify every component of the PYROLYS block. In this block, dried coal was broken down into CO, H₂, CH₄, CO₂, N₂, H₂O, C₆H₆, and char. The gas–solids separator SEP-2 block separated the upstream product into two streams, namely CHAR and PYRO-GAS. This reaction was also considered instantaneous.

3. Decomposition: CHAR was downstream of the CHAR-DEC block. CHAR, as a NC component, must be transformed to participate in the gasification reaction. In this study, block RStoic was
chosen to simulate the decomposition process. CHAR was decomposed into C, H₂, O₂, N₂, S, and ash for the solid–gas reactions. The stoichiometric coefficients of the elements mentioned above were determined automatically according to char’s ultimate analysis in the CALCULATOR block. The output was separated by the gas–solids separator SEP-3 block into two streams of CHAR-GAS (including H₂, O₂, and N₂) and CHAR-SLD.

4) Gasification: The air, steam and the stream CHAR-GAS gaseous products, were mixed in MIX-GASIN. Then, the stream CHAR-SLD together with MIX-GASIN and the stream PYRO-GAS from the upper block PYROLYS was reacted in the RCSTR reactor, named as block GASIF-1/2. We used two RCSTR reactors to simulate the dense and the dilute regions of the fluidized bed. The uncatalyzed kinetic parameters are shown in Table 1, which were written in an external FORTRAN subroutine and was linked to the simulation. The gaseous outputs were mainly CO₂, CO, H₂, CH₄, and C₆H₆.

5) Catalytic effects: In fact, catalysts, such as alkali metals, will respectively increase the reaction rates of the chemical Equations (2)–(7), mentioned in Section 2.2, during the gasification process. Adding catalytic effects into the gasification model requires correcting of the kinetic parameters compared with the uncatalyzed simulation. We assumed that alkali metals merely increase the rate of the carbon-steam reaction (3), which is the step-determining step in the steam/air gasification process after the char is decomposed [31]. A correction factor is introduced based on the kinetics of catalytic coal gasification with alkaline organic wastewater in the fluidized bed. The correction factor was obtained via the following method: it equaled the ratio of \( k_{\text{exp}} \) to \( k_{\text{n}} \), where \( k_{\text{exp}} \) is the reaction rate constant from the catalytic gasification experiment, and \( k_{\text{n}} \) is the reaction rate constant without catalytic effects calculated from Table 1 as used in Equation (8).

\[
f = \frac{k_{\text{exp}}}{k_{\text{n}}}
\]  
(8)

2.4. Characteristics of Feed Coal and Operation Parameters

We selected Yongding Fujian anthracite as the raw material, using steam/air as gasification agents with catalytic effect correction factors of 10% waste alkali in Sections 3.2 and 3.3. The results of proximate and ultimate analyses along with the operation parameters are shown in Tables 3 and 4, respectively. While the validation of models was carried out on the basis of previous literature in Section 3.1, the characteristics of feed coal and the reaction conditions can be seen experimentally in their researches [32,33].

Table 3. Proximate and ultimate analyses of Yongding Fujian anthracite [31].

| Proximate Analysis | Ultimate Analysis (d) |
|--------------------|-----------------------|
| Mₐd                | A_d                   | V_d | C   | H   | N   | S   | O   |
| 5.69               | 72.04                 | 17.88 | 75.86 | 1.26 | 1.33 | 1.78 | 0.77 |

a by difference.

Table 4. Operation parameters used in the simulation.

| Types of Coal                | Yongding Fujian Anthracite |
|------------------------------|-----------------------------|
| Coal-feeding flow rate       | 0.6 kg/h                    |
| Steam flow rate              | Steam/coal = 0 to 5         |
| Air flow rate                | ER = 0 to 1                 |
| Gasification temperature     | 550 to 900 °C               |
| Pressure                     | 0.1 MPa                     |
| Fluidized bed volume         | 0.001 + 0.001               |
| Void fraction                | 0.25 to 0.65 (dense phase and dilute phase) |
2.5. Calculation of CCG, CGE, and LHV Values

The carbon conversion efficiency (CCE), cold gas efficiency (CGE), and the lower heating value (LHV) are chosen as quality indicators of syngas. CCE, CGE, and LHV are defined and calculated as follows [34,35]:

$$CCG = \frac{\text{carbon content in the syngas} \times \text{syngas flow rate}}{\text{carbon content in the feed coal} \times \text{coal flow rate}} \times 100\%$$ (9)

$$CGE = \frac{\text{LHV of syngas} \times \text{syngas flow rate}}{\text{LHV of the feed coal} \times \text{coal flow rate}} \times 100\%$$ (10)

$$\text{LHV}(\text{MJ/Nm}^3) = \frac{10.79n_{H_2} + 12.63n_{CO} + 35.818n_{CH_4}}{100}$$ (11)

3. Results and Discussion

3.1. Model Validation

3.1.1. Validation of Fluidized Bed Model without Catalytic Effect

Experimental data from two lab scale gasifiers were used and named as cases 1 and 2 [32,33]. Both experimental and simulation results under same operation conditions are compared in Figures 3 and 4. In case 1, the agents for bituminous coal were steam and air, and the gasification temperature was set to 840–910 °C. The results show that the CO content during the simulation was a bit lower than the experiment value. In case 2, air/oxygen was employed for the gasification agents. The gasification temperature was about 860 °C in the dense phase zone, which decreased to 760 °C in the dilute phase zone. The results show that CO content was over-predicted paralleled with the experimental data, while H\textsubscript{2} and CO\textsubscript{2} were lower. The largest absolute error occurred in nitrogen content with a deviation of 5.7%. In summary, the model outcomes were reasonably close to what were seen experimentally.

![Figure 3. Syngas distribution comparison in case 1 (Steam: 0.76 kg/h, Air: 2.18 m\textsuperscript{3}/h).](image-url)
3.1.2. Validation of the Fluidized Bed Model with a Catalytic Effect

We introduced the catalytic effects to update the original model. The apparent kinetics of catalytic anthracite gasification with 10% industrial alkaline organic wastewater have been studied by Lin et al. [31]. The kinetic parameters obtained in their study describe the overall gasification process, in which all chemical reactions are involved. A simplification in that only the carbon-steam reaction is promoted in our simulation is made based on the assumption mentioned in Section 2.3.2. The correction factor was calculated using Equation (8) as shown in Table 5. We acquired a fitting formula between reaction temperatures and correction factors through the curve-fitting method in Origin program and it was linked to the model by user-defined subroutine.

$$f = 2.55 \times 10^9 \times e^{-0.014T}$$  \hspace{1cm} (12)

where \( f \) is the correction factor, and \( T \) is the gasification temperature.

| Temp. (K) | \( k_{exp} \) | \( f \) |
|-----------|----------------|-------|
| 1023      | 0.0216         | 1593  |
| 1073      | 0.0266         | 699   |
| 1123      | 0.037          | 380   |
| 1173      | 0.0416         | 180   |

Predicted trends for every component were also compared to those gained experimentally with rising steam/air ratio in Figure 5 [31]. The \( \text{H}_2 \) yield increased while \( \text{CO}_2 \) and \( \text{CO} \) decreased when the steam/air ratio was increased. The largest deviation, of 8.6\%, occurred in \( \text{H}_2 \) and \( \text{CH}_4 \) contents at a ratio of 1.4. The deviation demonstrated that the catalytic effect played a role in other reactions, such as the water-shift reaction (6), and \( \text{H}_2 \) will affect the methanation reaction (7). Another possible reason for the seemingly high error of \( \text{CH}_4 \) is that pyrolysis is the determining factor for \( \text{CH}_4 \) yield and the experimental data we used to simulate pyrolysis process was one specific coal type with similar pyrolysis characteristics [36].
Figure 5. Syngas distribution comparison under different steam-to-air ratios.

The experimental data of CCE (50–80%), CGE (79.22–85.73%), and LHV (5.31–6.03 MJ/m³) were collected under a gasification temperature range of 750–900 °C [31]. From Figure 6, CCG and CGE values were reasonably matching with those observed experimentally. While lower LHV values occurred because of the lower CH₄ content in the syngas. To sum up, the simulation results showed a good agreement with what can be seen experimentally.

Figure 6. CCE, CGE, and LHV values in validation.
3.1.3. Calculation of Root Mean Square Error (RMSE)

To quantify the accuracy of the model, the simulation results were compared with all experimental data using the sum squared deviation method. We calculated the RMSE of syngas composition, such as CO, H\textsubscript{2}, CO\textsubscript{2}, CH\textsubscript{4}, and N\textsubscript{2}, for 12 sets of experimental data through Equation (13) \cite{37}.

\[
\text{Root Mean Square Error (RMSE)} = \sqrt{\frac{1}{N} \sum_{i=1}^{N} \left( \frac{y_{ie} - y_{ip}}{y_{ie}} \right)^2}
\]  

(13)

where \(y_{ie}\) and \(y_{ip}\) are experimental and simulation compositions of the gasification product gas.

As shown in Table 6, the distribution of errors was 0.07–0.29. N\textsubscript{2} showed the lowest error, while CH\textsubscript{4} showed the largest error of 0.2883. The deviation in this simulation is reasonable and the correction factors were available for catalytic gasification.

| Composition | CO      | H\textsubscript{2} | CO\textsubscript{2} | CH\textsubscript{4} | N\textsubscript{2} |
|-------------|---------|---------------------|---------------------|---------------------|-------------------|
| RMSE        | 0.2714  | 0.1667              | 0.1526              | 0.2883              | 0.0728            |

3.2. Influence of Operating Conditions on Gasification Performance

3.2.1. Effect of Gasification Temperature

The effect of gasification temperature on the simulation results is presented in Figures 7 and 8. Figure 7 shows H\textsubscript{2} content was increased with higher gasification temperature, while CO content increased first and then decreased when the gasification temperature raised gradually, with a turning point of 650 °C. CO\textsubscript{2} content presented with the opposite trend of CO and CH\textsubscript{4} content declined slightly. These phenomena are explained by the endothermic steam gasification reaction (3) and the Boudouard reaction (4) and were motivated with ascending temperature. In addition, lower temperature was beneficial to the exothermic methanation reaction (5).

![Figure 7. Effect of gasification temperature on syngas composition (Simulation, ER = 0.2, S/C = 2).](image)

The contents of the effective gas components (CO + H\textsubscript{2} + CH\textsubscript{4}) were relatively high, above 700 °C. As shown in Figure 8, CCE (44.8–78.0%), CGE (41.9–81.4%), and the LHV (4.97–6.26 MJ/Nm\textsuperscript{3}) are all improved with elevated gasification temperature. More syngas can be obtained at gasification.
temperatures >700 °C. Higher gasification temperatures were more favorable for the overall gasification process. Moreover, an appreciable carbon conversion of 65–70% was achieved due to the catalytic effect at a low temperature range of 650–750 °C.

Figure 8. Effect of gasification temperature on CCE, CGE, and LHV (Simulation, ER = 0.2, S/C = 2).

3.2.2. Effect of the Steam to Coal (S/C) Ratio

The effect of the steam to coal ratio on the simulation results is presented in Figure 9. As expected, H₂ increased rapidly in the S/C range of 0–5.0. The steam-carbon reaction (2) was the largest contributor to H₂ yield, which was accelerated tremendously with adequate steam source and catalytic effects. CO content decreased while CO₂ content showed a completely opposite tendency with the rise in S/C, indicating that the steam enhanced the water–gas shift reaction (6), which generated H₂ and CO₂, while consumed CO. The steam did not have a great impact on CH₄, which remained almost immobile.

Figure 9. Effect of the steam to coal ratio on syngas composition (Simulation, ER = 0.2, T = 700 °C).

CCE (44.5%–72.7%), CGE (39.6%–83.1%), and LHV (5.13%–6.63 MJ/Nm³) were all improved with larger S/C ratio (Figure 10). Adding extra steam to the system helps enlarge the volume of wastewater that needs to be treated but it also requires additional energy input [38], which is one of the constraint
conditions according to the technological economics. The effects of operating parameters on energy consumption will be discussed in detail in Section 3.3.

![Figure 10](image1.png)

**Figure 10.** Effect of the S/C ratio on CCE, CGE, and LHV (Simulation, ER = 0.2, T = 700 °C).

### 3.2.3. Effect of the ER Ratio

The effect of the ER ratio on the distribution of syngas component is presented in Figure 11. H₂ content dropped sharply as ER increased, while CO and CO₂ contents decreased slightly. It is apparent that the equivalence ratio had two opposing effects on the gasification process. Adding air to the system promoted the combustion reaction but increased the gasification temperature, which is helpful to improve the composition of effective gases as mentioned in Section 3.2.1. But the combustion of carbon and the oxidation of reducing gas (such as H₂, CO) will be dominant in the gasification process if excessive air is added.

![Figure 11](image2.png)

**Figure 11.** Effect of ER on syngas composition (Simulation, S/C = 2, T = 700 °C).

Figure 12 shows that CGE and LHV decreased with ascendant ER ratio which declared the effective gas contents were transformed by extra O₂. The maximum of CGE was 84.05% when the ER ratio was >0.4, CGE was <64.72%, which diverged from the desired value. LHV was 10.45–2.17 MJ/Nm³, which
could reach and even surpass the maximum values in previous statement when the ER ratio was less than 0.2. And it is not difficult to understand why CCE increased with the rise in the ER ratio resulted in a highest CCE of 84.98% at a ratio of 1.0. The ideal gasification process emphasizes high CCG, CGE, and LHV at the same time. Thus, the ER ratio should be <0.4 to ensure syngas quality.

3.3. Energy Analysis

Energy consumption is one of the limiting conditions for system optimization, as we mentioned in Section 3.2.2. Figure 13 is a heat transfer flow chart of the coal catalytic gasification system. Based on the model we established, heat from each reactor (Q-DRY, Q-PYRO, Q-DECOM, Q-GASI1, and Q-GASI2) was introduced and summed in the Q-TOTAL stream, which is the total heat released by the system. The Q-TOTAL value should be greater than or equal to zero in Equation (14) to guarantee that the gasification system maintains self-sufficiency.

![Heat transfer flow chart in the model.](image)

\[
Q_{-DRY} + Q_{-PYRO} + Q_{-DECOM} + Q_{-GASI1} + Q_{-GASI2} = Q_{-TOTAL} \tag{14}
\]
Figures 14–16 show the effects of temperature, the S/C ratio, and the ER ratio on the heat output from this system, respectively. When exploring the effects of one variable, the other two variables remain unchanged, and the basic parameters were set as $T = 700\, ^\circ\text{C}$, $S/C = 2.0$, and $ER = 0.2$.

![Effect of Temperature](image1.png)

**Figure 14.** The effect of temperature on the simulation system heat output.

![Effect of S/C](image2.png)

**Figure 15.** The effect of S/C on the simulation system heat output.

It is inevitable that the increased temperature reduced system heat output as a result of maintaining a high gasification temperature, which absorbs a large amount of heat. Improving the S/C value had an adverse impact on heat output of this system because adding more aqueous water to the system requires more heat to convert it into steam, which led to a waste of energy. The phenomenon that heat output increased when ER < 0.6 and decreased when ER > 0.6 owing to the increased air-promoted oxidation and combustion to release heat while extra air input consumed energy during the preheating process, which declined the heat output.
Figure 16. The effect of ER on the simulation system heat output.

Sensitivity analysis was applied to seek the optimal operating conditions, which was a three-variable problem. Table 7 lists the cases that satisfied Q-TOTAL > 0 with different operating parameters. The ER ratio should be no less than 0.4 to achieve self-sufficiency with a high S/C ratio, which has been proven to be a negative condition. The distribution of effective gas components shows the basic relationship of CO > CO₂ ≥ H₂ > CH₄, the CO content of the effective gas component was higher than 10%, and the CCE was 67–76%. In general, using the wastewater to catalyze coal gasification satisfies self-sufficiency at a relatively low temperature. The parameters of T =700 °C, S/C ratio = 1.0 and ER = 0.4 attained the best gasification performance with higher CCE and LHV considering agglomeration and coking would not occur under such a low temperature range.

Table 7. Cases satisfied self-sufficiency in sensitivity analysis.

| T (°C) | S/C | ER | CO (%) | CO₂ (%) | H₂ (%) | CH₄ (%) | Q (W) | LHV (MJ/Nm³) | CCE (%) | CGE (%) |
|--------|-----|----|--------|---------|--------|---------|-------|---------------|---------|---------|
| 650    | 0.5 | 0.2| 17.5   | 10.6    | 16.0   | 3.9     | 11.7  | 5.4           | 50.8    | 35.7    |
| 650    | 0.5 | 0.4| 15.9   | 8.4     | 6.9    | 2.5     | 345.4 | 3.6           | 67.8    | 44.0    |
| 650    | 1   | 0.4| 15.2   | 8.7     | 8.8    | 2.4     | 156.9 | 3.7           | 69.1    | 56.7    |
| 700    | 0.5 | 0.4| 16.8   | 8.1     | 7.3    | 2.4     | 271.4 | 3.8           | 70.2    | 47.6    |
| 700    | 1   | 0.4| 15.7   | 8.9     | 9.7    | 2.3     | 75.9  | 3.9           | 72.1    | 63.8    |
| 750    | 0.5 | 0.4| 17.0   | 8.4     | 7.5    | 2.4     | 240.1 | 3.8           | 71.8    | 49.1    |
| 750    | 1   | 0.4| 15.6   | 9.6     | 10.2   | 2.3     | 48.3  | 3.9           | 74.2    | 67.3    |
| 800    | 0.5 | 0.4| 16.7   | 9.1     | 10.2   | 2.4     | 235.9 | 3.8           | 72.7    | 62.1    |
| 800    | 1   | 0.4| 15.0   | 10.6    | 10.6   | 2.3     | 50.6  | 3.9           | 75.5    | 69.6    |

4. Conclusions

In this study, a fluidized bed gasification model was established and verified using Aspen Plus. A fitting formula of catalytic correction factors was derived according to the experimental data which was thereafter linked to update the original model. Notably, such a correction factor fitting formula can be used on the same type of coal and the same catalyst concentration under similar reaction conditions. The simulation results of this catalytic model agreed well with experimental data from the literature.

The effects of reaction temperature, S/C ratio, and ER ratio on gasification process were analyzed. Higher gasification temperatures were more favorable for the gasification process and an appreciable carbon conversion of 65–70% was achieved due to the catalytic effect at a low temperature range of 650–750 °C. A mass of H₂ content was consumed as ER increased, which indicated exorbitant ER ratios would be detrimental. Steam had positive effects on gasification, which appeared as much
more H₂ was produced, while excessive steam caused energy waste from the angle of technological economics. The optimal conditions are summarized based on a self-sufficient system via sensitivity analysis: gasification temperature of 700 °C, S/C = 1.0, and ER = 0.4.

We will use additional catalytic experimental data and the same method to enhance the adaptability and robustness of this model in future work by deriving the function relationship concerning catalyst concentration.

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**Nomenclature**

\( M_{ad} \) moisture of the coal sample under air dry basis (%)

\( V_{d} \) volatiles of the coal sample under dry basis (%)

\( A_{d} \) ash of the coal sample under dry basis (%)

\( T \) reaction temperature (K)

\( k_{film} \) mass transfer coefficient for gas film diffusion (gm-mole/cm³·sec·atm)

\( k_{ash} \) mass transfer coefficient for ash diffusion (gm-mole/cm³·sec·atm)

\( \varepsilon_p \) porosity of ash

\( r_{core} \) average radius of shrinking unreacted coal particles (cm)

\( r_{particle} \) average radius of feed coal (cm)

\( [C] \) concentration of char

\( C \) mole concentration of the subscripted substance (mol/m³)

\( P \) partial pressure of the subscripted substance (atm)

\( P^* \) back reaction equilibrium pressure of the subscripted substance (atm)

\( x \) mole fraction of the subscripted substance (%)

\( F_w \) ash correction factor

\( k_{large} \) equilibrium constant of the water–gas shift reaction

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