CaO-Assisted Alkaline Liquid Waste Drives Corn Stalk Chemical Looping Gasiification for Hydrogen Production

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ABSTRACT: The chemical looping gasification (CLG) process is a promising pathway to produce hydrogen-enriched syngas with biomass. It is urgent to enhance the reactivity and thermal stability of oxygen carriers (OC) and capture the inherently separated CO2. This work presents the strategy of simultaneous modification of a Fe2O3/Al2O3 oxygen carrier and the supplement of an oxidant for corn stalk chemical looping gasification by introducing KNO3-containing ethanol liquid waste. CaO is employed to capture the generated CO2 and promote the reaction balance toward hydrogen production in a fuel reactor (FR). The highest carbon conversion reaction rate of $1.1 \times 10^{-4}$ mol/g could be obtained at the ratio of CaO to fuel carbon and the reaction temperature of 1.5 and 600 °C, respectively. The kinetics and thermodynamics analyses under the optimized condition are further discussed to verify the possibility and high efficiency of using alkaline organic liquid waste to boost solid fuel gasification for hydrogen production. This CLG strategy shows multifunctional merits, including organic liquid waste treatment, biomass CLG promotion, and hydrogen production enhancement.

1. INTRODUCTION

Biomass chemical looping gasification (CLG), derived from chemical looping combustion (CLC), is established as a promising biomass gasification technology, attracting interest over the last decades.1 CLG utilizes an oxygen carrier (OC) (e.g., the metal oxides of Cu, Ni, Fe, Mn) rather than O2 to transfer oxygen to partially oxidize biomass into syngas.2–4 As shown in Figure 1, a CLG system consists of two interconnected reactors. In a fuel reactor (FR), OC plays multiple roles, including catalyzing tar and hydrocarbon reforming and oxidizing biomass and volatile compounds into CO, CO2, CH4, and H2O.5,6 Syngas can be used to synthesize hydrocarbons under the Fischer–Tropsch process. Then, the reduced OC is transferred into the air reactor (AR), where it is oxidized by air for the next CLG cycle. Among the numerous metal oxides, Fe2O3 has attracted much attention due to its low cost and environmental friendliness.7,8 Fe2O3 can transfer the lattice oxygen in it for the chemical looping process under reasonable temperatures, like driving biomass gasification at 700–900 °C.9 Nevertheless, pure Fe2O3 suffers from limited reactivity and low thermal stability.11 Fe2O3 supported on Al2O3 can improve the thermal stability and reactivity for H2 production.12 Multicomponent modification can also increase the activity of Fe2O3, like Ni–Fe@CNF/porous carbon13 and Ca2Fe2O5,14–16 and obviously improve biomass CLG efficiency. Especially, alkali modification of Fe2O3-based OC can greatly enhance the reactivity for biomass gasification.17–20

Figure 1. Chemical looping gasification schematic diagram.
Further, steam and CO₂ can act as gasification agents, assisting in the solid fuel chemical looping reaction and improving char gasification and tar gasification into CO. Organic liquid waste from food, coal mining, medicine, and chemical industries contains high concentration of alkali and organic matter. The traditional incineration method can burn off organic matter, but alkali metals are likely to cause sintering. However, research has shown that the chemical looping method could be used for gasification of organic liquid waste to produce syngas. Moreover, organic liquid waste can introduce sufficient steam for biomass CLG to produce H₂. Therefore, not only organic matter in alkaline organic waste liquid can be gasified but the steam can also act as a gasification agent and alkali metals can theoretically modify Fe₂O₃-based OC to improve the reactivity. It is reasonable to introduce alkaline organic liquid waste to promote biomass gasification, while CaO can assist in capturing carbon dioxide during CLG.

In this research, we will introduce a KNO₃-containing ethanol solution as the model alkaline organic liquid waste to one-step activate Fe₂O₃/Al₂O₃ and provide sufficient steam as an oxidant for promoting corn stalk CLG, while CaO is utilized for the capture of CO₂. The objectives of this research study are to optimize the operation parameters of the CLG reaction by comparing different reaction conditions and confirm the possibility of using CaO to assist the CLG of the KNO₃-containing ethanol solution and corn stalk for H₂ production through reaction kinetic analysis and thermodynamic analysis.

2. RESULTS AND DISCUSSION

2.1. Composition of Syngas during Corn Stalk CLG.

Since Ω = 0.2 resulted in the highest H₂ yield from biomass CLG reported in our previous work, Ω was set to 0.2 to perform CLG experiments under different T, mKNO₃ and CaO/C ratios. (Here, the oxygen excess number, Ω, is defined as the ratio of the lattice oxygen of OC to the oxygen required for complete oxidation of the corn stalk.) Figure 2 shows the results of CLG at the condition of Ω = 0.2, T = 650 °C, mKNO₃ = 6%, and CaO/C = 1.5. A large amount of syngas (mainly H₂, CH₄, and CO₂) is generated in the CLG reaction, where H₂ yield was far higher than CO₂ and CH₄ yields. The corn stalk CLG mechanism could be illustrated using the formulas 1–5 of the reaction. Pyrolysis of CH₃CH₂OH and stalk produces CO, CO₂, H₂, H₂O, hydrocarbon C₅H₊ (including CH₄), and tar, while tar and char were mainly oxidized by H₂O into CO, CO₂, and H₂ (formula 3). Further, the generated CO and the reduced Fe₂O₃ (Fe₂O₃-x) could be oxidized by H₂O to release H₂ (formula 4 and 5). It was found that CO₂ was increasingly produced, although the total flow of syngas decreased after 35 min. It could be attributed to the decomposition of CaCO₃ as reported previously.

\[
\text{H}_2 + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{H}_2 + \text{CO} + \text{C}_n\text{H}_m + \text{CO}_2 + \text{tar} + \text{char} + \text{H}_2\text{O} \quad (1)
\]

\[
\text{C}_n\text{H}_m/\text{CH}_3\text{CH}_2\text{OH} + \text{Fe}_2\text{O}_3 \rightarrow \text{CO} + \text{CO}_2 + \text{H}_2\text{O} + \text{Fe}_2\text{O}_3-x \quad (2)
\]

\[
\text{H}_2\text{O} + \text{C}/\text{char} \rightarrow \text{H}_2 + \text{CO}/\text{CO}_2 \quad (3)
\]

\[
\text{H}_2\text{O} + \text{CO} \rightarrow \text{H}_2 + \text{CO}_2 \quad (4)
\]

\[
\text{Fe}_2\text{O}_3-x + \text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 + \text{H}_2 \quad (5)
\]

2.2. Effect of KNO₃ Concentration. The effect of mKNO₃ (ranging from 4 to 10%) on H₂ yield was investigated under T = 800 °C, CaO/C = 0, and Ω = 0.2. As shown in Figure 3, when mKNO₃ = 6%, the H₂ production is the highest, indicating that the increasing concentration of KNO₃ can promote the gasification reaction in the system, but excessive KNO₃ will block the pore structure of the oxygen carrier surface. KNO₃ can react with biomass char to improve gasification efficiency. In addition, the released gas can not only oxidize the char accumulated on the surface of OC but also influence the dispersity and pore structure of OC. A reasonable amount of KNO₃ is important for CLG, since less KNO₃ corresponds to the lower catalytic activity for the CLG reaction and more KNO₃ results in slagging on Fe₂O₃/Al₂O₃.

\[
\text{KNO}_3 + \text{C} \rightarrow \text{KNO}_2 + \text{K}_2\text{O} + \text{CO}_2 + \text{N}_2 \quad (6)
\]
2.3. Effect of CaO. CLG experiments at different CaO/C of 0, 0.5, 1, 1.5, and 2 were performed under $T = 650 \, ^\circ C$, $m_{KNO_3} = 6\%$, and $\Omega = 0.2$ to investigate the effect of CaO on CLG. The total volumes of the main component (H$_2$, CO, CH$_4$, and CO$_2$) in syngas are indicated in Figure 4. CH$_4$ formation curve is similar to that of H$_2$. Also, CO was not detected with the addition of CaO. The high catalytic activity of CaO promotes the conversion of tar, resulting in more gaseous products.\textsuperscript{35} As shown in Figure 5, the effect of CaO on corn stalk CLG displays a nonlinear relationship between CaO/C and the parameters. The highest H$_2$ yield was obtained at a CaO/C of 1.5. CaO/C has a significant effect on H$_2$ production, which is due to the catalytic dehydrogenation of CaO.\textsuperscript{39} In addition, CaO can absorb CO$_2$, promote CO$_2$ and subsequently favor H$_2$ and H$_2$O formation.\textsuperscript{38} More CaO catalytic active sites are conducive for efficient catalytic gasification and reforming to generate H$_2$.\textsuperscript{35} However, too much addition of CaO may lead to the specific surface area loss of OC and influence the initiate adsorption, redox, and catalytic reactions in corn stalk CLG. The H$_2$ production curve shows a maximum formation rate at a CaO/C of 1.5, which is similar to the experimental results of Hanaoka et al.\textsuperscript{40} Results show that a reasonable CaO/C ratio of around 1.5 favors the CLG reactions and H$_2$ production.

2.4. Effect of Temperature. CLG experiments under various temperatures (600, 650, and 700 °C) were performed at CaO/C = 1.5, $\Omega = 0.2$, and $m_{KNO_3} = 6\%$. The yields of H$_2$, CO, CH$_4$, and CO$_2$ are presented in Figure 6. The H$_2$ formation rate decreases with the increasing temperature, while CO$_2$ generation increases. The plausible explanation may reside in that the decomposition of the CaCO$_3$ reaction, which is an endothermic reaction, is enhanced at higher temperature.\textsuperscript{41,42} CO$_2$ adsorption by CaO may experience a rapid surface reaction and slow diffusion of CO$_2$ through the CaCO$_3$ layer formed during surface carbonation.\textsuperscript{43,44} In addition, high temperature is not conducive for CO$_2$ adsorption,\textsuperscript{45} leading to sorbent sintering and inhibiting further adsorption of CO$_2$.\textsuperscript{46} In comparison with the cases under higher temperature, 600 °C favors the adsorption of CO$_2$ by CaO, forming CaCO$_3$,\textsuperscript{35} and promoting the production of H$_2$. The increasing temperature can promote the release of gas in the initial stage of devolatilization and production of H$_2$ in the subsequent reaction stage, including tar cracking/reforming, and char gasification.\textsuperscript{46,47} However,
sintering of CaO on the surface of OC may occur at high temperature, which will hinder the oxidation of biomass, hydrocarbon reforming, and other reactions, thereby inhibiting the production of H₂. The results show that the proper temperature can not only promote the absorption of CO₂ but also alleviate the decomposition of CaCO₃, which promotes the production of H₂.

Correlations between H₂ volume and temperature are illustrated in Figure 7, where CaO shows better assistance properties under 600 °C for H₂ generation than the other cases. A higher temperature is not conducive for adsorption of CO₂. This result reflects not only the temperature sensitivity, but also the synergistic effect of CaO on H₂ production.

2.5. Reaction Stoichiometry. The stoichiometry of the CLG reaction at the optimal condition was analyzed. Based on the integral calculation of \( Q_{\text{CH}_4}, Q_{\text{CO}}, \) and \( Q_{\text{CO}_2}, \) the volume \( Q_C \) of the total carbon-containing gas was calculated by the following formula

\[
Q_C = Q_{\text{CH}_4} + Q_{\text{CO}} + Q_{\text{CO}_2}
\]  

(8)

The molar amount of carbon converted with reaction time, \( n_C \), could be calculated as

\[
n_C = \frac{Q_C}{24.45}
\]  

(9)

The carbon conversion rate in terms of per unit mass of OC, \( r_c \), could be calculated as

\[
r_c = \frac{dn_c}{m_{\text{OC}}dt}
\]  

(10)

According to the above formula, the time-dependent \( r_c \) could be obtained. Under different CaO/C, the relationship between \( n_C \) and \( t \) is illustrated in Figure 8a. \( n_C \) gradually increases with increasing CaO/C up to 1.5. \( n_C \) gradually decreases with the increase in CaO/C from 1.5 to 2. The rate of ethanol solution addition is constant over time, and the peak value of \( r_c \) at the beginning of the corn stalk CLG can be attributed to the pyrolysis of corn stalk to quickly release volatiles. \( r_c \) increased from 0 to 30 min. Then, \( r_c \) decreased continuously after ethanol solution addition was stopped, indicating that it is difficult to convert the fixed carbon of

Figure 6. Flow rate (left coordinate) and volume (right coordinate) of the main component of syngas under various temperatures under CaO/C = 1.5 and a temperature of (a) 600 °C, (b) 650 °C, and (c) 700 °C.

Figure 7. Correlations between the volume of H₂ and temperature under CaO/C = 1.5, \( \Omega = 0.2 \), and \( m_{\text{KNO}_3} = 6\% \).
corn stalk without sufficient steam as a gasification agent. The certain rate \( r_c \) was still observed after 70 min, which may relate to the decomposition of CaCO\(_3\) in the reaction system to generate CO\(_2\).35

2.6. Thermodynamics Analysis. As discussed above, in the case of CaO/C of 1.5, the highest H\(_2\) yield could be achieved. Thermodynamic analysis of the CaO-promoting ethanol-driven corn stalk CLG process was performed. Thermodynamic parameters utilized for the related calculations\(^ {36} \) are listed in Table 1. Based on the product gas distribution, the electronic equilibrium analysis indicated that 0.01805 moles of electrons reduce Fe\(^ {3+}\) to Fe\(^ {2+}\), which was

| physical parameters | unit | value |
|---------------------|------|-------|
| \( \Delta H_m^\circ (\text{Fe, 298.15 K}) \) | kJ/mol | 0 |
| \( \Delta H_m^\circ (\text{Fe}_3O_4, 298.15 K) \) | kJ/mol | -1118.38 |
| \( \Delta H_m^\circ (\text{FeO}_2, 98.15 K) \) | kJ/mol | -271.96 |
| \( \Delta H_m^\circ (\text{Fe}_2O_3, 298.15 K) \) | kJ/mol | -824.25 |
| \( \Delta H_m^\circ (\text{C}_2\text{H}_6\text{O}(l), 298.15 K) \) | kJ/mol | -236.92 |
| \( \Delta H_m^\circ (\text{CO}_2, 298.15 K) \) | kJ/mol | -393.51 |
| \( \Delta H_m^\circ (\text{CO}, 298.15 K) \) | kJ/mol | -110.525 |
| \( \Delta H_m^\circ (\text{CH}_4, 298.15 K) \) | kJ/mol | -74.81 |
| \( \Delta H_m^\circ (\text{H}_2\text{O}(l), 298.15 K) \) | kJ/mol | -241.82 |

\( C_{\text{mp}}(\text{Fe}_3O_4, 298.15 K) \) J/(mol\( \cdot \)K) 143.43

\( C_{\text{mp}}(\text{Fe}_2O_3, 298.15 K) \) J/(mol\( \cdot \)K) 145.43

\( C_{\text{mp}}(\text{C}_2\text{H}_6\text{O}, 298.15 K) \) J/(mol\( \cdot \)K) 272.37

\( C_{\text{mp}}(\text{CO}_2, 298.15 K) \) J/(mol\( \cdot \)K) 26.537 + 7.6831 \times 10^{-3} \times T - 1.172 \times 10^{-6} \times T^2

\( C_{\text{mp}}(\text{CO}, 298.15 K) \) J/(mol\( \cdot \)K) 26.537 + 7.6831 \times 10^{-3} \times T - 1.172 \times 10^{-6} \times T^2

\( C_{\text{mp}}(\text{CH}_4, 298.15 K) \) J/(mol\( \cdot \)K) 26.537 + 7.6831 \times 10^{-3} \times T - 1.172 \times 10^{-6} \times T^2

\( C_{\text{mp}}(\text{H}_2\text{O}, 298.15 K) \) J/(mol\( \cdot \)K) 26.537 + 7.6831 \times 10^{-3} \times T - 1.172 \times 10^{-6} \times T^2

\( C_{\text{mp}}(\text{corn stalk, 298.15 K}) \) J/(mol\( \cdot \)K) 63.43

Figure 8. (a) \( n_c \) and (b) \( r_c \) at different reaction times during the CLG process under \( T = 650 \text{ °C}, m_{\text{KNO}_3} = 6\% \), and \( \Omega = 0.2 \).

Table 1. Related Thermodynamic Parameters, Including Standard Molar Reaction Enthalpy (\( \Delta H_m^\circ \)) and Molar Isobaric Hot Melt (\( C_{\text{mp}} \)), for Various Components

![Figure 9](https://dx.doi.org/10.1021/acsomega.0c02787)

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Figure 9. (a) XRD patterns and (b) scanning electron microscopy (SEM) images of the pure Fe\(_2\)O\(_3\)/Al\(_2\)O\(_3\) and the K-modified Fe\(_2\)O\(_3\)/Al\(_2\)O\(_3\).
equivalent to a mixture of $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ at a molar ratio of 2:3. Therefore, the reaction equation could be written as

$$\text{C}_{25}\text{H}_{20}\text{O}_5 + 3.3\text{C}_2\text{H}_4\text{O} + 7.3\text{Fe}_2\text{O}_3 + 10.4\text{H}_2\text{O} \rightarrow 19.7\text{H}_2 + 2.8\text{CH}_4 + 10.8\text{CO}_2 + 4.4\text{Fe}_3\text{O}_4 + 1.5\text{FeO} (\Delta H) = 298.572\text{kJ/mol}$$ (11)

$$2.9\text{Fe}_3\text{O}_4 + \text{FeO} + 0.9\text{O}_2 \rightarrow 4.9\text{Fe}_2\text{O}_3 (\Delta H) = -788.15\text{kJ/mol}$$ (12)

It can be found from the above calculations that corn stalk CLG is an endothermic process and requires heat of 1.006 kJ. Oxidation of reduced OC is an exothermic process and releases heat of 3.983 kJ. The heat released by the oxidation of the reduced OC can meet the heat required for the gasification process, which implies the self-heating balance for the strategy of using CaO-assisted alkaline liquid waste to drive corn stalk CLG for H$_2$ production.

2.7. Structural Characterizations. As shown in Figure 9a, the diffraction peaks of the X-ray diffraction (XRD) pattern correspond to different facets of Fe$_2$O$_3$, indicating that the prepared Fe$_2$O$_3$/Al$_2$O$_3$ is highly crystalline, and the absence of Al$_2$O$_3$ diffraction peaks in the fresh OC implies that the support Al$_2$O$_3$ is covered by Fe$_2$O$_3$ crystals. However, modification with an 8% KNO$_3$ solution changes the XRD patterns obviously to show some crystal facets of Al$_2$O$_3$ and KNO$_3$. The heat treatment led to the decomposition of KNO$_3$ into KNO$_2$, changing the distribution of Fe$_2$O$_3$ and exposing partial Al$_2$O$_3$ crystal facets. In Figure 9b, the crystals are arranged regularly on the surface of the fresh OC, while the surface of the alkaline modified OC is uneven with particles of different sizes, which could be attributed to the decomposition of KNO$_3$. The released gas could change the dispersity and pore structure of Fe$_2$O$_3$, hence altering the reactivity of the OC as discussed above. In addition, good structural regeneration and cycle performance of iron-based OC have been proven. However, after three cycles, the accumulation of Si in the biomass ash will reduce the H$_2$ production in CaO-assisted CLG. Although the introduction of KNO$_3$ can improve the H$_2$ production, it is necessary to determine the optimal reaction pressure and structure of OC to improve the circulation of CaO-assisted OC in the CLG process.

3. CONCLUSIONS

Corn stalk chemical looping gasification for H$_2$ production boosted by a CaO-assisted KNO$_3$-containing ethanol solution was experimentally investigated, which shows that $\Omega = 0.2$, $m_{\text{KNO}_3} = 6\%$, $600 \degree \text{C}$, and CaO/C = 1.5 leads to the highest hydrogen production of 3.0 L/g of corn stalk driven by 20 mL alkaline liquid waste. Compared to the case without CaO, the addition of CaO increases the H$_2$ production and carbon conversion of corn stalk by 61.3 and 44.7%, respectively. Reaction kinetic analysis and thermodynamic analysis further confirmed the possibility of using CaO to assist the CLG of the KNO$_3$-containing ethanol solution and corn stalk CLG for H$_2$ production, which not only treats organic liquid waste but also favors energy conversion.

4. MATERIALS AND METHODS

4.1. Materials. Feedstocks involved in the CLG system include corn stalks and a 6% ethanol solution. Proximate analysis and ultimate analysis of corn stalk are listed in Tables 2 and 3, respectively. The molecular formula of corn stalks was calculated to be C$_{6}$H$_{10}$O$_{5}$ according to the ultimate analysis (shown in Table 3). Herein, as a laboratory-level experimental study, KNO$_3$ was added in the process for preparing Fe$_2$O$_3$/Al$_2$O$_3$ by an impregnation method to improve dispersion of K in the OC system, where the ratio of the Fe$_2$O$_3$ mass fraction to the Al$_2$O$_3$ mass fraction in OC is 3:2. The 6% ethanol solution was used to perform CLG experiments as the model organic liquid waste. First, Fe(NO$_3$)$_3$·9H$_2$O was added into the ionized water and the suspension was stirred to obtain Fe(NO$_3$)$_3$ saturated solution. Then, Al$_2$O$_3$ powder was added and the mixture was continuously stirred for 1 h. The mixture was dried at 100 $\degree$C for 8 h and then placed in a muffle furnace and calcined at 900 $\degree$C for 1.5 h, and the corrosive gas containing the nitrogen element generated by pyrolysis was processed and discharged through a ventilation duct. The mixture was ground into powder of 30–50 meshes for the following CLG experiments. The prepared OCs were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD).

4.2. Experimental Procedure. The fixed-bed reaction system, as previously mentioned, was designed for corn stalk CLG. The CLG system consists of a reactor (quartz tube), a gas supply system, a detection system, and a heating system. As shown in Figure 10, the height and internal diameter of the quartz tube reactor were 900 and 18 mm, respectively. To perform CLG experiments, quartz wool was loaded on a porous plate, which was 450 mm above the bottom of the reactor. The mixture of corn stalk, OC, and CaO was placed on the quartz wool above the porous dam plate. The reactor was sparged with N$_2$ at a rate of 160 mL/min. 6% ethanol solution (10 mL) prepared by dissolving ethanol in deionized water was injected into the reactor at a rate of 0.333 mL/min from the top through an injection pump at various reaction temperatures. The outlet gas was tested every 5 min by a gas chromatograph (Agilent Micro GC 490). The detailed parameters of the CLG experiment are shown in Table 4. Here, the oxygen excess number, $\Omega$, is defined as the ratio of the lattice oxygen of OC to the oxygen required for complete oxidation of the corn stalk.

4.3. Data Evaluation. Since the nitrogen flow rate ($Q_{\text{N}_2}$) was fixed to be 0.16 L/min, the outlet gas flow rate at reaction time ($t$), $Q_t$, could be calculated using the following equation.

\[
Q_t = Q_{\text{N}_2} + Q_{\text{H}_2}
\]
\[ Q_{\text{H}_2} = \int Q_{\text{H}_2}(t) \, dt \]  
\[ Q_{\text{CO}} = \int Q_{\text{CO}}(t) \, dt \]  
\[ Q_{\text{CH}_4} = \int Q_{\text{CH}_4}(t) \, dt \]  
\[ Q_{\text{CO}_2} = \int Q_{\text{CO}_2}(t) \, dt \]  

The carbon conversion rate, \( \eta \), is defined as the molar ratio of carbon in the syngas to that in fuel material and was calculated by the following formula:

\[ \eta = \frac{(Q_{\text{CO}} + Q_{\text{CH}_4} + Q_{\text{CO}_2}) \times \frac{273}{273 + 60}}{22.4 \times (n_{\text{fuel}})} \]  

where “60” is the hue gas chromatograph injection temperature 60 °C and \( n_{\text{fuel}} \) is carbon molar amount in corn stalk and ethanol solution.

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Notes
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