CO$_2$ utilization for combined gasification and sorption enhanced water-gas shift for syngas production of biochar

Supanida Chimpae$^1$, Suwimol Wongsakulphasatch$^1$*, Supawat Vivanpatarakij$^2$, Thongchai Glinrun$^3$, Fasai Wiwatwongwana$^3$, Suttichai Assabumrungrat$^4$

$^1$Department of Chemical Engineering, Faculty of Engineering, King Mongkut’s University of Technology North Bangkok, Bangkok, 10800, Thailand,
$^2$Energy Research Institute, Chulalongkorn University, Phayathai Road, Wang Mai, Phatumwan, Bangkok Thailand,
$^3$Department Chemical Engineering, Faculty of Engineering, Pathumwan Institute of Technology, Rama 1 Road, Wang Mai, Phatumwan, Bangkok, Thailand,
$^4$Center of Excellence in Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok, 10330, Thailand.

Corresponding author: suwimol.w@eng.kmutnb.ac.th (S. Wongsakulphasatch)

Abstract: Searching for alternative renewable energy to serve high demand of energy consumption has been of interest for decades. However, the production of energy comes with an emission of large amount of CO$_2$, the main cause of global warming problem. As a consequence, improvement of energy production process in terms of increasing high efficiency and reducing CO$_2$ emission are required [1]. This research verified the combined systems: biochar gasification and sorption-enhanced water gas shift reaction for the production of synthesis gas. The effect of calcium precursor on CaO-based sorbents, type of metal on multifunctional materials, and amount of co-feed CO$_2$ as gasifying agent on process performances were focused on this work. Fixed-bed reactors were used for both gasification and sorption-enhanced water-gas shift experiments. Performances of the system were analyzed in terms of %biochar conversion, H$_2$/CO ratio, and CO$_2$ emission. The temperature used in the gasification process was fixed at 900°C and sorption-enhanced water-gas shift was 600°C at 1 atm. The results showed the sorbent CaO/Ca$_{12}$Al$_{14}$O$_{33}$ derived from calcium nitrate displayed the best performance for CO$_2$ capture, whose CO$_2$ capture capacity is 0.34 gCO$_2$/g sorbent at 30%CO$_2$ v/v at 600°C. For the combined gasification and sorption-enhanced water-gas shift reaction, 98% biochar conversion can be obtained. Ni/CaO-Ca$_{12}$Al$_{14}$O$_{33}$ offered higher H$_2$/CO ratio and CO$_2$ emission when compared to Cu/CaO-Ca$_{12}$Al$_{14}$O$_{33}$ at fixed feed molar ratio of H$_2$O:CO$_2$:O$_2$:C = 0.5:0.5:0.125:1. The utilization of CO$_2$ as gasifying agent at feed molar ratio of H$_2$:O:CO$_2$:O$_2$:C = 0.5:0.1:0.125:1 demonstrated the reduction of CO$_2$ emission with the production of H$_2$/CO ratio = 0.23.

1. Introduction

Synthesis gas (syngas) is a substance consists of carbon monoxide (CO) and hydrogen (H$_2$), which can be used as a primary substrate to produce hydrogen, ammonia, methanol or hydrocarbon fuels. The syngas can be used for various applications, depending upon the ratio of hydrogen to carbon monoxide [2]. Syngas can be obtained from various raw materials, such as natural gas, coal, hydrocarbon and biomass. Gasification of biomass is actually used as steam and O$_2$ gasifier agent. [3]. Nowadays,
concerning on CO₂ emission, a cause of global warming is an essential issue. Since the traditional process for syngas production also produces substantial amounts of carbon dioxide, therefore, capturing or recycling carbon dioxide produced from syngas production process is of interest.

This research verified the combined systems: biochar gasification and sorption-enhanced water gas shift (SEWGS) for the production of synthesis gas. The effect of calcium precursor on CaO-based sorbents, type of metal on multifunctional materials, and amount of co-feed CO₂ as gasifying agent on process performances were focused on this work.

2. Materials and Methods

2.1. Synthesis of sorbent/catalyst material

The 70/30%wt of CaO/Ca₁₂Al₁₄O₃₃ was prepared by sol-gel methods followed [4] and various of calcium precursor, using Calcium nitrate tetrahydrate (Ca(NO₃)₂•₄H₂O), Calcium gluconate (C₁₂H₂₂CaO₁₄), and Calcium acetate monohydrate: Ca(CH₃COO)₂•H₂O as calcium precursor. First, aluminum precursor, and calcium precursor were dissolved in DI water with the addition of citric acid using molar ratio citric acid to Al³⁺, Ca²⁺ of 1.2 and DI water to citric acid of 50. The solution was adjusted to pH 1-2. Then, the solution was heated up and stirred at 80 °C under reflux for 2 hr. After that, ethylene glycol was added into the solution and allowed the solution to stir under reflux at 105 °C for 5 hr. The solution was dried at 110 °C for 12 hr and calcined at 850 °C for 2 hr under dried air.

A multi-functional sorbent/catalyst material, using 70/30%wt of CaO/ Ca₁₂Al₁₄O₃₃ and added 12.5 %wt. of Ni or Cu, was prepared by sol-gel method followed [4].

2.2. characterization of sorbent/catalyst material

X-ray diffraction (XRD) to determine crystal structure or molecule of compound, element, kind of material and Scanning electron microscope (SEM) to study the morphology and characteristics of the surface of the sample.

2.3. Experimental Test

2.3.1 CO₂ sorption test.

CO₂ sorption test was carried out by using fixed-bed reactor (see Figure 1). A sorbent (CaO/Ca₁₂Al₁₄O₃₃) was fixed by 0.5 g in fixed-bed reactor (inside diameter of 11 mm and outside diameter of 12 mm). Prior to running experiment, sorbent was pretreated by Ar with flow rate of 50 ml/min at 850°C for 60 min. CO₂ sorption test was varied CaO-based sorbents under 15 mL /min gas flow containing 30% CO₂ (balanced Ar) at 600°C atmospheric pressure.

In order to compare the CO₂ sorption performance of various CaO-based sorbents, using parameter, CO₂ sorption capacity is defined as follows:

\[
\text{CO}_2\text{ sorption capacity} (\text{g CO}_2/\text{g sorbent}) = \frac{F_{\text{CO}_2,in} \int_{t_0}^{t_f} (1 - \frac{C_{\text{CO}_2,\text{out}(t)}}{C_{\text{CO}_2,\text{in}}}) \, dt}{W}
\]

where,
- \(F_{\text{CO}_2,in}\) = CO₂ feed flow rate (g/min)
- \(C_{\text{CO}_2,\text{in}}\) = inlet concentration of CO₂ (mol/mL)
- \(C_{\text{CO}_2,\text{out}(t)}\) = outlet concentration of CO₂ (mol/mL)
- \(W\) = weight of sorbent (g)

2.3.2 Syngas production test.

Syngas production test was carried out by using two-connected fixed-bed reactors, one for biomass gasification and another one for sorption-enhanced water gas shift reaction (see Figure 1). A 0.7-g biochar was packed in the gasification reactor and a 3.5-g multi-functional material was packed in another fixed-bed reactor. Biochar was pretreated by Ar at 600°C for 60 min. Multi-functional material
was pretreated by Ar at 850°C for 30 min followed H₂ at 850°C for 30 min. In this work, gasification temperature was fixed 900°C at atmospheric pressure. The evaluating parameters are reported using %Biochar conversion, H₂/CO ratio, and CO₂ emission ratio, respectively.

% Biochar conversion:

\[
\text{% Biochar conversion} = \frac{\text{Biochar}_{\text{in}} - \text{Biochar}_{\text{out}}}{\text{Biochar}_{\text{in}}} \times 100
\]

H₂/CO ratio:

\[
\text{H₂/CO ratio} = \frac{\text{mol of H₂ produced}}{\text{mol of CO produced}}
\]

CO₂ emission ratio, CO₂ EMR:

\[
\text{CO₂ emission ratio (CO₂ EMR)} = \frac{\text{CO₂ emission}}{\text{CO₂ total}}
\]

Figure 1. Process flow diagram for syngas production from gasification combined with sorption enhanced water gas shift of pyrolyzed biochar.

3. Results and discussion

3.1. Sorbent/catalyst characterizations

XRD patterns of the synthetic sorbent of CaO/Ca₃Al₂O₆ are shown in Figure 2(a). As seen, the results show XRD peaks corresponding to CaO ,Ca₃Al₂O₆ and Ca(OH). In Figure 2(b) is shown the synthetic multi-functional materials of NiO and CuO on CaO-Ca₃Al₂O₆. The results show XRD peaks corresponding to CaO, Ca₃Al₂O₆, NiO, CuO, Ca(OH). SEM micrographs of fresh samples are depicted in Figure 3, the results show CaO-xerogel/ Ca₃Al₂O₆ has oval-like particle with smooth surface morphology, CaO-xerogel/ Ca₃Al₂O₆ has small particles, whereas closed packing of particles was observed with CaO-xerogel/Ca₃Al₂O₆. The multi-functional materials, 12.5%wt-NiO/CaO-Ca₃Al₂O₆ and 12.5%wt-CuO/CaO-Ca₃Al₂O₆ as shown in Figures 3(d)-(e), show small-size particles connected loosely to each other with void space.
Figure 2. XRD patterns of (a) CaO/Ca$_{12}$Al$_{14}$O$_{33}$ various of calcium precursor and (b) different metal (Ni,Cu) on CaO-Ca$_{12}$Al$_{14}$O$_{33}$.

Figure 3. SEM images of fresh samples; (a) CaO/Ca(NO$_3$)$_2$/Ca$_{12}$Al$_{14}$O$_{33}$, (b) CaO/C$_{12}$H$_{22}$CaO$_{14}$/Ca$_{12}$Al$_{14}$O$_{33}$, (c) CaO/Ca(CH$_3$COO)$_2$/Ca$_{12}$Al$_{14}$O$_{33}$, (d) 12.5%wt-NiO/CaO-Ca$_{12}$Al$_{14}$O$_{33}$ and (e) 12.5%wt-CuO/CaO-Ca$_{12}$Al$_{14}$O$_{33}$.

3.2. CO$_2$ sorption capacity test

Different calcium precursors show different performance on CO$_2$ sorption. The result in Figure 4 shows that CaO$_{converso}$/Ca$_{12}$Al$_{14}$O$_{33}$ provides the highest CO$_2$ sorption capacity, followed by CaO$_{converso}$/Ca$_{12}$Al$_{14}$O$_{33}$ and CaO$_{converso}$/Ca$_{12}$Al$_{14}$O$_{33}$, respectively.
3.3. Syngas production test

3.3.1. Effect of catalyst type.
In the WG reactor, the effect of catalyst types was investigated: (1) Ni-based: Ni/CaO-Ca₁₂Al₁₄O₃₃, and (2) Cu-based: Cu/CaO-Ca₁₂Al₁₄O₃₃.

As shown in Figure 5, conversion of biochar reaches almost 100% for all catalyst types investigated in this study. Figure 6 presents the effect of H₂/CO ratio and CO₂ emission ratio for different metals of Gasification and SEWGS. As seen, using of Ni-Based as catalyst shows high CO₂ emission because CO can be converted into H₂ from water gas shift reaction (5).

Water-gas shift reaction

\[
\text{CO (g) + H₂O (g) } \rightleftharpoons \text{CO₂ (g) + H₂ (g)} \Delta H = -41 \text{ kJ/kmol} \tag{5}
\]

Figure 5. Biochar conversion (%) at different metal(Ni,Cu) on CaO-Ca₁₂Al₁₄O₃₃, using a H₂O:CO₂:O₂:C feed molar ratio of 0.5:0.5:0.125:1, gasification at 900°C and SEWGS at 600°C.
3.3.2 Effect of gasifying agent.

In this work, the effect of introducing CO as gasifying agent was studied in order to utilize the produced CO. The combined gasification and SEWGS reactor shows that CO from gasifier can be converted into H from water-gas shift reaction (3.1) in SEWG reactor and reduces CO from sorption by CaO as shown by high H/CO ratio and less CO emission ratio when ratio of CO/C was decreased to 0.1.

4. Conclusion

The sorbent CaO/Ca._Al._O._ derived from calcium nitrate displayed the best performance for CO capture, whose CO capture capacity is 0.34 gCO/g sorbent at 30%CO_v/v at 600°C. For the combined gasification and sorption-enhanced water-gas shift reaction, 98% biochar conversion can be obtained. Ni/CaO-Ca._Al._O._ offered higher H/CO ratio and CO emission when compared to Cu/CaO-Ca._Al._O._. The utilization of CO as gasifying agent at feed molar ratio of CO:C = 0.1:1 demonstrated the reduction of CO emission with the production of H/CO ratio = 0.23.
Acknowledgements

The authors would like to acknowledge funding support from the Ratchadapisek Sompoch Endowment Fund 2016 of Chulalongkorn University (CU-59-003-IC), and King Mongkut’s University of Technology North Bangkok (contract no. KMUTNB-KNOW-61-029). S.W. and S.A. also wish to acknowledge the “Research Chair Grant” of the National Science and Technology Development Agency (NSTDA).

References

[1] Rafieea A, Khalilpourb K R, Milanid D and Panahie M 2018 J. Environ. Chem. Eng. 6 5771-94
[2] Moneti M, Di Carlo A, Bocci E, Foscolo P U, Villarini M and Carlini M 2016 Int. J. Hydrog. Energy 41 11965-73
[3] Koppatz S, Pfeifer C and Hofbauer H 2011 Chem. Eng. J. 175 468-83
[4] Changjun Z, Zhiming Z, Cheng Z and Fang X 2016 Appl. Catal., B 196 16-26