

Electronic Supplementary Information

**Deoxygenation-enhanced chemical looping gasification: A
new pathway to produce hydrogen from biomass**

Zhao Sun,^{*a} Hanpeng Liu,^a Sam Toan,^b Weizhi Shi,^a Dongfang Cheng^c and Zhiqiang Sun ^{*a}

^a School of Energy Science and Engineering, Central South University, Changsha 410083, China

^b Department of Chemical Engineering, University of Minnesota, Duluth, MN 55812, United States.

^c Department of Chemical and Biomolecular Engineering, University of California, Los Angeles, CA 90095, United States.

*Email:

zhaosun@csu.edu.cn (Zhao Sun)

zqsun@csu.edu.cn (Zhiqiang Sun)

1. CLG and DE-CLBG

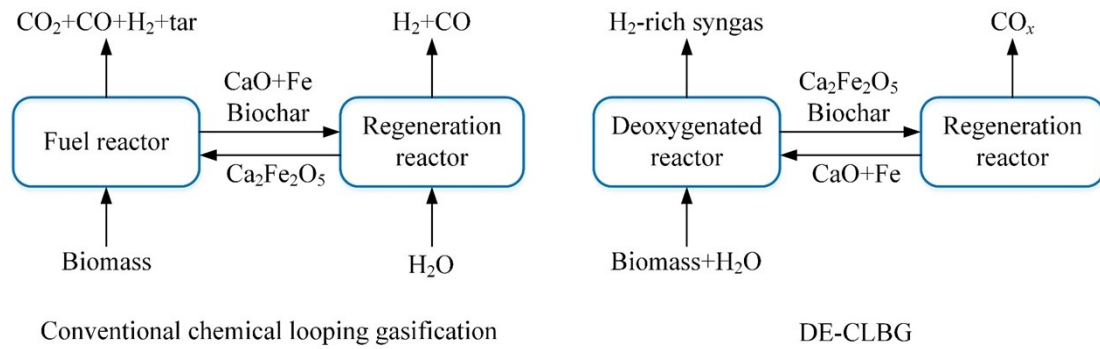


Fig. S1. Comparisons of conventional chemical looping gasification and DE-CLBG.

For conventional chemical looping gasification of biomass, the oxygen carrier provides lattice oxygen with syngas production, in which the oxygen carrier is reduced during biomass gasification. For the regeneration stage, the OC is oxidized with the achievement of H₂O splitting; while for DE-CLBG, the redox looping is exactly reverse to the conventional chemical looping gasification. Specifically, the deoxidizer is oxidized ($\text{Fe}^0 \rightarrow \text{Fe}^{3+}$) during deoxygenated gasification stage due to the existence of steam, and the deoxidizer is reduced at the regeneration stage, accomplishing the deoxygenated looping ($\text{Fe}^{3+} \rightarrow \text{Fe}^0$).

2. Effect of D/B mass ratios on the product distribution

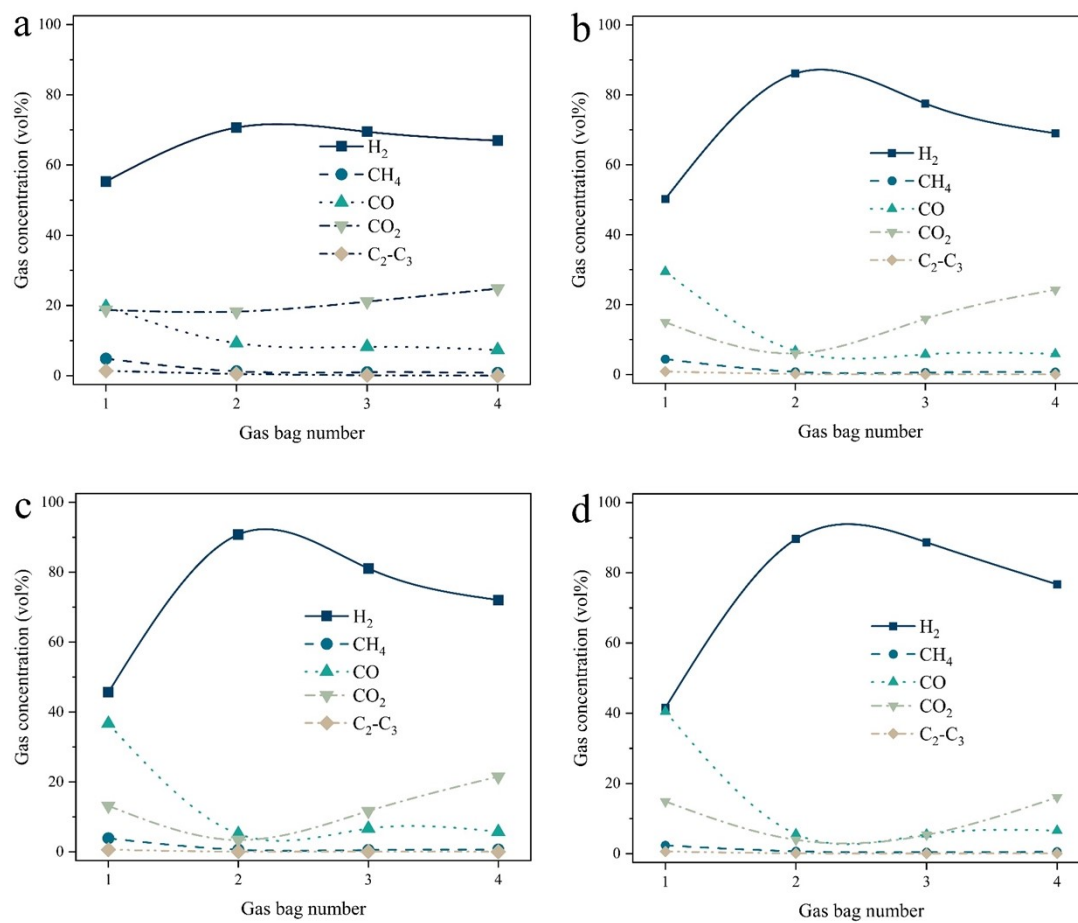


Fig. S2. Effect of D/B mass ratios on gas concentrations: (a) D/B=0, (b) D/B=0.1, (c) D/B=0.2, and (d) D/B=0.3. (Deoxygenation temperature: 680°C, water injecting velocity: 0.010 mL/min).

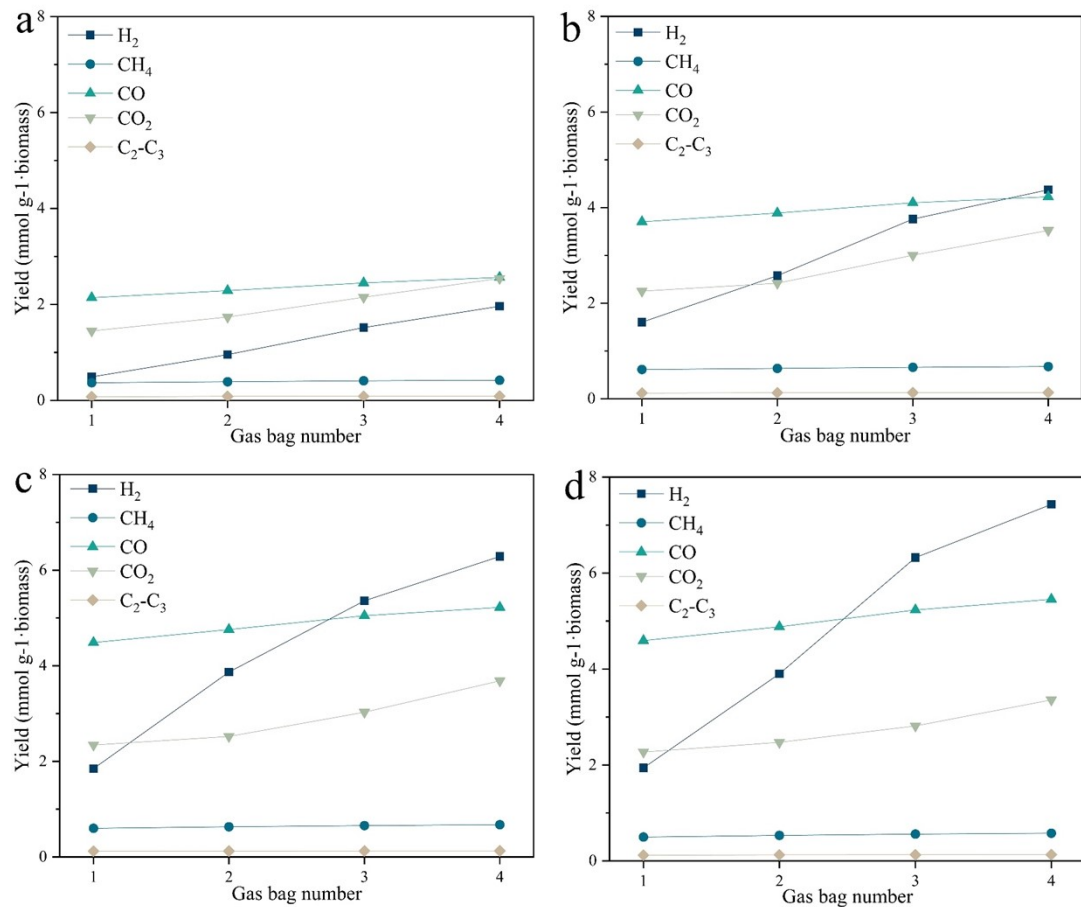


Fig. S3. Effect of D/B mass ratios on gas yields: (a) D/B=0, (b) D/B=0.1, (c) D/B=0.2, and (d) D/B=0.3. (Deoxygenation temperature: 680°C, water injecting velocity: 0.010 mL/min).

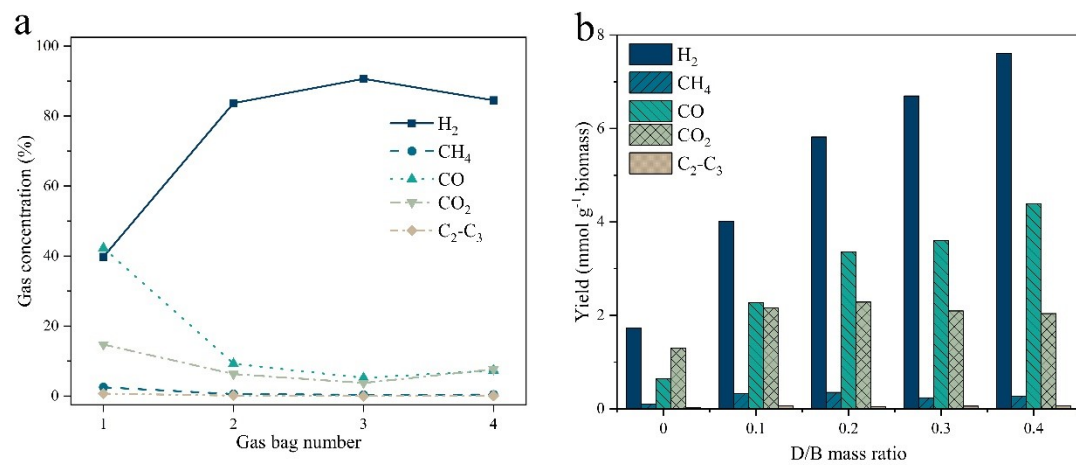


Fig. S4. (a) gas concentration on D/B=0.4 condition, and (b) gas yields with different D/B ratios.

It can be seen that the yields of H₂ and CO under D/B=0.4 increased by 13.50% and 21.48%, respectively, compared with that of D/B=0.3. Moreover, the highest hydrogen concentration reaches 90.66% during the third gas bag collection. However, it is to be noted that the excessively high content of deoxidizer addition may result in the incomplete reduction of the deoxidizer during regeneration stage, owing to limited amount of biochar left. Therefore, D/B=0.3 would be a suitable selection. To sum up, both the yields of H₂ and CO were promoted with the increase in the D/B mass ratio.

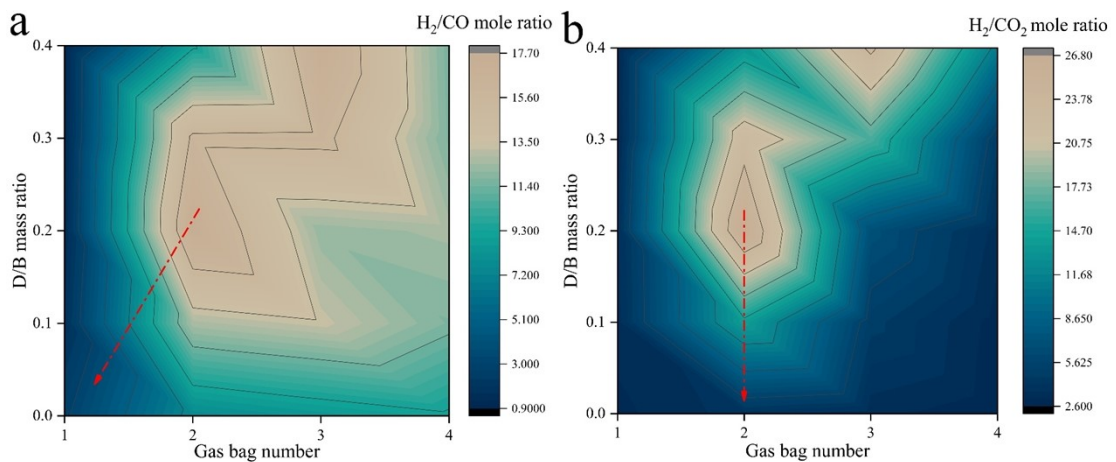


Fig. S5. Effects of different D/B mass ratios on the a) H₂/CO ratio; b) H₂/CO₂ ratio during gasification.

3. Effect of deoxygenation temperature on the product distribution

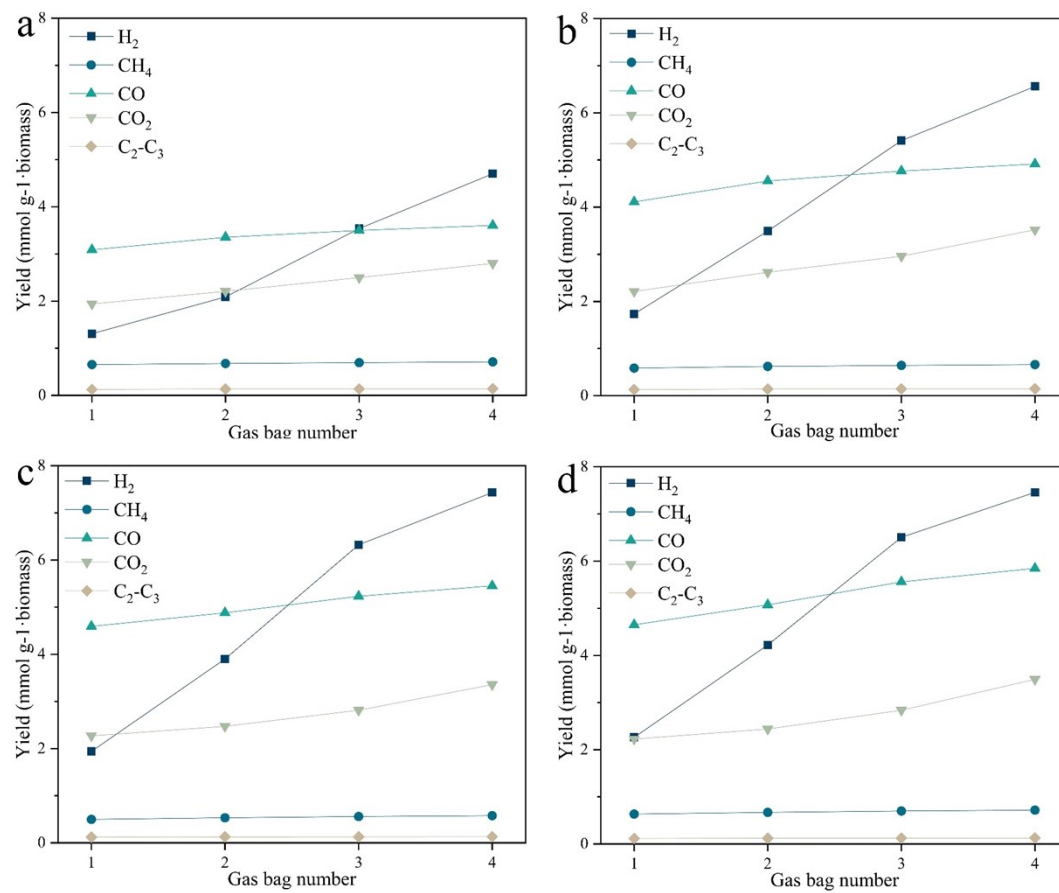


Fig. S6. Effect of deoxygenation temperature on gas yields: (a) 620°C, (b) 650°C, (c) 680°C, and (d) 710°C. (D/B=0.3, water injecting velocity: 0.010 mL/min).

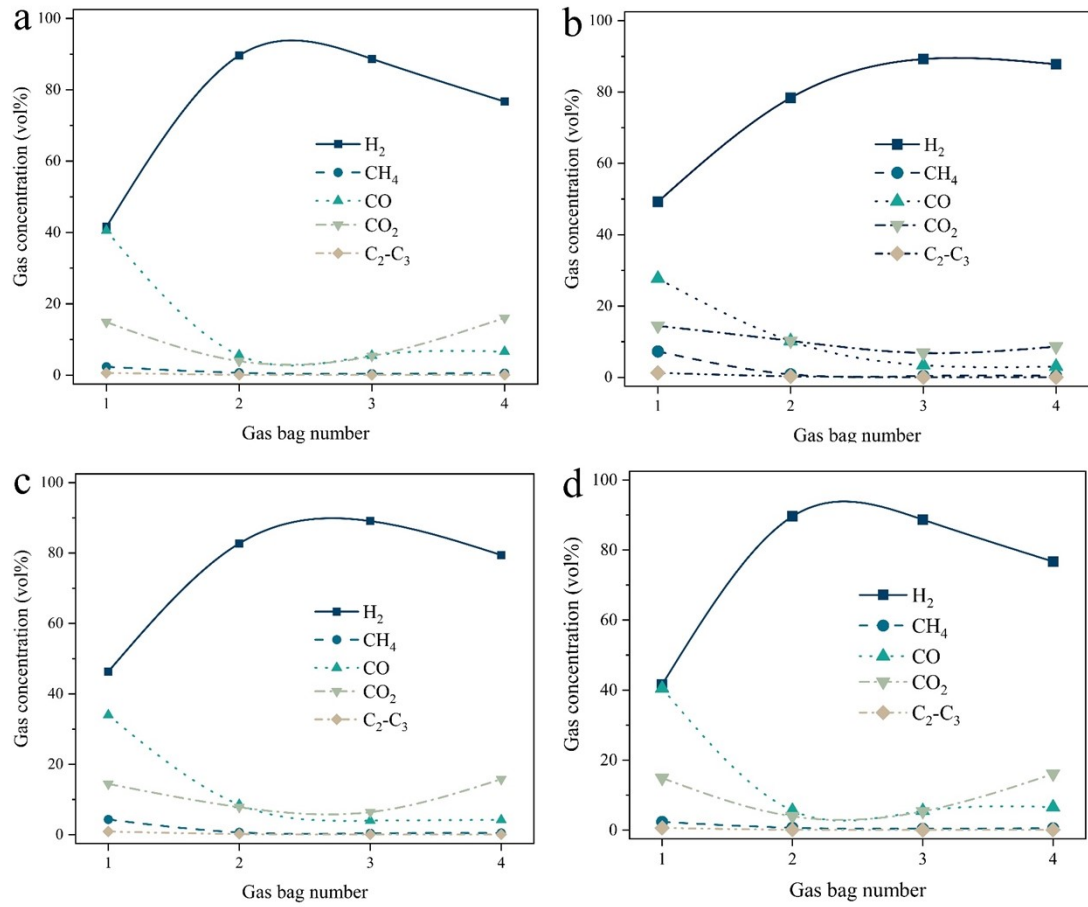


Fig. S7. Effect of deoxygenation temperature on gas concentrations: (a) 620°C, (b) 650°C, (c) 680°C, and (d) 710°C. (D/B=0.3, water injecting velocity: 0.010 mL/min).

4. Effect of water injecting velocity on the product distribution

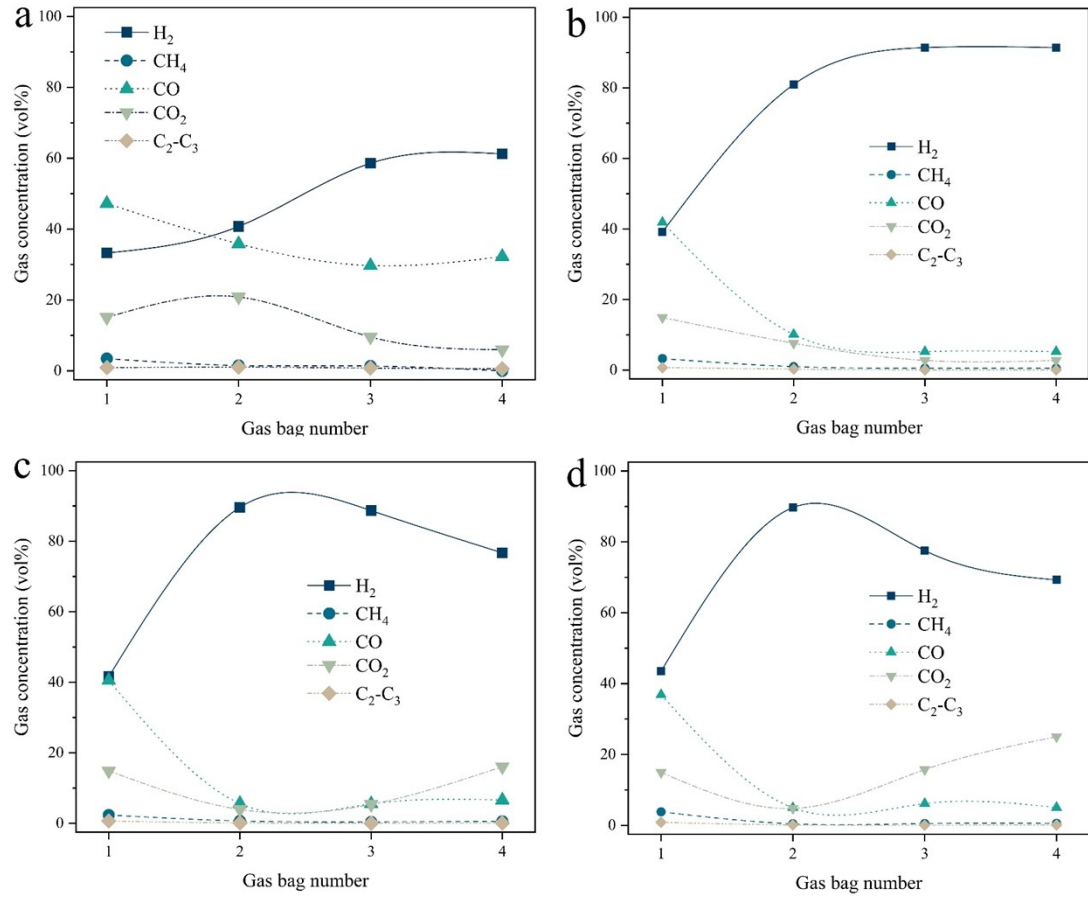


Fig. S8. Effect of water injecting velocity on gas concentrations: (a) 0 mL/min (b) 0.005 mL/min, (c) 0.010 mL/min, and (d) 0.015 mL/min. (D/B=0.3, deoxygenation temperature: 0.010 mL/min).

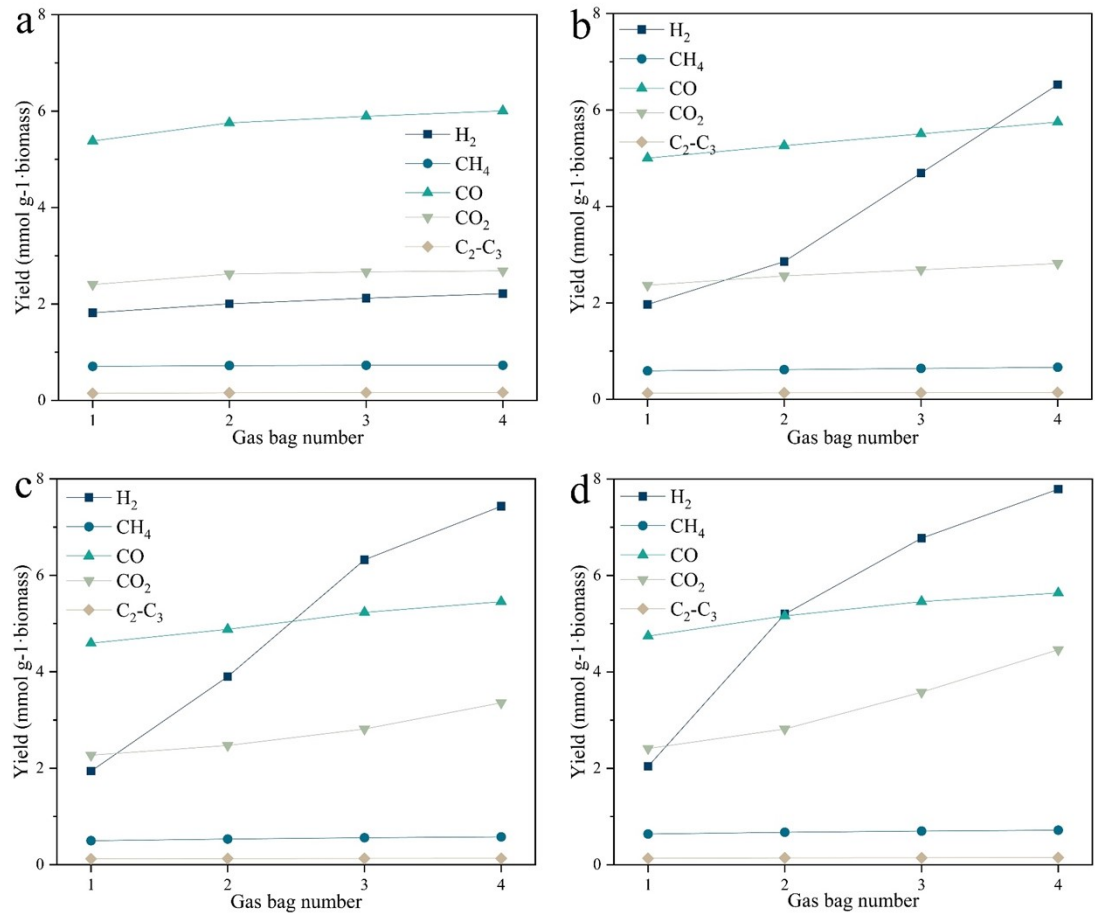


Fig. S9. Effect of water injecting velocity on gas yields: (a) 0 mL/min (b) 0.005 mL/min, (c) 0.010 mL/min, and (d) 0.015 mL/min. (D/B=0.3, deoxygenation temperature: 0.010 mL/min).

5. Characterizations

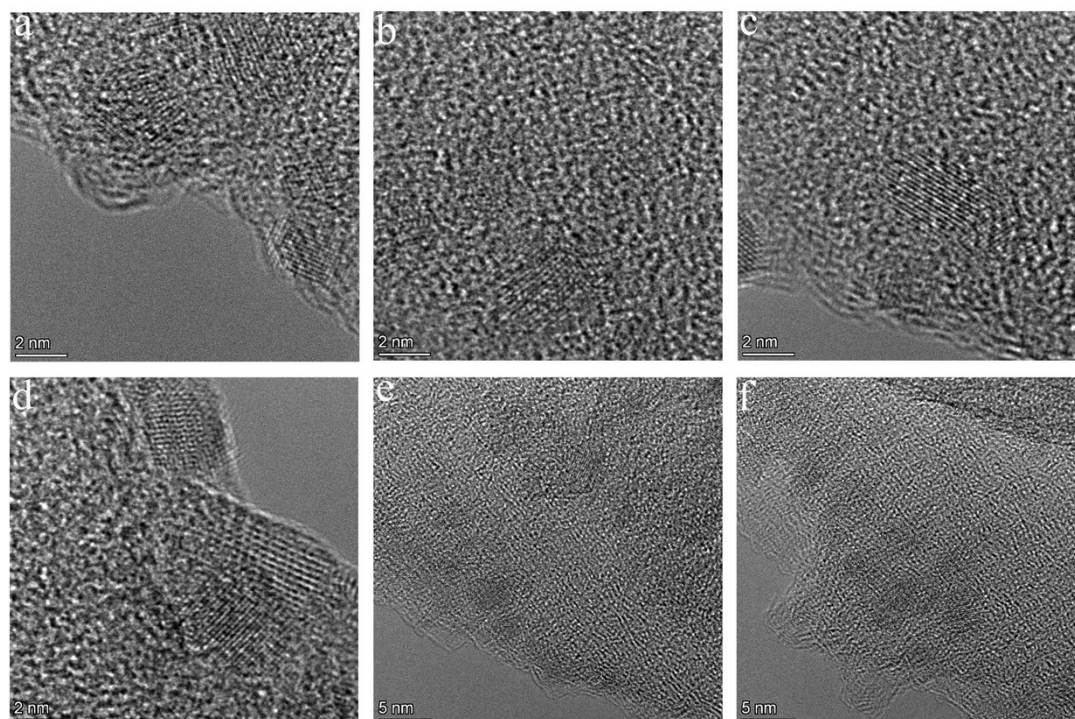


Fig. S10. The TEM images of the deoxidizer after 10 minutes' deoxygenated gasification (D/B mass ratio at 0.3, water injecting velocity at 0.010 mL/min, gasification temperature at 680°C).

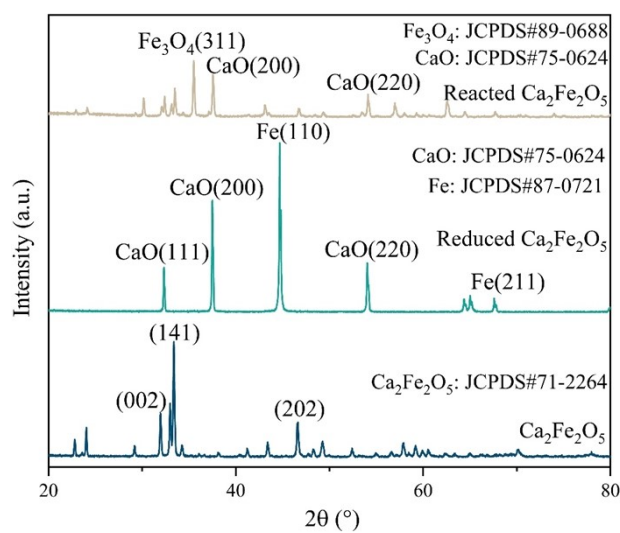


Fig. S11. The XRD patterns of $\text{Ca}_2\text{Fe}_2\text{O}_5$, reduced $\text{Ca}_2\text{Fe}_2\text{O}_5$, and reacted $\text{Ca}_2\text{Fe}_2\text{O}_5$.

6. Biochar conversion

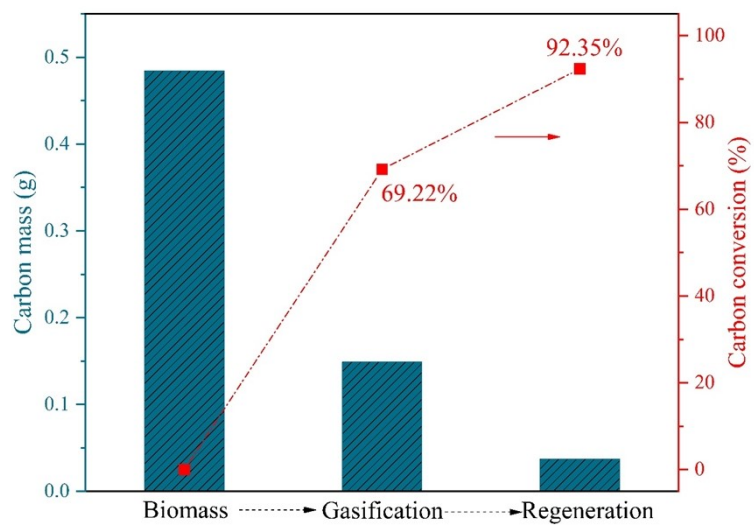


Fig. S12. Carbon mass and conversion during DE-CLBG process.