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Combustion of Coal-Derived CO with Membrane-Supplied Oxygen Enabling CO_2 Capture

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A variety of technologies are under development to capture greenhouse gas CO_2 from the combustion of coal and other fossil fuels. Among these technologies, combustion using pure oxygen rather than air, as the oxidant offers a promising means for sequestration of CO_2 in the exhaust gas stream. The main difficulty with this approach lies in the consumption of large quantities of expensive pure oxygen that is currently produced through cryogenic air separation process. A recent development in oxygen separation technology is the use of a mixed oxygen ion and electron conducting oxide as an oxygen-permeable membrane.[1–4] The membrane allows oxygen to permeate at elevated temperatures, while imperious to nitrogen and other gases. Such membranes have been explored for partial oxidation of methane to a mixture of hydrogen and carbon monoxide, a key feedstock to produce chemicals and fuels.[5,6] The other potential application of the membranes is in the integration of oxygen separation from air with the combustion of fossil fuels.[7,8]

In this article, we propose a membrane-based coal combustion process as shown in Figure 1. In this process, coal is first gasified by CO_2 through the reverse Boudouard reaction $C + CO_2 + \text{heat} = 2CO$, and the as-derived CO is burned with oxygen supplied by an oxygen-permeable ceramic membrane via a reaction $2CO + O_2 = 2CO_2 + \text{heat}$; the overall reaction is $C + O_2 = CO_2 + \text{heat}$. This process results in a hot CO_2-rich gas stream, part of which is recycled back to gasify the coal, and the rest is discharged for heat extraction and CO_2 sequestration.

Experimental Section

The experimental setup used is shown in Figure 2. For production of CO fuel, a reactor was constructed with an alumina tube of inside diameter of 1.8 cm. Coal (anthracite with composition of fixed carbon of 75.21%, moisture in the dried sample of 1.16%, volatile matter of 12.22%, and sulfur of 0.34%), or carbon powder were sieved to 0.025–0.2 mm, and filled into the alumina tube to form a bed of height of 10 cm. The reactor was heated by an electrical furnace, and the bed was located in the isothermal zone of the furnace. As a CO_2 gas stream was fed into the alumina tube, coal (carbon) was gasified, resulting in a CO-rich gas stream. For combustion of the as-derived CO, an oxygen-permeable membrane tube was used to supply the needed oxygen. The membrane tube consisted of $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ 2 (90 mol %), and $SrZrO_3$ (10 mol %), which was manufactured by extrusion followed by sintering at 1,250°C for 20 h. The membrane tube was sealed between two alumina tubes using Pyrex glass rings, and to ensure the gas tightness, a pressure was applied by a spring attached to the upper alumina tube. The compositions of the gas streams at the outlets of the gasification and combustion stages were analyzed by online gas chromatograph (Shimadzu GC-14C).

Results and Discussion

First, a coal sample was used to verify the proposed gasification-combustion process. The packed-bed reactor of coal was operated at a temperature of 950°C, and CO_2 feed rate of 20 $cm^3\ min^{-1}$. Before feeding CO_2, the coal underwent pyrolysis in a flowing helium stream to remove volatile species. As shown in Figure 3a, the gas stream at the outlet of the reactor is rich in CO. The CO production rate decreases with time, which is 30 $cm^3\ min^{-1}$ at the time of 5.5 h, and drops to 15 $cm^3\ min^{-1}$ after operation of 33 h, corresponding to the decrease of CO_2 throughput conversion from 76 to 39%. The continuous decrease in CO_2 conversion and CO production rate is due to the accumulation of the ash and the decreased amount of the coal present in the reactor. The as-derived CO was fed into a membrane tube of thickness

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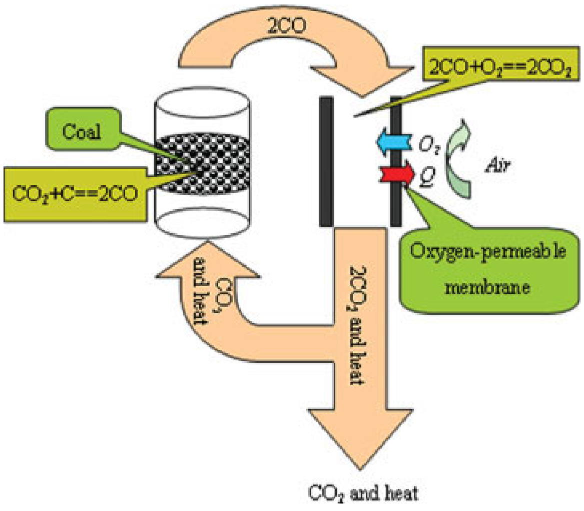

Figure 1. Combustion of coal-derived CO by membrane-supplied oxygen.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

0.12 cm, and inner surface area 7.75 cm^2. As shown in Figure 3b, after a few hours of activation for the membrane tube, CO_2 becomes the primary component at the outlet of the membrane combustion tube, and CO accordingly decreases to below the detection level, showing completion of combustion of the coal-derived CO. The stability of the membrane may pose problems. The coal-derived CO contains H_2S and other impurity gases and particulates, which might be detrimental to the operation of the membrane. In this study with the coal sample, no effect of sulfur-containing species on the performance of the membrane tube has been observed. The problem, if it occurs, may be coped with by modifying the membrane surface with sulfur-tolerant V or Mo- containing oxides,[9,10] and/or applying a cleaning step to the coal-derived CO fuel before feeding it into the membrane.

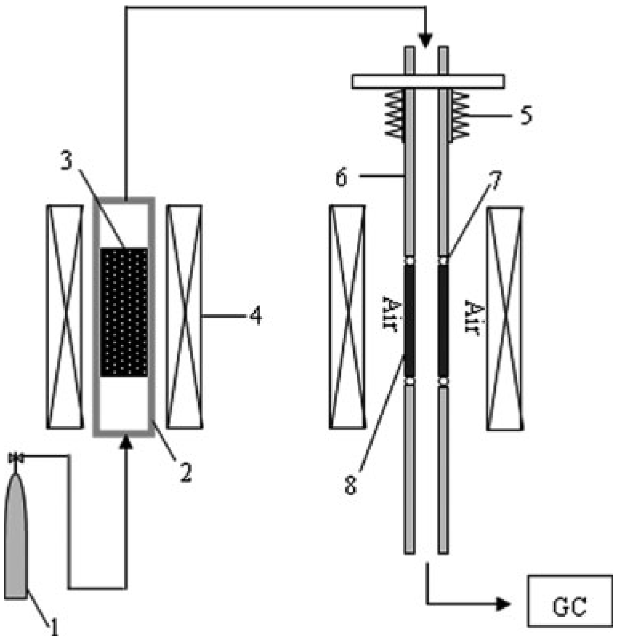

Figure 2. Experimental setup: 1, cylinder gas; 2, alumina tube; 3, coal layer; 4, furnace; 5, spring; 6, alumina tube; 7, glass sealant; 8, oxygen-permeable membrane tube.

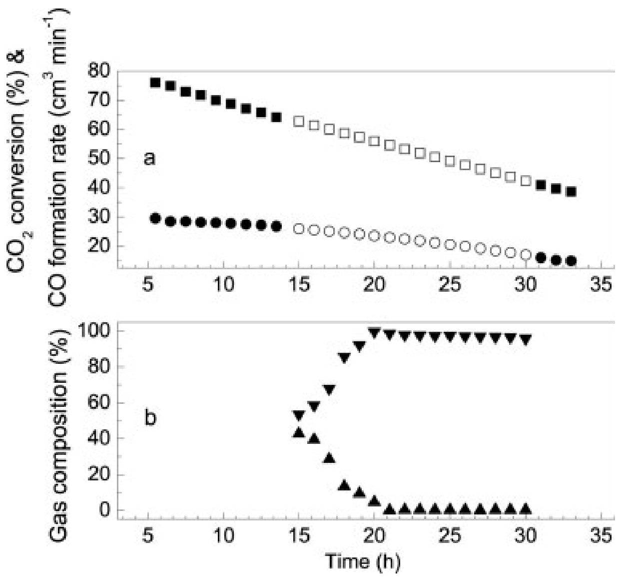

Figure 3. Verification of the gasification-combustion process with coal powders at 950°C and CO_2 feed rate of 20 cm^3 min^{-1}.

(a) Gasification stage. Square denotes CO_2 throughput conversion, circle denotes CO production rate. Full symbol denotes the data measured at the outlet of the coal gasification stage, and the open symbol denotes the data derived from the compositions of the effluents at the outlet of the membrane combustion tube and the CO_2 feed rate, and (b) Combustion stage. (▼) CO_2 content, and (▲) CO content.

The process was also verified with carbon powders. Unlike the case of coal, the rate of CO production from carbon powder now can be kept constant with respect to time, because little ash is left after gasification of the carbon, and carbon

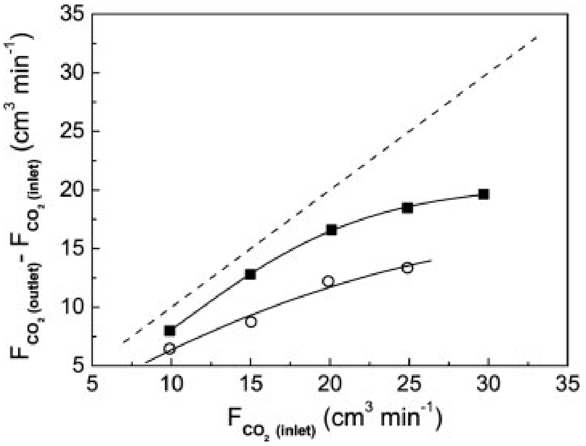

Figure 4. Verification of the gasification-combustion process with carbon powders.

Temperature: (■) 1,000°C, and (○) 950°C.

can be added into the reactor continuously. Figure 4 shows the output of CO_2 minus the input as a function of CO_2 feed rate. According to the overall reaction as shown in Figure 1, the net CO_2 output corresponds to the amount of carbon burned. It can be seen from Figure 4 that the amount of carbon burned increases with increasing CO_2 feed rate and temperature. At 1,000°C and CO_2 feed rate of 20 $cm^3\ min^{-1}$, 0.7×10^{-3} mol of carbon was burned per min, with a membrane tube of surface area 7.5 cm^2, equivalent to 16.1 kg carbon per square meter membrane surface area per day.

When the CO_2 fed into the reactor are completely converted to CO (in the presence of excess carbon), and the as-produced CO are all burned in the membrane tube, the net CO_2 output is equal to the input of CO_2 as denoted by the dashed line in Figure 4. However, it is clear from Figure 4 that the net CO_2 output is less than the input CO_2, revealing that the reaction of input CO_2 with carbon in the gasification stage and/or the reaction of CO with the permeated oxygen in combustion stage does not reach completion. To determine which stage is responsible for the previously observed deviation, the compositions of the effluents of each stage need to be analyzed.

Analysis of the effluents of the gasification stage shows that the reaction of CO_2 with carbon indeed does not reach 100%. As can be seen from Figure 5, with an increase of the CO_2 feed rate, and, thus, the decreased residence time, the CO_2 conversion decreases. As CO_2 feed rate increases from 10 to 25 $cm^3\ min^{-1}$, the conversion decreases from 74 to 58% at 950°C; at a higher temperature of 1,000°C, the corresponding conversion of CO_2 is 92 and 83%. Thermodynamic calculations shows that the conversion of CO_2 to CO is above 95% in the presence of excess carbon at given temperature. Apparently, the reaction of carbon (coal) with CO_2 is in the dynamically-controlled region. To improve the reaction kinetics, one may consider adopting a fluidized-bed reactor, which allows a better mixing of the solids, as well as improved heat and mass transfer. The addition of alkali and alkaline earth metals into the carbon may also catalyze the gasification reaction.

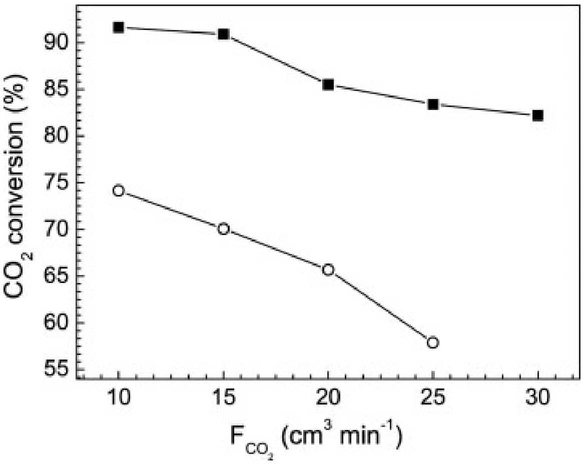

Figure 5. Reaction of input CO_2 with carbon in an alumina tube at temperature 1,000°C (■), and 950°C (○).

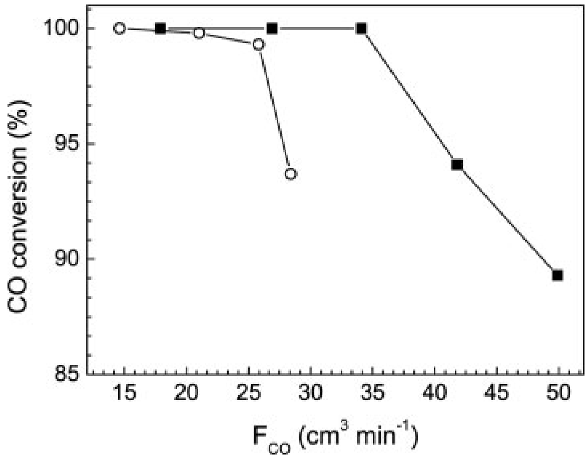

Figure 6. Reaction of CO with the permeated oxygen in the membrane tube at temperature (■) 1,000°C, and (○) 950°C.

Analysis of the effluents of the combustion stage shows that the combustion of CO neither reaches completion at higher CO fuel feed rate. As can be seen from Figure 6, at a lower CO feed rate, virtually no CO is present in the effluent gas stream, and a small amount of oxygen appears, indicating over-supply of the permeated oxygen. Whereas at a higher CO rate, oxygen is no longer detectable and some CO appears in the effluent gas stream, indicating that the oxygen is under-supplied. For an optimal combustion neither O_2 nor CO is present in the exhaust gas. As shown in Figure 6, the amount of CO that can be burned fully by the membrane combustion tube is ~35 $cm^3\ min^{-1}$ at 1,000°C, which is decreased to ~25 $cm^3\ min^{-1}$ at a lower temperature of 950°C. Obviously, the performance of the combustion stage is mainly determined by the capacity of the membrane to supply oxygen. In this regard, the most suitable form of the membrane is hollow fibers, which have very high value of membrane area per unit volume (up to 5,000 m^2 per m^3, based on the densest packing of fibers with outside diameter of 0.75 mm). However, recent progress in fabrication of the hollow-fiber membranes is likely to stimulate the application of the oxygen-separation membranes.[11,12]

Conclusions

In this work, we have proposed and experimentally verified a novel coal combustion process. In this process, coal is gasified by CO_2, and the as-produced CO is burned with oxygen supplied by a dense ceramic membrane from air. The resulting exhaust gas stream is rich CO_2, enabling efficient and convenient separation of CO_2 and clean utilization of coal. Further research and development is needed to improve the reaction kinetics of CO_2 with coal, and to enhance the capacity of membranes to supply oxygen for combustion of coal-derived CO fuel.

Acknowledgment

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