In Situ Gasification of a Solid Fuel and CO_2 Separation using Chemical Looping

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Introduction

Electricity generation accounts for ~38% of global anthropogenic carbon emissions to the atmosphere or ~2,400 Mt/y (carbon basis), projected to exceed 4,000 Mt/y by 2020.[1] To control its environmental impact, there is an urgent requirement to sequester CO_2 from the combustion of coal, or fuels derived from it, in the earth.[2] The cost of sequestration is small (for example \$4–8/t C) compared to the costs of separating CO_2 from typical flue gases[2] (\$100–200/t C), so that disposal approaches viability only if pure CO_2 is produced, largely free of nitrogen and other inert gases. One means of obtaining pure CO_2 from a power plant, burning a gaseous fuel, for example, natural gas, is to use chemical looping combustion[2] (CLC). The fuel in gaseous form is oxidized with a metal oxide, MeO, in

$$(2n + m)\text{MeO} + C_nH_{2m} \rightarrow (2n + m)\text{Me} + mH_2O + nCO_2, \tag{1}$$

to produce largely CO_2 and steam. Consequently, almost pure CO_2 is left after the steam has been condensed. The reduced form of the metal oxide, Me, can then be transferred to a different reactor, where it is reoxidized in

$$\text{Me} + 1/2O_2 \rightarrow \text{MeO} \tag{2}$$

The gas leaving this second reactor is N_2 and unused O_2. Taking reactions Eqs. 1 and 2 together, the net effect is that the fuel has been combusted, but the resulting CO_2 has been separated from the nitrogen in the air. Of course, the total heat evolved is the same as for combustion of the fuel in air. This technique for the combustion of natural gas is an active research area.[2,3] Schemes for using CLC with a solid (as opposed to a gaseous) fuel assume that the solid will first be gasified to syngas in a separate reactor before being used in a CLC cycle.[4] However, there has been no research published on using CLC with *solid* fuels directly, that is, gasification of the solid fuel *in situ* within the chemical looping reactor, largely because the solid fuel and metal oxide cannot readily be separated during the oxidation phase.

One way of applying chemical looping to solid fuels is in say a fluidized bed containing the metal-oxide. Such a reactor could be operated in a steady cycle of three consecutive periods, t_1, t_2 and t_3. During t_1, the bed would be fluidized by steam or CO_2 (or both), and coal would be fed steadily to the bed (at ~ 900°C) so that:

- the coal undergoes gasification by the steam or CO_2 to yield a synthesis gas containing mainly CO and H_2:

$$C_{(s)} + H_2O_{(g)} \rightarrow CO_{(g)} + H_{2(g)} \tag{3}$$

$$C_{(s)} + CO_{2(g)} \rightarrow 2CO_{(g)} \tag{4}$$

- the syngas reacts with the surrounding MeO particles to give CO_2 and steam by a version of reaction Eq. 1

$$\text{MeO}_{(s)} + H_{2(g)} \rightarrow \text{Me}_{(s)} + H_2O_{(g)} \tag{5}$$

$$\text{MeO}_{(s)} + CO_{(g)} \rightarrow CO_{2(g)} + \text{Me}_{(s)} \tag{6}$$

This system can only function down to a certain degree of chemical reduction of the metal oxide. Thus, after time t_1, the feed of coal ceases and the remaining inventory of bed carbon

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Table 1. Analysis of Hambach Lignite and its Char by Microanalysis (as received basis)

Material	C (wt%)	H (wt%)	N (wt%)	Incombustible residue (wt%)	Balance (mainly oxygen)
Hambach Lignite	48	5.9	0.66	3.2	42
Hambach Lignite Char	85	0.71	0.70	12	1.4

is allowed to gasify for a further period t_2, until the inventory is sufficiently small. At the end of t_2, the bed is fluidized by air instead of steam and CO_2 for a period, t_3, during which reaction Eq. 2 proceeds to regenerate the bed of oxide. During t_3 some residual carbon might be burned off, leading to a small release of CO_2 with the regenerating air, but very much less than that from the direct combustion of coal in air.

This article reports preliminary experiments to test the feasibility of the earlier technique using iron oxide (Fe_2O_3), and a lignite fuel gasified by CO_2.

Experimental

Materials. The chemical looping agent was produced from Fe_2O_3 powder (Aldrich > 99% purity), which was mixed with a small amount of distilled water, in a food mixer. The resulting particles were sieved to +300, −710 μm, and any larger lumps broken up. The procedure was repeated until a sufficient quantity of particles was in this size range. The agglomerated particles of Fe_2O_3 were then placed in a furnace, heated to 900°C, and maintained at this temperature for 5 h. The resulting particles were then sieved into two size ranges, 300 to 425 μm and 425 to 710 μm.

The fuels used were a lignite (Hambach) and its char. The char was manufactured in a bed of silica sand (sieved to 355–425 μm) contained in a quartz reactor, initially at 900°C, fluidized by N_2. The lignite (1.4 to 1.7 mm) was added slowly (~ 15 g) over ~ 30 min. The bed was then allowed to regain a temperature of 900°C, and then cooled (while fluidized by N_2) until the char could be recovered. The reactivity of a char is known to be affected by its heating history; hence, this method of producing the char would not be ideal if detailed measurements of the char's reactivity were the object of this work. However, for this study the method is sufficient. Once recovered, the char was sieved to 1.18–1.4 mm. Analyses of the char and the parent coal are given in Table 1.

Chemical Looping Experiments. Experiments were performed in a fluidized bed of either (1) 20 ml of silica, sand (+355, −425 μm) or (2) 10.308 g of Fe_2O_3 (+300, −425 μm) made up to 20 mL with silica sand (+355 μm, −425 μm), so the total mass of particles in the bed was 30.971 g. These particles were contained in a quartz tube (i.d. 30 mm) with a sintered disk for a distributor. It was fluidized by N_2 (85 mL s^{-1} at STP) mixed with either pure CO_2 (32 mL s^{-1} at STP) for gasification, or air (28 mL s^{-1} at STP) to regenerate the Fe_2O_3. U/U_{mf} was between 9 and 12. The reactor was placed in a tubular furnace and the bed was heated to 900°C, as monitored by a K-type thermocouple within the bed.

The off-gases were sampled continuously into two NDIR analyzers, one measuring [CO_2] and [CO] (with ranges of 20 mol% and 1 mol%, respectively), and the other [CH_4] and [CO] (with ranges of 6 mol% and 11 mol%, respectively), via a trap at 0°C (to remove tars, etc) with a glass wool filter and a Permapure® membrane drier (MD 070 44P), which was purged at 5 L min^{-1} with dry nitrogen. Each analyzer received 1 L min^{-1} of sample gas.

The first experiments used the bed of silica sand alone and served as a control. With the hot bed fluidized by the mixture of N_2 and CO_2, a batch (~ 0.1 g) of the char was added to the bed. The char was allowed to gasify until completion in every experiment. The experiment was repeated several times. The second set of experiments used the bed containing the particles of Fe_2O_3 mixed with silica sand. As in the first experiments, a batch of char (~ 0.1 g) was added to the bed and gasified to completion. Further batches of char were added, until it was clear that the chemical looping agent (Fe_2O_3) had been used up. At this point, the bed was reoxidized with the mixture of air and N_2; then the gasification experiment was repeated. Finally, following a further regeneration of the Fe_2O_3, the gasification experiments were repeated with the parent coal (sieved to 1.4 to 1.7 mm) added, instead of its char.

Results

Gasification of Char in an Inert Bed of Silica Sand. A typical result from such an experiment is shown in Figure 1, indicating that gasification of the char was complete within ~ 400 s. The peak rate of gasification in Figure 1 corresponded to a concentration of 1.8 mol% of CO in the off-gas from the bed. The conversion of the carbon in the char to CO, as measured from the area under the curve in Figure 1, was between 90.0% and 91.7% in 4 replicated experiments. Since a small amount of fine carbon was collected by the trap in the sampling line, the discrepancy of ~ 10% in the mass balance can be partly attributed to the elutriation of fine particles of char, once most of a batch had been gasified.

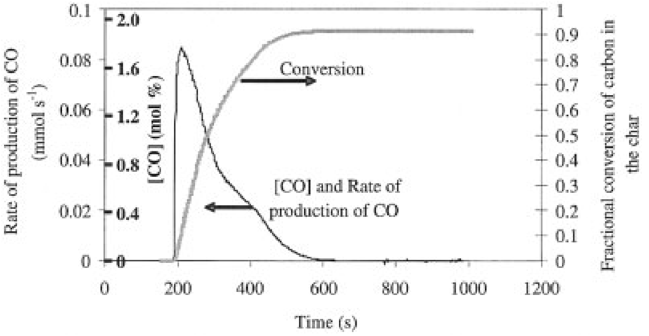

Figure 1. Rate of production of CO from a bed of sand (that is, the product of the total molar flow rate and mole fraction of CO) in which a single batch of char (0.0904g) was gasified in 27.5 mol% CO_2 at 900°C.

The corresponding mole fraction of CO and fractional conversion are also shown.

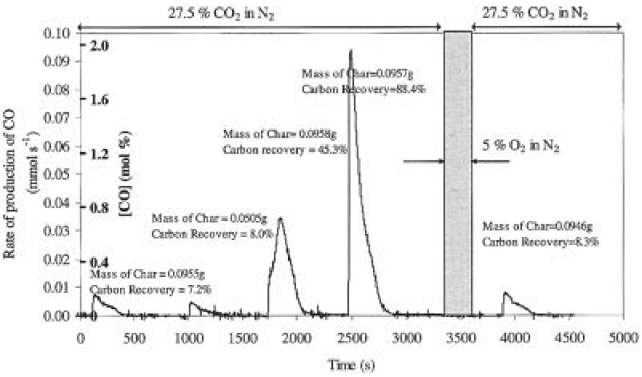

Figure 2. Series of experiments in which successive batches of char were gasified in the active bed of Fe_2O_3 and silica sand.

The bed was regenerated after the fourth batch using 5% O_2 in N_2. In each case the mass of char in the batch is shown, together with the recovery of carbon.

Gasification of Char in an Active Bed of Fe_2O_3 and Silica Sand. Figure 2 shows the results of experiments in which a batch of char was gasified in CO_2, in a bed initially of sand and Fe_2O_3 particles. In this case reaction Eq. 4 again produces CO, which is subsequently oxidized in reaction Eq. (6), by the solid particles of Fe_2O_3. The recovery is here defined as the number of moles of CO actually produced in the off-gases to the amount which would have been produced had all the carbon in the char been gasified to CO. The bed was not regenerated between the first four experiments; consequently, the ability of the Fe_2O_3 particles to react with CO was gradually reduced. The largest peak concentration in Figure 2 corresponds to ~2 mol%; it occurs when the Fe_2O_3 was fully reduced and exhausted. This is evident from the fact that the maximum [CO] agrees well with the 1.8 mol% observed with a bed of sand, in Figure 1. The very last plot for CO in Figure 2 is identical to the first, showing that all the Fe_2O_3 had been regenerated after being exposed to 5 mol% O_2 for ~5 min.

Gasification of Raw Lignite in an Active Bed of Fe_2O_3 and Silica Sand. When a batch of parent coal was added to the bed of Fe_2O_3 and sand, there was an initial, very rapid production of volatile matter, corresponding to the initial sharp spikes on the broader peaks shown in Figure 3. During devolatilization, a small amount of methane was also detected, together with the CO. The extent to which the volatiles reacted with the Fe_2O_3 in the bed is not totally clear at this stage. However, the fact that the first CO spike in Figure 3, that is associated with the volatiles, was much smaller than say the third peak, indicates that the volatiles do react with Fe_2O_3. A similar difference was also seen for the methane produced, although this is not shown. It is also noteworthy that the sampling line's filter (located in an ice bath) did not contain any tarry material. This again suggests, qualitatively, that the earlier procedure results in the improved conversion of volatile matter, including its tarry components. Of course, it is possible that the volatile matter, before it is oxidized by the Fe_2O_3, is also cracked by it.

Discussion

The earlier preliminary experiments demonstrate that it is possible to use a solid fuel, such as coal, directly within a chemical looping cycle, involving gasification of the char, as well as combustion of both the volatiles and the products of gasification by reaction with Fe_2O_3. Despite the fact that the chemical looping agent used (pure Fe_2O_3) was not optimized, it was still able to burn most of the CO produced by the gasification of the carbon. Mattison et al.[5] found that natural hematite (Fe_2O_3) became porous and fractured when subjected to several cycles of reduction in methane, followed by oxidation in air. There is a wealth of literature on the production of particles suitable for chemical looping, using iron[5,6] and other metallic oxides.[7] Thus, there is considerable scope to engineer particles suitable for chemical looping, using iron or other metals.

In this work, the same active bed was used for all experiments. In fact, although the iron-oxide particles were actually reoxidized three times in Figures 2 and 3, the particles did not appear to degrade during these reduction-oxidation cycles, in that the bed recovered its initial reactivity when reoxidized. Further experiments are being done to determine how many oxidation/reduction cycles the Fe_2O_3 can usefully endure.

If it is assumed that the Fe_2O_3 in the bed reacts to form Fe_3O_4 in reactions Eqs. 3 and 6, so that the overall reaction in the system is

$$C + CO_2 + 6Fe_2O_3 \rightarrow 2CO_2 + 4Fe_3O_4 \qquad (7)$$

the theoretical capacity of a bed (containing 10.308 g of Fe_2O_3 as above) is 0.0106 mol of carbon. The assumption that the Fe_2O_3 reacts to form only Fe_3O_4 (rather than $Fe_{0.947}O$ or metallic Fe) can be justified by the following thermodynamic argument. For the reaction

$$0.788CO + 0.947Fe_3O_4 \rightarrow 0.788CO_2 + 3Fe_{0.947}O \qquad (8)$$

the equilibrium constant $K_p = (p_{CO_2}/p_{CO})^{0.788} = 1.749$ (using NASA-Glenn thermodynamic coefficients[8]) at 900°C. Thus, at 900°C, for the Fe_3O_4 to be reduced to $Fe_{0.947}O$ would require $p_{CO}/p_{CO_2} > 0.49$, which it was not. A rough estimate of the actual capacity of the bed can be calculated by noting that in Figure 2, the Fe_2O_3 had been depleted after the third batch had been added. Using the difference in yields of CO between the inert bed of sand and the active bed containing Fe_2O_3, the amount of carbon consumed by reaction Eq. 7 was 0.0117 mol, in close agreement with

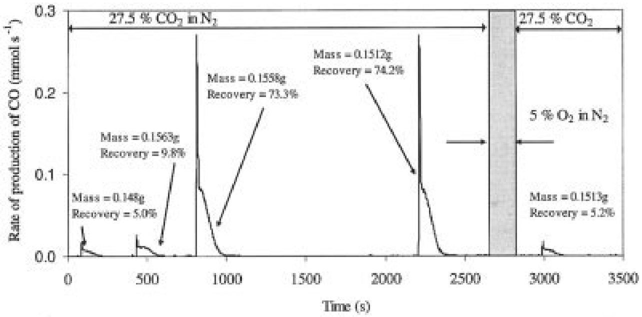

Figure 3. Series of experiments in which batches of coal (+1.4 mm, −1.7 mm) were gasified in the active bed of Fe_2O_3 and silica sand.

The bed was regenerated after the fourth batch using 5% O_2 in N_2. The mass of coal used in each experiment is shown.

the earlier theoretical value of 0.0106 mol. Although this calculation is relatively coarse, it does indicate that the Fe_2O_3 goes completely to Fe_3O_4. In future work, the composition of the solid will be measured directly by x-ray diffraction.

Conclusions

- It is possible to use chemical looping with a solid fuel, such as coal, provided a gasification agent like CO_2 is introduced into the reactor. The gasification agent converts solid carbon to CO the gas phase, where it can be oxidized, together with any H_2 from reaction 3, by the solid oxygen carrier, for example Fe_2O_3.
- The heights and durations of the peaks for CO in Figures 1 to 3 indicate that gasification is probably the rate-limiting step. Consequently, the reaction of these sintered compacts of for example, Fe_2O_3, appears to be sufficiently rapid at 900°C to make the earlier cyclic process feasible and worthy of further investigation.

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BOOK REVIEW

COSMO-RS, From Quantum Chemistry to Fluid Phase Thermodynamics and Drug Design

By Andreas Klamt, Elsevier Science, 2005, 246 pp., $165.00.

This book gives a comprehensive overview of the wide range of problems that can be addressed with the COSMO-RS method for predicting thermodynamic properties of pure and mixed fluids which are important in many areas, ranging from chemical engineering to drug design. It is a high-quality reference book written in a clear and self-consistent style by the creator of this novel approach for predicting vapor-liquid equilibria, based on *ab-initio* calculations of molecular interactions in a fluid mixture.

After an excellent and concise description of models used for describing solvation effects in quantum calculations in which he summarizes the equations used in a easy to read format, the author clearly underlines the advantages of COSMO model in which the surrounding medium is modeled as a conductor rather than as a dielectric in order to establish the initial boundary conditions. The assumption that the solvent is well modeled as a conductor simplifies the electrostatic computations, and corrections may be made *a posteriori* for dielectric behavior. By adopting a stepwise and methodological approach for explaining the physics of the COSMO theory, the author reveals the logical sequence of the choices he has done, as well as their implications.

Charge surfaces and charge distributions profiles of isolated molecules obtained through QM-COSMO calculations are used as quantitative molecular descriptors for characterization of their electrostatic behavior in different solvents. The author introduces then the concept of COSMO-RS/COSMO*therm* methodology for predicting several macroscopic properties for a wide variety of molecular mixtures simultaneously in a unified framework with few parameters from COSMO molecular surface polarity distributions, unlike group contribution methods which depend on large experimental databases or quantitative structure-property relationships (QSPR).

The specific problem of predicting vapor-liquid equilibria of fluids and fluid mixtures, based on theory and realistic models requires a combination of different computational approaches, going from the quantum electronic-structure theory of the isolated molecule to statistical physics description of fluid mixtures. In bridging this gap, this text provides what I believe to be an original, comprehensive, careful, meticulous, and clear development.

The book combines advances in fundamental scientific knowledge with novel computational technology for industrial applications in fluid phase thermodynamics and drug design. It will be helpful to both students and academic researchers and industrial experts in computational chemistry, theoretical chemistry, molecular simulation, physical chemistry and chemical engineering. The book will also particularly suit those researchers who use commercial "molecular modeling" software, by allowing them to understand more fully what they can and cannot do with such packages. I believe that Andreas Klamt's book will substantially contribute to the recognition of the fact that computational chemistry is serious science that promises new ways to tackle the problems of real-world applications.

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