A PRACTICAL ROUTE FOR GREENING OF COAL

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Introduction

Global surface temperature anomaly yields serious consequences in the inhabited environment, which is considered responsible for the rising of sea levels, shrinkage of snow-covered areas, shortage of fresh water, and the disasters caused by abnormal weather. Accumulation of CO_2 in the atmosphere is considered responsible for the global temperature anomaly, and industrial activities have accelerated the CO_2 accumulation because of the combustion of fossil fuels. The rate of economic development is much faster in the early years of the 21st century than ever before. Therefore, the rate of CO_2 accumulation in the atmosphere is definitely much faster than past. Although coal is not clean, it is indispensable energy source of the world for quite a long time[1] as shown in Fig. 1. Therefore, more development of economy will result in heavier pollution of environment. However, complete greening of coal will radically solve environmental problems, and the fast knot between economic development and the environmental pollution is unlocked.
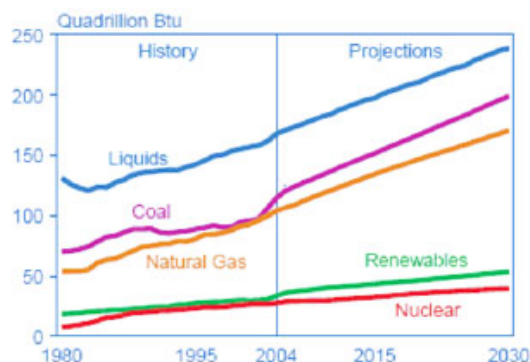

Fig. 1. World marketed energy use by fuel type for 1980-2030.

Complete greening of coal is different from any clean coal technology available presently. The latter cannot reduce CO_2 emission because the fuel still contains the element of carbon. The former changes coal to hydrogen, therefore, stops CO_2 emission. The Hymelt Process [2] is a typical technology of changing coal to hydrogen presently available. Coal is decomposed under the catalysis of molten iron and a gas mixture containing hydrogen is obtained. Some carbon is also produced in decomposition and the carbon is dissolved in molten iron. Oxygen reacts with molten iron in another reactor, and the dissolved carbon was taken out of iron yielding CO-rich gas. The process operates at temperatures as high as 1400-1800 ^{o}C. Such technologies feature in the fact that coal is the source of hydrogen, therefore, hydrogen is not the unique fuel obtained. The HydroMax process [3,4] produces pure hydrogen, but uses molten iron to react with steam and uses solid carbon to reduce iron

oxide back to pure metal. The latter operation is just a typical metal smelting process. Another water-splitting process basing on the Fe_3O_4/FeO cycle [5,6] releases oxygen at an elevated temperature to realize the cycle. Extra energy is paid for keeping operations cycling between two temperatures, and the huge thermal capacity of real reactors renders the cycle a very slow process.

Proposed Strategy

The process
In the complete greening technology of coal, coal is assumed to convert to inorganic carbon. Hydrogen is produced in a cycle consists of three reactions:
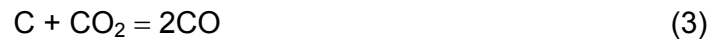
1. Oxidation of FeO by steam at about 800^oC. The product is pure hydrogen and Fe_3O_4/Fe_2O_3.

$$H_2O + 3\ FeO = H_2 + Fe_3O_4 \tag{1}$$
Or
$$H_2O + 2\ FeO = H_2 + Fe_2O_3 \tag{1a}$$
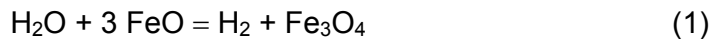
2. CO is used to reduce Fe_3O_4/Fe_2O_3 at same temperature. The product is FeO and CO_2.

$$Fe_3O_4 + CO = 3\ FeO + CO_2 \tag{2}$$
Or
$$Fe_2O_3 + CO = 2\ FeO + CO_2 \tag{2a}$$
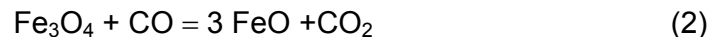
3. The above produced CO_2 reacts with carbon at about 900^oC generating the CO required in Reaction 2.

$$C + CO_2 = 2CO \tag{3}$$
Summing up reactions (1-3), a general reaction is obtained:
$$H_2O + C = H_2 + CO \tag{4}$$
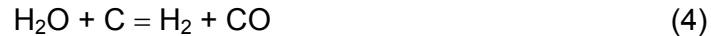
Theoretical energy balance
To evaluate the viability of a novel process, theoretical energy gain (TEG) of the process was defined as the ratio of theoretically releasable energy by the process products over the theoretically invested energy in order to acquire the products. A process must not be energetically feasible if the TEG is less than unity. The theoretical energy input and output is calculated on the basis of general reaction and formation enthalpies at 298 K.[7] The energy input of the process is: (-110.54)-(-285.83) = 175.29 kJ. The theoretically releasable energy of the products is determined from the combustion reactions:

$$H_2 + 1/2O_2 = H_2O$$
$$CO + 1/2O_2 = CO_2$$

The enthalpy change of the above reactions is -285.83 and –282.97 (-393.51+110.54) kJ, respectively. The energy gain is, therefore, (285.83+282.97)/175.29 = 3.24. The energy input required by the whole process, 175.29 kJ, is only 62% of that releasable by CO (282.97 kJ), therefore, the process is energetically more than autarky.

Experimental proof
Practical feasibility of the process was experimentally proven.[8] Pure hydrogen could be continuously produced in a process shown schematically in Fig. 2. In order to increase the reaction interface, iron oxide was dispersed on the surface of silica SBA-15. Composition of the effluent stream from a reactor was analyzed with a mass- spectrograph. Pure hydrogen

was produced in the oxidation period, and it was really obtained as is shown in Fig. 3.The reduction period is very important for the continuous production of pure hydrogen, though the period does not produce hydrogen. The reduction extent of iron oxides must be under control to avoid the product of metal iron since fresh iron is very tiny particulate and easily carried out from the reaction zone. The temperature and atmosphere of the reduction must be carefully tuned. Both oxidation and reduction reactions were kept at 800 ^{o}C, and a proper ratio of CO vs. CO_2 was maintained in the reduction period. Carbon is consumed as the source of carbon monoxide, but not as reductant to favor the control of reduction extent and to keep the hydrogen pure. The production rate of hydrogen will be stable in so doing as shown in Fig. 4. Avoidance of forming metal iron avoids the formation of iron carbide because metal iron is the prerequisite condition of forming iron carbide for temperatures higher than 628 ^{o}C.[9] Iron carbide can hardly form at 800 ^{o}C even H_2 joined the reducing gas.[8,10]
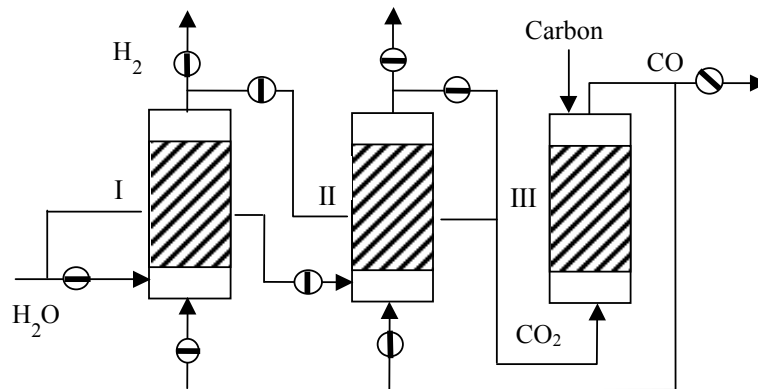

Fig. 2. A process for continuous operation. Reactors I and II are packed with iron oxide support and Reactor III is packed with carbon.
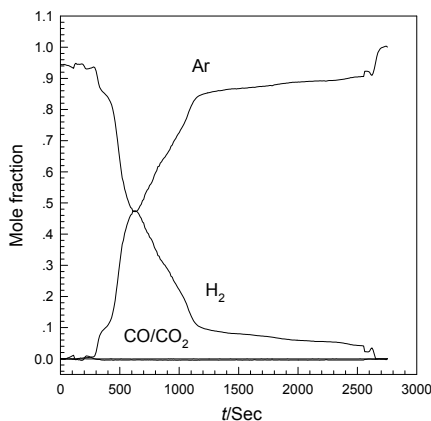

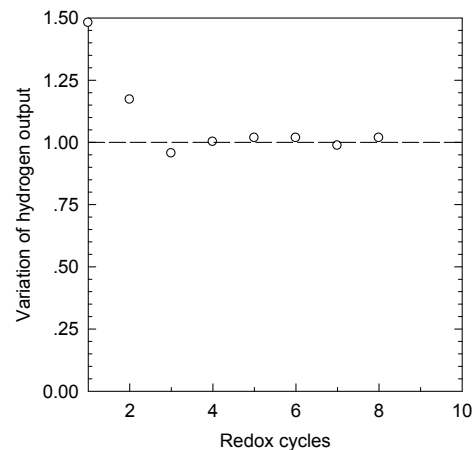**Fig. 3.** Composition of the effluent stream during oxidation period (Ar is carrier gas).

Fig. 4. Stability of hydrogen production in consecutive reduction/oxidation cycles using a mixture of CO and CO_2 as reducing gas.

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Scenario of green energy unit

To satisfy the energy requirement of the hydrogen production process, 62% of the produced CO is burnt, and CO_2 is generated. Aside from CO_2, N_2 is also enriched in the flue gas of the combustion. Therefore, CO_2 and N_2 are by-products of the process if a separation operation is applied for flue gas. The 38% of produced CO is output as another by-product. CO is one of the initiating chemicals of many green synthesis processes and has eight times higher market value than hydrogen. Therefore, the process is economically profitable. The combined processing units may look like that shown in Fig. 5.
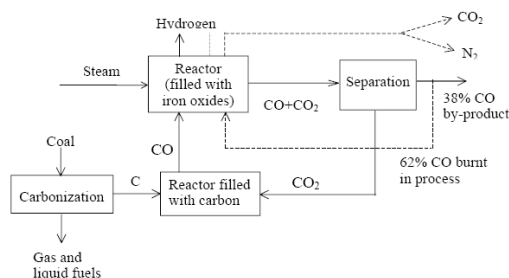

Fig. 5. Combined processing units.

There are three green ways to dispose the produced CO_2. One is to inject CO_2 into some oil fields aiming to increase oil recovery.[6] Another is to inject CO_2 into the reservoirs of natural gas and five times higher output was observed[11] while CO_2 is concealed in the reservoir. The third one is to inject CO_2 into the sediments of flammable ice to replace CH_4 as the guest gas of hydrates.[12] Therefore, there would be not CO_2 emitting into atmosphere.

The process is technically simple, and there is not any technical barrier towards industrialization. Coal is not the exclusive source of carbon, but is the one a national economy can rely on. The carbonization technology of coal is already matured, though the advanced technology has not been widely applied. More liquid and gaseous fuels are produced in the process of coal carbonization if supercritical extraction is utilized,[13] and the ever increasing petroleum price would subject a heavy impact if the proposed energy strategy be seriously considered. Coal bears the largest ratio of carbon to hydrogen compared to liquid or gaseous fuels, and the decrease of CO_2 emission is more than proportional if coal is replaced with hydrogen. A fast improvement in the world environment is definitely promising.

Acknowledgements

References

1. International Energy Outlook 2007, web site www.eia.doe.gov/oiaf/ieo/index.html.
2. T.D. Trowbridge, D.P. Malone (2001), "The Hymelt Process - Potential for revolutionizing the hydrogen industry," [325d] Annual AIChE Meeting, Nov. 4-9, At Louis, Missouri, USA.

3. http://www.alchemix.net. "Alchemix Corporation Hydrogen Technology."

4. J.K. Kindig, R.R. Odle, T.E. Weyand, B.R. Davis (2002), "Method and apparatus for the production of hydrogen gas," US Patent Application Publication Sep.12, Pub. No. US 2002/0127178A1.

5. F. Lemort, P. Charvin, C. Lafon, M. Romnicianu (2006), "Technological and chemical assessment of various thermochemical cycles: From the UT3 cycle up to the two steps iron oxide cycle," *Int J Hydrogen Energy*, 31, 2063-75.

6. Ministry of Petroleum and Energy, Norway (2007), "Use of CO_2 to increase oil recovery," web site http://www.regjeringen.no/ published August 20.

7. J.A. Dean (1999), Lange's Handbook of Chemistry, 15th Ed. New York, McGraw-Hill.

8. Y.P. Zhou, C.X. Jia, Y. Zhang, C.F. Liu, D.S. Huang, Y. Sun, L. Zhou (2008), "Experimental Study on a New Process of Producing Hydrogen in Consumption of Water and Coal," *AIChE J*, 54 (5) 1388-1395.

9. L.K. Liang, Y.C. Che (1990), "*Metallurgy Thermodynamics and Dynamics* (in Chinese)," Shenyang, Northeast Institute of Technology Press.

10. D.Y. Wang, Y. Min, C.J. Liu, P.Y. Shi, M.F. Jiang (2007), "Study on iron carbide production with CO-CO_2-H_2 mixing gas," (in Chinese) *The Chinese J Process Eng*. 7, 332-336.

11. C.M. Oldenburg, K. Pruess, S.M. Benson (2001), "Process modeling of CO_2 injection into natural gas reservoir for carbon sequestration and enhanced gas recovery," *Energy Fuels*, 15, 293-298.

12. J.H. Yoon, T. Kawamura, Y. Yamamoto, T. Komai (2004), "Transformation of Methane Hydrate to Carbon Dioxide Hydrate: In Situ Raman Spectroscopic Observations," *J Phys Chem A*, 108, 5057-5059.

13. S.C. Guo (1991), *Chemical Technology of Coal*, Beijing, Metallurgical Press.