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HYDROGEN PLANT**

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Adding Value to Coal as Feedstock for a Hydrogen Plant

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Coal is the largest fossil energy resource and, in spite of its 19th century image, coal has proven itself in the last quarter of the 20th century as a modern and remarkably cost-effective fuel for generating electric power. Today, with increasing concern over greenhouse gases, coal needs to overcome the obstacle of being the most carbon intensive energy source there is. To clear this hurdle and provide a modern and environmentally viable energy resource based on abundant coal reserves is the goal of Vision 21. The strategy of Vision 21 rests on the production of high-quality gaseous fuels like hydrogen that could either leave the plant or could be in the production of electricity by highly efficient fuel cell stacks.

Here we outline three processing steps, that combined or separately can greatly reduce greenhouse gas emissions from coal, (see Figure 1). First, we propose to perform the gasification and water-gas shift reaction for producing hydrogen from coal with calcium oxide as a getter for carbon dioxide. This provides an efficient means to collect the carbon dioxide for reuse or disposal. Simultaneously, the carbonation facilitates the formation of hydrogen and provides the energy necessary to drive the hydrogen producing reaction to completion. In the second step, the calcium oxide would be regenerated either by a conventional calcination process or, as we propose to investigate, in a solar furnace. The latter approach would lead to a novel hybrid solar/fossil power plant that derives about 30% of its energy output from solar energy. Finally, we propose to develop a solar driven process, that generates methanol from waste carbon dioxide. In a photolytic process, CO₂ is broken up into CO and O₂. The CO is then reacted with water in a conventional process to form methanol. This process, which appears cost-effective, would provide a high quality feedstock or transportation fuel and thereby drastically reduce greenhouse gas emissions from coal use.

Figure 1: Sketch of the proposed process steps in the context of a Vision 21 plant. The calcium oxide based shift gasifier replaces the gasifier and shift reactor in the standard design. Instead of an air separation plant, this design requires a calcination furnace that is either heated by a standard combustion process or, as suggested here, by a solar furnace. The photolytic production of methanol provides a renewable fuel that effectively gets a second use from the fossil carbon. Note that in this design the only energy inputs are in the calcination unit and in the photolysis unit. The chemical energy stored in the coal is carried over in its entirety into the hydrogen product. To complete the hydrogen production, the energy has been augmented by the heat of the calcination or carbonation process. Overall the energy available per unit of carbon has been greatly increased. For a mass and energy balance see the text below.

In the long term, Vision 21 for the use of coal is likely to succeed, simply because of the large reserves and ready availability of coal. In the short term, natural gas is a formidable competitor with the advantage of a much higher heat of combustion per mole

of carbon. Combined with the higher efficiency of a combined-cycle gas turbine power plant, carbon dioxide emissions are roughly half that of conventional coal fired power plants. This advantage, however, can be offset by the intrinsically lower cost of coal.

For coal to remain a long term competitor, it is important to view coal not as a fuel but as a chemical feedstock that is used to manufacture high-grade fuels like hydrogen or liquid hydrocarbons for use in transportation. Coal as well as other fossil fuels can provide high quality "designer fuels." Developing such fuels is desirable; they are cleaner, they allow for higher efficiency, and by making fossil fuels virtually interchangeable, they increase competition, which in turn lowers fuel prices. Such a scenario is highly desirable for the economy at large; and coal is a strong competitor in this arena due to its high availability and low cost.

In view of the global climate challenge and the desire to reduce greenhouse gas emissions, it is very important to reduce the overall emissions of CO₂ from coal-based fuels. Greenhouse emissions can be reduced in three fundamentally different ways, all of which we intend to contribute to. First, increased efficiency of fuel production and fuel use reduces carbon dioxide production. Second, supplementing fossil power production with renewable energy, wherever the latter is particularly efficient, also lowers greenhouse emissions. Finally, sequestration and disposal or reuse of carbon dioxide provides a very direct avenue for the elimination of greenhouse gases. Using carbon dioxide as feedstock for a synthetic fuel produced with renewable energy is a particularly promising way of combining renewable and fossil energy. This approach essentially doubles the carbon efficiency of the fuel.

The ideas outlined below are based on the interactions between two different projects that have been underway at Los Alamos for some time. One is the disposal of carbon dioxide in mineral form, the other is the photolytic production of methanol from carbon dioxide. The investigators realized some time ago, that both concepts have in common the need for an efficient collection of carbon dioxide from a power plant. This led to the idea of using calcium oxide for capturing the CO₂ from a power plant. The CO₂ once captured is released in a subsequent calcination step which allows the reuse of the

calcium oxide and the further processing of the carbon dioxide. We soon realized that this approach would be of particular advantage in generating hydrogen from coal. In this case it would not only provide carbon dioxide in a convenient form, but it also could make the process more efficient. A major advantage is that our approach completely avoids the pure oxygen driven gasification step that is currently envisioned and which requires the costly and energy consuming separation of oxygen from air. By increasing the energy efficiency of hydrogen production, we reduce the overall greenhouse emissions from the power plant.

In the photolytic production of methanol, carbon dioxide is heated to high temperatures with solar energy. Thus it became evident, that solar energy could also be used in the calcination of the carbonate product from the power plant. The solar calcination furnace also provides a stepping stone towards the methanol production. It would demonstrate the ability to design cost-effective, high-temperature solar furnaces on an industrial scale. This is an important prerequisite for the photolytic methanol production. The solar furnace is, however, valuable in its own right, as it would provide the heat of calcination from solar energy rather than from additional coal. This would reduce the greenhouse gas emission of the plant by 30% without affecting its hydrogen or power output.

Finally, the photolytic process to generate methanol would allow a second use of the carbon that is oxidized in the power/hydrogen plant. This reuse reduces greenhouse emissions even further. Thus, our three-pronged research approach, which includes the development of the calcium oxide supported water-gas shift reaction, the solar calcination of calcium carbonate, and the solar driven photolytic production of methanol from carbon dioxide, provides an integrated research approach that fits exceedingly well with the goals of Vision 21. A successful conclusion of this work would augment carbon dioxide sequestration options because it provides a particularly elegant method of collecting the carbon dioxide that is to be disposed. Our work would not only strengthen the existing effort in mineral sequestration of carbon dioxide at Los Alamos, but also any other sequestration option that needs a cost-effective means of collecting the carbon dioxide.

Calcium Oxide in the Water Gas Shift Reaction

Calcium oxide is an efficient getter for carbon dioxide. The carbonation reaction is quite exothermic and below 900°C to 1280°C (at 1 bar to 110 bar respectively) it is thermodynamically favored.

Combined with the water gas shift reaction, one obtains the following reaction,

Again this reaction is favored by free energy over a wide temperature and pressure

Figure 2: Free Energy of the reaction $\text{CaO} + \text{C} + 2\text{H}_2\text{O} \rightarrow \text{CaCO}_3 + 2\text{H}_2$ as function of temperature.

regime. The free energy change is independent of pressure, as the number of gas molecules is the same on both sides of the reaction. The Gibbs free energy of the reaction is shown in Figure 2 as a function of the temperature. As can be seen from the Figure, in the temperature regime of interest thermodynamics favors the formation of calcium carbonate and hydrogen.

A major advantage of the calcium oxide supported gasification is that the hydrogen generation can be performed at lower temperatures and pressures and

most importantly it does not require any additional oxygen to provide the energy balance. The additional energy balance is now provided by the heat of carbonation which amounts to about 40% of the heat of the combustion from carbon to carbon dioxide.

Since large sources of natural calcium oxide are not available, the energy of carbonation needs to be provided externally. We envision that the calcium oxide is

recycled and reused after calcination. The calcination could be performed in a conventional manner or, as we outline below, in a solar furnace.

The major research issue in this part of the project is to demonstrate the CaO driven hydrogen formation, to determine the kinetics of the reaction, and to provide the CaO in a form that is stable against sintering and other degradation phenomena that might otherwise slow down the reaction rate in repeated use. In addition one would have to study the interaction with coal impurities. Relative to other alternatives our method may be particularly well suited to deal with this problem since limestone is already considered as a material to remove sulfates and sulfides from the process stream.

Prior to having developed detailed designs, we use stoichiometric constraints to estimate the size of the various material flows. We aim for a design that generates 1000 MW of power from hydrogen fuel cells at a fuel cell efficiency of 74%. This implies a flow of 5000 moles of hydrogen per second. Starting with a typical coal that effectively contains CH plus ash, the process requires 2000 moles of calcium oxide per second. In terms of product carbonate that amounts to 200 kg/sec or roughly 17 ktons/day. If the fluidized bed can be held to a residence time of 5 minutes this amounts to 60 metric tons of solid, or about 60 m³ of bed volume. Note that the energy balance at this point contains a contribution of 360 MW of heat energy that is provided by the calcium oxide which ultimately needs to be supplied from elsewhere, i.e., the resulting calcium carbonate needs to be calcined under input of energy. The amount of coal being burned in the gasification step corresponds to 2000 moles of carbon. For ash content of a typical US coal, this amounts to about 33 kg of coal per second. This provides about 950 MW of heat. In this simple discussion we have ignored energy losses in the hydrogen production and thus return to an overall efficiency of 74%. Of course, a realistic discussion will account for additional losses in the hydrogen generation, reducing the actual efficiency to 60 to 65%.

Based on the numbers given for the Vision 21 plant, the reaction in the gasifier can be approximated roughly by

Thus, the calcium oxide process eliminates the use of 1100 moles of oxygen per second or 3000 tons per day. Because of the high cost of separating air, in monetary as well as energetic terms, this provides a strong incentive to develop the calcium oxide based method.

In order to contrast the two approaches we discuss the energetics of the basic conversion reactions. The overall process that one would like to accomplish can be written as

This process is very endothermic and the energy has to be provided by some additional reaction. One way to accomplish this is to provide this energy by combustion of carbon,

This way, one needs an additional 0.46 mole of carbon and oxygen to provide the necessary energy. Normalizing back to one mole of carbon we therefore expect to use at a minimum 0.32 moles of O_2 per mole of carbon in order to let the hydrogen producing reaction go to completion. This is not in bad agreement with the actual value of 0.55 suggested above. The latter is higher for two reasons. (1) We have ignored the binding energy between carbon and hydrogen in the coal. For methane this would be a significant effect, here it is somewhat smaller. (2) The thermodynamics of the intermediate gasification step requires a certain energy input which does not necessarily lead to a perfect energy balance in the overall reaction. With less oxygen available, not all the coal would gasify. As a result, the gas product has more than enough internal energy to drive the hydrogen production. The overall excess introduces an inefficiency into the system.

From this discussion we can conclude, that to a good approximation the input of oxygen in the currently envisioned hydrogen production method is a means of providing the additional energy that is required to produce hydrogen from coal. In our case, the enthalpy as well as the free energy are already provided for by the reaction of carbon dioxide with calcium oxide,

Instead of burning additional coal we envision to provide CaO in a fluidized bed reactor for the mixture of coal and water to react with. CaO serves two separate functions. It provides the energy for the reaction and by constantly removing carbon dioxide from the reactant mixture, CaO drives the equilibrium towards the carbon free hydrogen gas. Membranes that simultaneously remove hydrogen from the system will speed up the reaction even more. However, the overall system is likely to be more efficient than alternative membrane designs because the membrane pull is supplemented by the carbonation push.

Calcination in a Solar Furnace

The above process could well be implemented without any further innovation regarding the necessary calcination step. The calcium carbonate could be calcined in a conventional process that also burns fossil fuels. The carbon dioxide from the calcination is certainly available for further processing and additional CO₂ from the combustion supporting the calcination could also be recovered. However, at this point one may want to consider a more ambitious approach of using solar energy to perform the calcination. Such a plant would be a hybrid solar/fossil power plant. There are major advantages over conventional solar plants. First, the carbonate can be stored easily, thus the unavoidable fluctuation in insolation can be averaged out over large time scales. Secondly, the electricity is generated completely at a fuel-fired site, eliminating idling of expensive generating equipment for about 2/3 of the time.

The solar energy would add another 40% percent to the energy output of the power plant. The challenge for this approach of using solar energy is the relatively high temperature one would need to achieve in what is presumably a gas-solid heat exchange. One would need to achieve temperatures in excess of 900°C. The energy is used to calcine calcium carbonate. The resulting calcium oxide in turn provides the energy required for forming hydrogen. In an indirect fashion, this is a means of forming

(additional) hydrogen from solar energy. The conversion efficiency of a fuel cell is very high, thus leading to a very high overall efficiency of the solar collection system. The high down-stream efficiency of the solar energy conversion which is unique to the hybrid design makes the use of solar heat collectors much more cost-effective.

For an implementation, we envision a field of mirrors that aims at a central tower. The temperature goal is more ambitious than for past power plant designs, but it is clearly within reach of currently available technology. To lower the cost we would expect to develop mirrors that use optical feedback to accurately aim the sunlight onto the central tower even if wind forces try move the mirror surfaces. Such feedback can substitute for structural strength and thus can significantly reduce the cost of a mirror system that already requires tracking. Much more ambitious feedback loops have been designed for astronomical mirrors and mirrors used in SDI that use adaptive optics to accommodate fluctuations in the atmosphere.

Photolytic Methanol Production from Carbon Dioxide

By raising the temperature of the solar capturing system even further, we can develop a novel, high throughput photochemical method of forming methanol from CO_2 . We have already demonstrated that hot CO_2 becomes an efficient absorber of sun-light. At low temperatures, the carbon dioxide is transparent to the visible light where the bulk of the solar energy is delivered. However, starting at about 1700°C the absorption becomes strong and sunlight can be used to photolytically disassociate carbon dioxide into carbon monoxide and oxygen. Thermally quenching the product gas back to 1200°C by the introduction of excess unheated CO_2 stabilizes the gas mixture. It is well known that the reaction between oxygen and carbon monoxide is arrested under these conditions, so that a stable gaseous product has been prepared.

The resulting carbon monoxide is separated, partially shifted with water and used in a conventional method to form methanol. Thus, this solar plant producing methanol would effectively get a second use out of each carbon atom. If the methanol becomes feedstock for plastics, this can be viewed as long term sequestration, if it becomes a fuel, the carbon replaces original fossil carbon and thus raises the carbon efficiency of the system.

Because of the high heat of combustion of methanol, this second use actually provides more energy than the first. In addition, the process generates oxygen that needed to be separated from the methanol in any case and could now be used elsewhere within the Vision 21 plant.

Conclusion

With the world's very heavy dependence on fossil fuels and the very beneficial cost effectiveness of those fuels compared to alternative energy sources, it is evident that fossil fuels, especially coal, will continue to be heavily used into the indefinite future. That combined with the current high level of CO₂ emissions from fossil fuels, makes it imperative that the goals of Vision 21 be adopted. In the work outlined above, we discuss a three part research effort that aims at a unique hybrid technology that combines fossil and solar energy into one inseparable unit. Each of these three research topics individually offers a significant improvement in the energy production efficiency from coal while simultaneously providing a means of either reusing CO₂ or providing a convenient means of its intermediate separation and storage before final permanent sequestration. Combined they perform even better and simultaneously provide an effective means of beginning to incorporate alternative energy sources into today's energy distribution network at relatively low cost.

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