

# COPRODUCTION OF HYDROGEN AND ELECTRICITY : CATALYTIC APPLICATIONS

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There is a growing need for new technology for more economical manufacture of hydrogen and for generation of electricity, dictated by increasingly stringent environmental requirements.

Environmentally benign transportation fuels almost always require hydrogen for their manufacture. Hydrogen is needed for production of high-performance oxygenate fuels - alcohols and ethers. Hydrogen is needed for hydrodesulfurization. Also, it is expected that hydrogen will be needed for conversion of aromatics to naphthenes to meet environmental requirements. There is a growing recognition that there will be a significant future shortage of hydrogen supply.

The electric utility industry is most affected by the 1990 Clean Air Act Amendments requirements for the reduction of SO<sub>2</sub> and NO<sub>x</sub> to meet acid rain provisions (Title IV) and by control of NO<sub>x</sub> in ozone nonattainment areas ( Title I ). The CAAA requires reduction of SO<sub>2</sub> to half of 1980 levels.

These needs provide the motivation for the present paper which examines catalytic opportunities for advantageous *coproduction* of hydrogen and electricity from coal, petroleum coke and/or biomass. The strategic concept involves modifications of the Integrated Gasification - Combined Cycle process. In IGCC, coal, petroleum coke or biomass is converted to synthesis gas, a mixture of H<sub>2</sub>, CO and CO<sub>2</sub>. This syngas is used as fuel for generation of electricity in a combined turbine and steam cycle. The IGCC plant process steps of **gasification, gas purification, and gas turbine and steam cycle** for production of electricity are illustrated in Fig.1. Including the Cool Water plant in California, four IGCC coal-based demonstration plants have been built and operated world-wide. Eight additional plants are in various state of development under the DOE Clean Coal Program. A 305MWe plant is under construction in Spain. IGCC plants based on petroleum coke are in advanced planning and commitment stages.

It has been proposed that the IGCC process be modified so that part of the synthesis gas is converted to chemicals and then the remainder of the syngas is used to generate electricity. Such a plant has been termed a powerplex. Technology for coproduction of electricity and methanol and dimethyl ether, (including once-through catalytic slurry-phase operation) have been proposed, and syngas conversion tested experimentally under appropriate conditions (1). The economics of oxygenates / electricity cogeneration evaluated and deemed to be favorable under certain conditions (2).

In this paper, various technologies for coproduction of hydrogen and electricity are proposed. Possible advantages are: pollution abatement; higher efficiency; and improved economics; and use of national resources of coal, petroleum coke and biomass. Emphasis is given to eight potential catalytic process applications, indicated in Fig. 1.

**1 Catalytic Gasification.** Gasification of solid fuels is carried out in the presence of steam by partial combustion at 900° - 1500° C. It has long been known that alkali hastens the critical slow reaction,  $C + H_2O \rightarrow CO + H_2$ . Extensive laboratory and pilot plant studies have established reaction mechanisms and practical process information (3). It was demonstrated that catalytic gasification of coal can be carried out at industrial rates at 600 - 700 °C. (3, 4).

**2 Integral Catalytic Gasification / Synthesis** ICG/S is the concept of carrying out integral, that is simultaneous, gasification and synthesis of desired fuel hydrocarbons or oxygenates. Gasification and synthesis of methane was first proposed. Fairly high yields of CH<sub>4</sub> becomes thermodynamically stable in the presence of steam and carbon at 700°C and higher pressures, Fig. 2 (5). Indeed, potassium is also a catalyst for methane formation and high methane levels were found in extensive catalytic coal gasification pilot plant operations carried out at Exxon with DOE support (3,4) This process has not been commercialized.

It is now suggested that a combination of gasification and oxygenate-synthesis catalysts be utilized to accomplish gasification and oxygenates synthesis. A problem is matching rates of gasification and thermodynamic constraints of oxygenate synthesis. at a common temperature and pressure. Synthesis of methanol is carried out at about 300° C. One option to increase synthesis conversion is to operate so as to produce methanol and dimethyl ether. Higher yields of MeOH and DME are thermodynamically possible at a fixed temperature/pressure conditions than for

methanol alone (6). Another option is gasification / production of mixed, higher alcohols. Higher alcohols, including isobutyl alcohol, were manufactured at temperatures as high as 500 °C. Production of hydrogen from oxygenates is discussed later.

**3 Catalytic Water Gas Shift** The composition of synthesis gas is sensitive to gasification conditions, including the presence of larger amounts of steam, used in the Texaco process. Another application of catalysis is the adjustment of gas composition to that most suitable for further synthesis processing. The catalytic water gas shift processes high, 350° C, and low, 200° C, are well established industrially for hydrogen manufacture by the reaction,  $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ . Incorporation of the WGS reaction presents useful options in synthesis process technologies now discussed.

#### **4. Catalytic Oxygenates Synthesis.**

Higher alcohols synthesis also offers opportunities for production of valuable coproducts, perhaps particularly isobutanol which has potential high value as an octane-enhancing gasoline additive. Several opportunities for improved higher alcohols synthesis has recently been presented.(7)

#### **5 Catalytic Reforming of Oxygenates for Hydrogen Manufacture.**

A problem in coproduction of hydrogen and electricity is fluctuating electricity demand which results in variable hydrogen generation rates. Gaseous hydrogen is not easily stored. If more easily-stored liquid methanol and dimethyl ether are produced, they can be utilized for production of hydrogen by catalytic decomposition or by catalytic steam reforming. Technology for reforming oxygenates for production of hydrogen is well established, has been used in certain instances, and may be a useful option component in an energyplex. Methanol decomposition is used for production of supplemental fuel gas in Berlin for peak demand conditions

The conversion of methanol (and DME ) to syngas is endothermic. The synthesis gas formed has higher heat of combustion than the methanol from which it is produced. It has been proposed that when *waste heat* is used to supply endothermic energy required for syngas formation, there would be an effective increase in heat value of the methanol, for automotive or electrical generation applications. Endothermic dissociation  $\text{CH}_3\text{OH}(\text{g}) \rightarrow 2\text{H}_2 + \text{CO}$ ,  $\Delta H_{298\text{K}} = 21,664 \text{ cal/g-mole}$ . Including the heating value increase in the methanol vaporization step, endothermic dissociation can increase the fuel heating value by over 20% over liquid methanol (8). If hydrogen is the sole desired fuel, methanol can be steam reformed.  $\text{CH}_3\text{OH}(\text{g}) + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO}_2$ ,  $\Delta H_{298\text{K}} = 11,826 \text{ cal/g-mole}$ . Including the heating value gained from methanol vaporization, the reformed methanol can have about 13% higher heating value than liquid methanol (8)

#### **6 Electrocatalytic Hydrogen Separation.**

A new technique for hydrogen separation is an outgrowth of fuel cell technology. An electrochemical cell is used which has highly efficient catalytic electrodes. Impure hydrogen is consumed at the anode of the cell and purified hydrogen generated at the cathode, Fig 3. By the application of a small potential across the electrodes of this cell, it is possible to ionize  $\text{H}_2$  at the anode and simultaneously to produce an equivalent amount of high purity  $\text{H}_2$  at the cathode. The effect of gaseous feed rate over an anode on hydrogen removal efficiency is illustrated in Fig. 4 showing data from an early publications from the Houdry Laboratory (9, 10). This concept has been much further developed with promising results. It has been shown that 80% of hydrogen recovery is feasible from very dilute  $\text{H}_2$ -containing streams, Fig 5 (11) It is a critical point that the catalytic electrodes are very efficient ( low overvoltage ). Therefore, only a small amount of electricity is required, namely 2to 10 kw-hr per 1000  $\text{ft}^3$  of hydrogen. In the present application hydrogen not separated is not wasted but is utilized as fuel in the combined cycle generation of electricity.

**7 Catalytic Fuel Cells.** Fuel cells are catalytic devices. It should also be pointed out that a fuel cell could be used advantageously to supply the needed electricity for the electrocatalytic hydrogen separation, utilizing a small part of the hydrogen produced. Fuel cells are not discussed further here except to note that they could be used instead of or in combination with combined cycle for electricity generation

#### **8 Membrane Separation, Separation/ Catalysis.**

Membranes offer special opportunities for separation of hydrogen from gaseous mixtures, based on diffusion, on sieving, or on permeation. The commercial Monsanto PRISM process utilizes hollow fiber membranes with an active siloxane layer. Active research is underway to develop membranes capable of separating gas mixtures based on molecular size, using molecular sieving mechanism. One direction is to begin with a mesoporous membrane ( > 50Å ) and to apply a layer of an inorganic oxides such as silica to produce a microporous structure.(12). A gas separation membrane multi-layer structure has been described (13). Another approach is to utilize carbon molecular sieve and to reduce the pore size to 3 or 4 Å, evaluated for separation of  $\text{CO}_2$  and  $\text{H}_2$  (14)

It is also possible to utilize a metal membrane. A special membrane is palladium which has almost infinite selectivity for passage of hydrogen. Here the mechanism is conversion to a hydride, migration of the hydride and reformation of molecular hydrogen. Palladium membrane have been used commercially for hydrogen purification. Pd alloyed with Ag or other metals has shown advantages (15). A metal-membrane-based process for production of hydrogen is based on a novel hydrogen-permeable composite membrane. Separation by permeation is also possible.

Combining separation and catalysis offers much potential. By removal of a reaction product for a thermodynamically limited reaction, the reaction can be driven further, as in the water gas reaction (16). Other reactions which could be combined are hydrodesulfurization or other hydrogenation reactions such as of aromatics to naphthenes.

**Pressure Swing Adsorption** Pressure Swing Adsorption, not a catalytic process, is used for separation in modern plants for manufacture of hydrogen. Microporous solids are used, in many ways structurally similar to catalysts. PSA offers a bench mark for comparison with alternative separation processes.

In summary, attention is drawn to a number of catalytic options which are deemed promising for needed new technology for production of hydrogen and electricity, technology which will be environmentally advantageous (16). Further, it is suggested that the electrical industry will be involved with catalytic chemistry and engineering.

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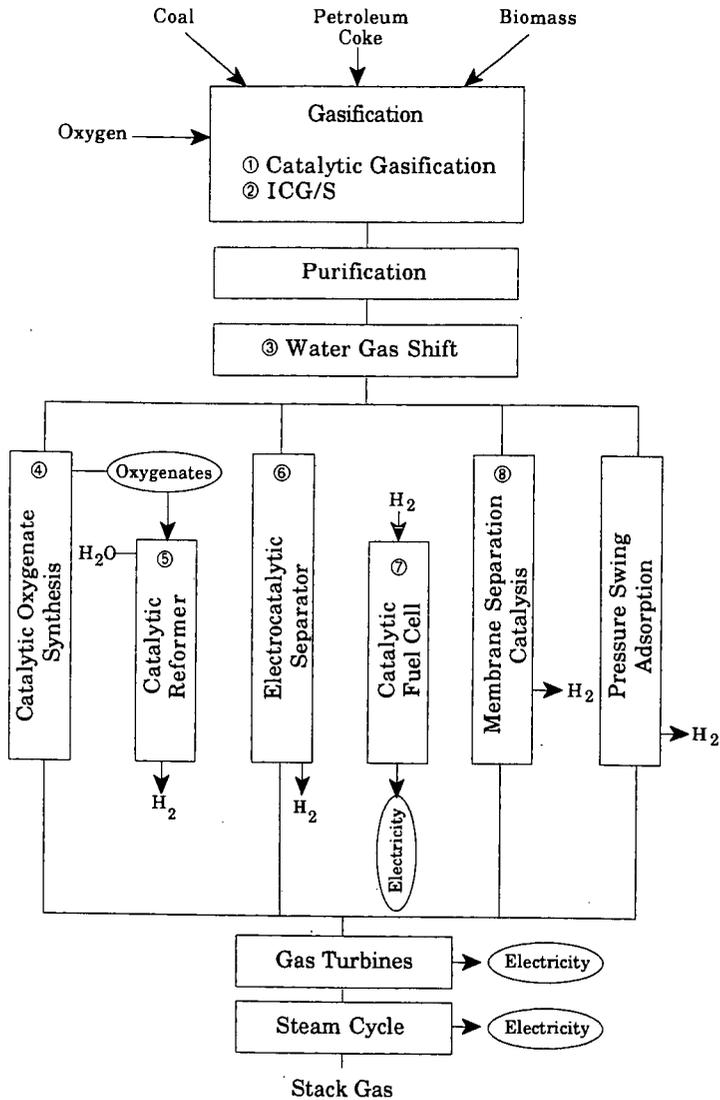


Fig. 1. Catalytic Modifications of IGCC for Production of Hydrogen and Electricity

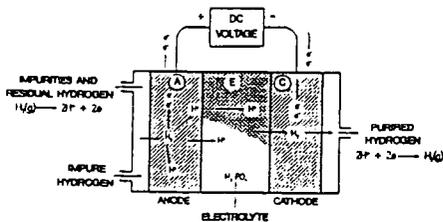


Fig. 3. Schematic of an electrocatalytic hydrogen separator (11).

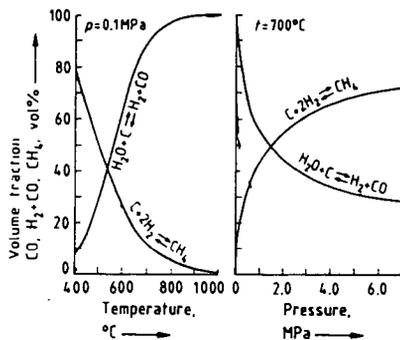


Fig. 2. Effect of temperature and pressure on equilibrium gas composition in the presence of carbon (5).

**Hydrogen Removal Efficiency from 12% H<sub>2</sub> Stream**

Plot No.	Feed Rate, Cc./Min.	% Efficiency
1	4.2	73.0
2	9.5	71.4
3	15.4	65.8

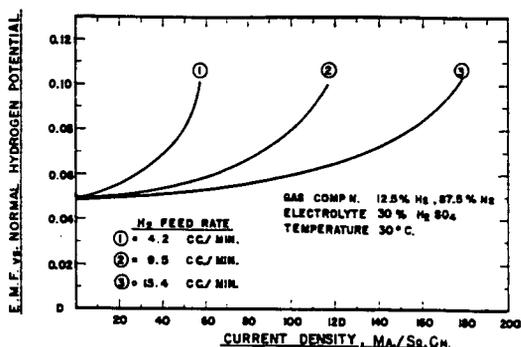


Fig. 4. Effect of feed rate on anode performance in electrocatalytic separation (9).

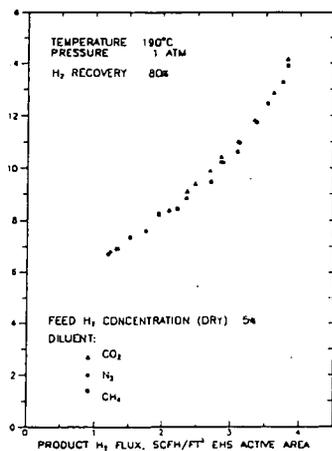


Fig. 5. Electrocatalytic Hydrogenation Separation performance with dilutants (11).