

**Symposium on "Chemistry of Renewable Fuels and Chemicals"**  
**Sponsored by the ACS Divisions of Fuel Chemistry and Cellulose, Paper and Textile**  
**217th ACS National Meeting, Anaheim, CA**  
**March 21-25, 1999**

**ATOM-ECONOMICAL PATHWAYS TO METHANOL FUEL CELL FROM BIOMASS**

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(Keywords: biomass, fuels, methanol fuel cell)

**ABSTRACT**

An economical production of alcohol fuels from biomass, a feedstock low in carbon and high in water content, is of interest. At Brookhaven National Laboratory (BNL), a Liquid Phase Low Temperature (LPLT) concept is under development to improve the economics by maximizing the conversion of energy carrier atoms (C,H) into energy liquids (fuel). So far, the LPLT concept has been successfully applied to obtain highly efficient methanol synthesis. This synthesis was achieved with specifically designed soluble catalysts at temperatures  $<150^{\circ}\text{C}$ . A subsequent study at BNL yielded a water-gas-shift (WGS) catalyst for the production of hydrogen from a feedstock of carbon monoxide and  $\text{H}_2\text{O}$  at temperatures  $<120^{\circ}\text{C}$ . With these LPLT technologies as a background, this paper extends the discussion of the LPLT concept to include methanol decomposition into 3 moles of  $\text{H}_2$  per mole of methanol. The implication of these technologies for the atom-economical pathways to methanol fuel cell from biomass is discussed.

**INTRODUCTION**

Though still controversial, global warming from increasing trace gases in the atmosphere is now generally accepted [1]. The role of  $\text{CO}_2$ , a greenhouse gas resulting from natural phenomenon and burning of fossil fuels, is particularly important. Due to its origin, biomass by definition is considered essentially  $\text{CO}_2$  neutral in the growth/usage cycle. It is, thus, of interest to develop efficient processes that utilize biomass feedstock to produce fuels and chemicals. Traditionally, ethanol production via biomass fermentation is widely recognized as an acceptable route. But fuels other than ethanol can be produced from biomass. This paper focusses on methanol and subsequent production of  $\text{H}_2$  with specific application to methanol fuel cell. A scheme is presented that can allow production of 3mol  $\text{H}_2$  per mol methanol via less intensive energy pathways i.e. via an atom-economical route.

**EXPERIMENTAL**

Materials

Sodium and potassium formates, metal complexes that served as catalysts, triethyleneglycol dimethyl ether (triglyme), and methanol were purchased from either Aldrich or Alfa.  $\text{CO}$ ,  $\text{H}_2$  gases ( $>99.9\%$  pure) were obtained from Scott Specialty Gases.

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## Batch Unit

All runs were conducted in a 0.5L AE Zipperclave constant stirred tank reactor (CSTR) available commercially from Autoclave Engineers (AE) but modified at BNL. The batch unit was fitted with a Dispersamax six-blade impeller and a removable metal ring inserted into the reactor to break up any vortices that may form during stirring. The heating / cooling was attained through a Parr temperature controller. The system had provisions for inlets and outlets for gases and liquids sampling during the run. The unit was rated at 20 MPa at 350°C.

## Run Procedure and Analysis

In a typical run related to water-gas-shift (WGS) reaction, sodium or potassium formate, metal complex catalyst and solvent mixture were loaded into the reactor under an inert atmosphere. The reactor was sealed, pressurized and heated at a desired temperature. Once isothermal condition was attained, evolved gases were identified and quantified by gas chromatographs.

## **RESULTS AND DISCUSSION**

Discussed below are novel technologies, under development at BNL, that could be adapted to biomass feedstock. Targeted is production of methanol and H<sub>2</sub> fuels with relevance to methanol fuel cells.

### Low Temperature Catalytic Methanol Synthesis



To sustain increasing natural gas usage, remote natural gas and non-conventional resources such as gas hydrates are being developed. The challenge is to retain atom-economy by developing technologies that allow processing and transport of available natural gas with minimum energy input. At BNL, the Liquid Phase Low Temperature (LPLT) concept has been developed to achieve this goal. A successful application of this concept to methanol synthesis utilized a designed alkoxide base-activated nickel catalyst (2). This catalyst system operates in homogeneous liquid phase and allows high synthesis gas conversion (>90%) per pass at high reaction rates (without optimization up to 9g-mol MeOH/g-mol cat.h) under thermodynamically allowed low temperature (<150°C) and low pressure (<5 MPa). These features simplify the overall methanol synthesis process in two ways:

- Natural Gas to Syngas - Step 1. The low pressure operation combined with inertness of the catalyst to N<sub>2</sub> permits partial oxidation of natural gas with air during syngas manufacture. This feature eliminates a need and, therefore, the cost of the AIR to O<sub>2</sub> separation plant.
- Syngas to Methanol - Step 2. A high syngas to methanol conversion (>90%) achieved with the designed catalyst eliminates syngas recycle.

With a target of 40% cost reduction over the conventional process for methanol synthesis, a second-generation methanol synthesis catalyst is being formulated and evaluated at BNL. A successful development of this atom-economical process would provide an economical edge over well advanced concepts of liquefied natural gas (LNG) and Fischer-Tropsch (F-T) liquids. Though not discussed in detail but relevant to this paper, syngas generated by gasification of biomass (3) could become the feedstock to produce methanol via the BNL low temperature methanol synthesis technology.

## Low Temperature Catalytic Methanol Decomposition



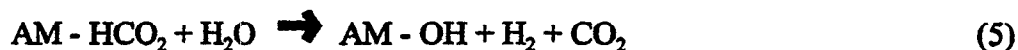
Several catalytic systems have been evaluated for methanol decomposition but high temperatures and side reactions present problems (4). By utilizing the LPLT concept, catalysts are being formulated at BNL that operate at a temperature of <150°C. At low temperatures, selectivity to desired products is enhanced. Though not discussed here, catalytic H<sub>2</sub> production via reaction (2) at low temperature is relevant.

## Low Temperature Water-Gas-Shift (WGS) Catalysis

The emphasis of the present paper is on development of water-gas-shift (WGS) catalysts (Equation 3) that effectively operate at low temperatures of <150°C:



Commercially, several heterogeneous metals (5) and homogeneous metal complexes (6) have been employed as catalysts. Under basic conditions, the reaction proceeds through a formate intermediate (Equations 4 and 5):



Thus, the ability of any catalyst to decompose an inorganic formate via reaction 5 is a measure of its effectiveness as a WGS catalyst. Table 1 lists several catalyst formulations that were evaluated to decompose potassium methyl formate. Since an equimolar amount of H<sub>2</sub> is expected per mol of KHCO<sub>2</sub>, the direct measurement of H<sub>2</sub> production vice gas chromatography allows assessment of reaction efficiency. Notable in Table 1 is Run 4 in which 94% decomposition was achieved at 120°C in <5 minutes and Run 9 where complete decomposition was achieved at 140°C in <2 minutes. The absence of CO (to <0.01% instrument sensitivity) is also noteworthy. The results show that the equilibrium reaction (3) can be driven essentially to the right with the low temperature catalysts developed at BNL (7).

## Methanol Fuel Cell Application

Methanol fuel cells are of commercial importance but several technological hurdles remain to generate pure H<sub>2</sub> feed from methanol feedstock. Methanol reforming with steam generates 3 mol H<sub>2</sub> and 1 mol CO<sub>2</sub> per mol methanol whereas methanol oxidation produces 2 mol H<sub>2</sub> and 1 mol CO<sub>2</sub> but both systems operate at high temperatures. Direct methanol fuel cells are also being evaluated (8). Work, ongoing at BNL, envisions an integrated system that operates at low temperatures. The system consists of two steps: 1) catalyzed methanol decomposition at T<150°C to produce 1 mol CO and 2 mol H<sub>2</sub> followed by; 2) fast and complete CO conversion to CO<sub>2</sub> with concomitant production of 1 mol H<sub>2</sub> via the present invention. Thus the BNL integrated system produces 3 mol H<sub>2</sub> per mol methanol at T<150°C compared to other schemes for methanol fuel cell system that are under development.

## CONCLUSIONS

The emphasis of this paper is to produce fuels and chemicals from biomass. The approach, presented here, involves biomass gasification to yield a dilute and "wet" syngas stream. The LPLT concept, developed at BNL, is applied to yield a low energy input pathway for catalytic conversion of syngas to methanol. A low temperature catalytic decomposition produces 2 mol H<sub>2</sub> and 1 mol CO. The produced CO is effectively converted to CO<sub>2</sub> and equimolar H<sub>2</sub> catalytically via WGS reaction. This scheme produces essentially a pure stream of 3 mol H<sub>2</sub> per mol methanol. If further purification (removal of any residual CO) of H<sub>2</sub> is required, methanol can be catalytically reacted with CO to produce methyl formate. Thus, methanol and H<sub>2</sub> are recognized as potential fuels from biomass. For application to fuel cells, H<sub>2</sub> can be further purified with coproduction of methyl formate, a specialty chemical. The overall emphasis at BNL is to develop technologies that are atom-economical thus retaining maximum energy of the original feedstock molecule in to fuel or chemical product.

## ACKNOWLEDGMENTS

Work at Brookhaven National Laboratory is supported by U.S. Department of Energy Contract No. DE-AC02-98CH10886.

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**Table 1. Decomposition of Inorganic Formates Catalyzed by Metal Complexes.**

0.5LAE Zipperclave batch reactor, Solvent: 5% H<sub>2</sub>O / 10% Methanol / 85% Triglyme = 130 mL,  
KHCO<sub>2</sub> = 50 mmol, T=120°C, P<sub>Ar</sub> = 1.4 Mpa.

| Run # | Catalyst | Final Gas Analysis<br>H <sub>2</sub> CO<br>mmol |   | Time<br>min | %KHCO <sub>2</sub><br>Decomposition |
|-------|----------|-------------------------------------------------|---|-------------|-------------------------------------|
| 1     | ----     | 1                                               | - | 140         | 2                                   |
| 2     | B-2      | 35                                              | - | 80          | 70                                  |
| 3     | NB-3     | 5                                               | - | 120         | 10                                  |
| 4     | RB-4     | 47                                              | - | <5          | 94                                  |
| 5     | RLB-5    | 40                                              | - | <30         | 80                                  |
| 6     | CLB-6    | 2                                               | - | 55          | 4                                   |
| 7     | PCL-7    | 43                                              | - | <10         | 86                                  |
| 8     | FLB-8    | 3                                               | - | 30          | 6                                   |
| 9     | RB-4-T   | 50                                              | - | <2          | 100*<br>*(T=140°C)                  |

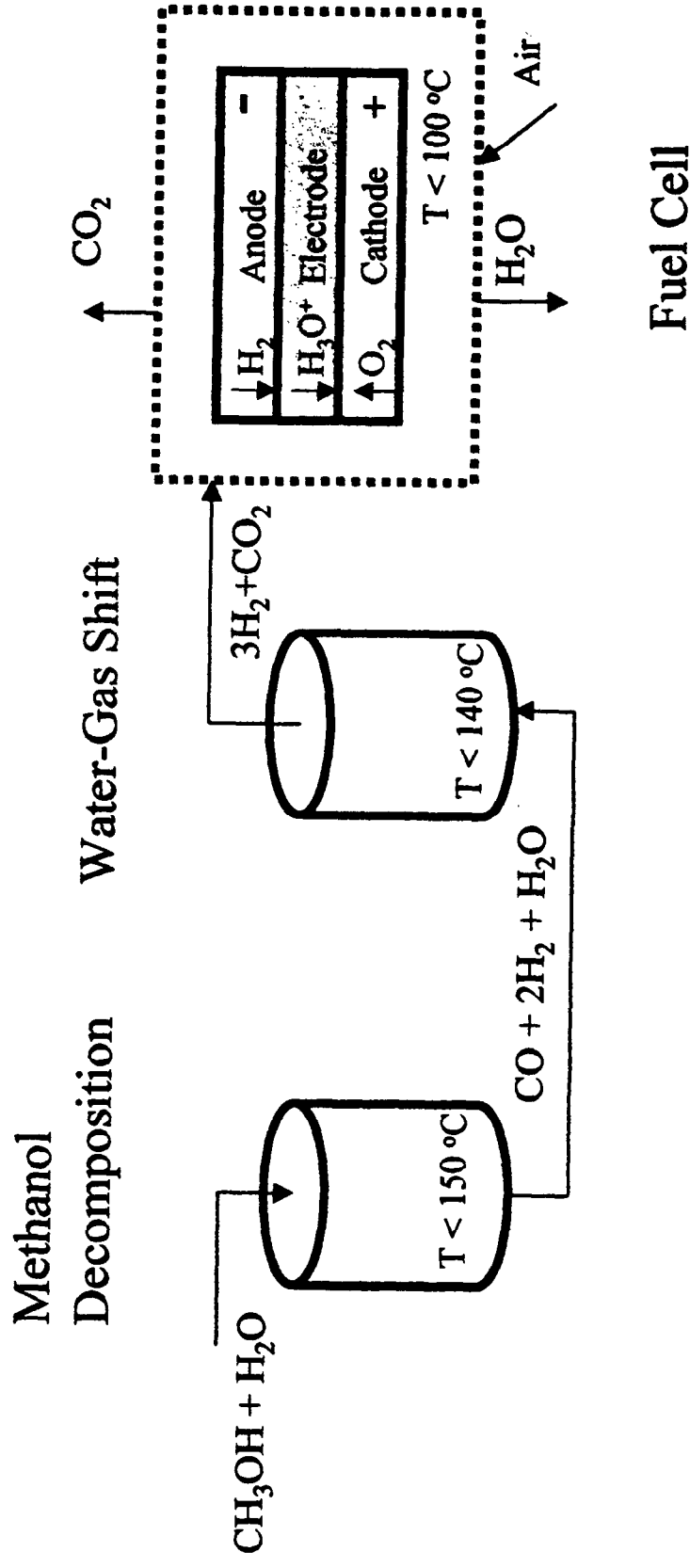


Figure 2. Scheme for High Efficiency Methanol Fuel Cell