

METHANOL FROM BIOMASS VIA STEAM GASIFICATION

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ABSTRACT

R & D at Wright-Malta on gasification of biomass, and use of this gas in methanol synthesis, has now reached the stage where a demonstration plant is feasible. The gasifier has evolved into a long, slender, slightly declined, graded temperature series of stationary kiln sections, with box beam rotors and twin piston feed. The methanol reactor is envisioned as a smaller, more declined, graded temperature, water-filled stationary kiln, with a multi-pipe rotor. Input to the demo plant will be 100 tons/day of green (45% water) wood chips; output is projected at 11,000 gal/day of methanol and 7500 lbs/hr of steam. The over-all biomass to methanol system is tightly integrated in its mechanical design to take full advantage of the reactivity of biomass under a slow, steady, steamy pressurized cook, and the biomass pyrolysis and methanol synthesis exotherms. This is expected to yield good energy efficiency, environmental attractiveness, and economical operation.

INTRODUCTION

The oral presentation at the biomass symposium will consist primarily of pictures, drawings, graphs, and flow charts, illustrating the novelty in the mechanical equipment aspects of the W-M technology, as it has evolved over the past quarter-century. There is some novelty, too, in the steam gasification chemistry, the raw gas reformation into syngas, and the projected methanol synthesis. These aspects of the development will be emphasized in this written preprint.

STEAM GASIFICATION RESEARCH

Process parameters were determined in two bench-scale equipments: a "minikiln" and a "biogasser". One provided batch experimentation, giving a differential look at the process and an end point; the other permitted continuous operation and gave integrated data.

The minikiln was a rotating autoclave, about 1 ft in diameter and 3½ ft in length, electrically heated, with provision for steam injection under the bed and for product gas sampling and analysis. Test material, such as wood chips, corn stalks, or solid waste and sewage sludge, was placed in the barrel, the door bolted on, heating and rotation started, and the material tumbled in place, gradually heating, going on a simulated trip down a long kiln. At the end of the run, the minikiln was cooled, and the residue removed and weighed.

The biogasser was a long (10 ft), slender (2 in. ID), auger reactor, heated electrically, with provision for continuous feed of moist sawdust through lock valves into the cool end, and controlled release of product gas at the hot end. The solid residue dropped into a pressurized receptacle and was subsequently weighed. Water and condensable organics, if any, were stripped from the gas by passage through a condenser. The gas was analyzed by chromatography; its composition was representative of that expected from a commercial kiln.

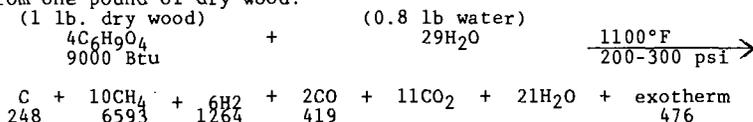
The bench-scale research showed that a slow, steady, pressurized cook, with alkaline catalyst and steam, under temperature gradually increasing to a top figure of 1100-1150°F is sufficient to gasify any type of biomass to 95-98% completion. No air or oxygen is required. It also showed that there is a broad optimum pressure at 200-400 psi. Lower pressure tends to slow the gasification process; higher pressure tends to throw the product mix toward higher molecular weight tar and coke, a la LeChatelier. It was determined that steam reformation of the intermediate pyrolysis liquids and steam gasification of the char go to completion under about the same conditions. Perhaps the vapors drift down the kiln, are absorbed into

char, and crack there. When conditions are right and char consumption is essentially complete, the gas also is clean, and burns with a pale blue, non-luminous flame.

The slow, steady temperature rise of the biomass charge, imposed by the inherently sluggish heat transfer of an indirectly heated kiln, is beneficial to the chemistry of steam gasification. Water itself is not sufficiently dissociated, even at 1100°F, to attack the decomposing biomass, although there will be some ionic hydrolysis in the region up to about 500°F. Rather, activation comes from the free radicals formed by breakage of chemical bonds in biomass polymers, starting at about 350°F, the weakest breaking first, then the next stronger, etc. Water participates in the radical chain reactions. With the slow temperature rise, radicals are generated in a slow, steady stream, on up through the brown and black charry stages. Char at, say, 900°F, is still not carbon; it is an amorphous high polymer with about one atom of hydrogen to two atoms of carbon, and still forms radicals (mostly atomic hydrogen) when heated to higher temperatures. And so the decomposing biomass reacts with water/steam all through its slow heat-up, and most of its substance, except inorganic matter, is gone by 1100°F.

(In contrast, a chip dropped into a fluid bed at 1100°F forms its radicals in a rush, wasting most of them. Steam reaction with the decomposing chip is thwarted, too, by the outpouring of gaseous products, and a substantial charry residue remains.)

The over-all gasification process is depicted in the balanced equation below. The proportions of the product gas are experimental data, being the nearest whole number composite of many runs in the biogasser at optimum conditions. (It is of interest to note that they are close to equilibrium even though equilibrium would not be expected at 1100°F in the absence of a metallic catalyst.) Wood is fresh white pine at 45% moisture. The numbers under the formulas represent the heat content in Btu's of each constituent, derived from one pound of dry wood.



Experimentation in the minikiln, using it in a differential thermal analysis mode, determined the magnitude and temperature occurrence range of the wood decomposition exotherm. Data obtained were in agreement with the calculated figure and with the literature. There was some degree of overlap between the water evaporation endotherm at higher pressures and the decomposition exotherm, but not enough to blunt it unduly. Calculation indicated that production equipment should be operable in regenerative mode without external heat supply, after initial warm-up and without a 2nd law pinch, provided that the moisture content of the feed material is not more than 50%. That is, the temperature differential between the backcoming gas in the heating pipes on the rotor vanes, and the on-going gasification process in the kiln, will be everywhere sufficiently large to sustain the process. This is particularly true in the methanol system, where the backcoming reformed gas will have unusually high enthalpy.

EQUIPMENT CHANGE AND SCALE-UP

The steam gasification process has been studied in five equipments in this order:

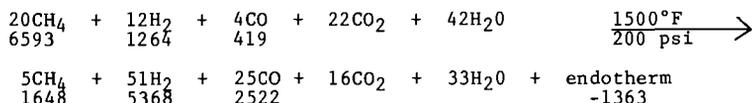
1. Bench-scale, batch type rotary kiln-15 lb charge.
2. Bench-scale continuous auger kiln-20 lbs/hr.
3. Process development unit, steam-heated auger kiln-500 lbs/hr.
4. Bench-scale, batch type rotor kiln-12 lb charge.
5. Mini-process development, rotor kiln-60 lbs/hr.

In all of the equipments, with comparable feed stocks, temperatures, pressures, heat cycles, and alkaline catalyst concentrations, the degree of gasification completeness and the composition of the product gas were, within experimental error, identical. There is no reason to expect this slow, steady process to change appreciably with further scale-up to

projected "standard" production units at, say, 12.5 green tons/hr.

REFORMING TO SYNGAS

If the gas is taken from the hot end of the kiln and raised in temperature from 1100 to 1500°F in the presence of an equilibrating catalyst, its composition will shift as shown in the equation below. This equation was derived from a W-M computer program which calculates the gas composition having the minimum Gibbs free energy as a function of temperature and pressure. Similar programs have been verified experimentally by other investigators in steam-reforming of natural gas.



Note that most of the methane has been steam-reformed to H₂ and CO, that some of the CO₂ has been reduced to CO, that most of the energy is now in the H₂ and CO, and that the ratio between these gases is now 2.04/1.00, just right for methanol synthesis. This gas composition shift is strongly endothermic, and the heat of reaction must be supplied by external heating.

(It is instructive to combine the gasification and shift equations, giving a situation which would prevail if the gasification were performed at a top temperature of 1500°F and 200 psi. The process is now 476-1363 = -887 endothermic. This does not mean that the wood decomposition exotherm has changed; it remains reasonably constant at about 700 Btu. It does mean that the over-all gasification process will range among varying degrees of endo- and exothermicity depending upon the final gas composition, which is in turn dependent upon temperature and pressure. Higher temperature and lower pressure throw it toward endothermicity and vice versa.)

Wright-Malta favors a lightly exothermic, self-sustaining gasification and a separate gas composition shift for reasons of equipment cost and process efficiency.)

METHANOL SYNTHESIS

As the syngas leaves the reformer, it gives a little of its sensible heat to the incoming gas, and then flows into the backcoming pipes on the gasifier vanes at about 1300°F. It exits the kiln at the feed end, is stripped of its water and all but a couple per cent of its CO₂, and is then compressed adiabatically from 200 to 1500 psi and 600°F.

Rather than use a scaled-down version of a commercial methanol process for the demonstration plant, W-M intends to use a new reactor design. It is, naturally, a stationary kiln (3 ft by 20 ft) declining about 15° from the horizontal, with about a 200 pipe rotor. In each pipe (1 in.) is a loosely fitting chain, and in each link is a copper catalyst pellet, kept bright and active by the mild chafing which occurs as the rotor slowly turns. Syngas drifts downward through the rotor pipes, condensing chemically into methanol vapor and physically into liquid, with the equilibrium shifting toward the right as the temperature falls. Water flows slowly, countercurrently up through the kiln, warmed by the methanol exotherm, its sensible heat, and heat of condensation, and boiling at the top end. Conversion of syngas to methanol is expected to be sufficiently accomplished (perhaps 60%) in a single, slow pass through the reactor so that recycling will be minimal.

The over-all biomass to methanol system is a tightly integrated package, taking full advantage of exotherms and sensible heat. The reformer will be heated by burning part of the purge gas (mostly methane); the remainder will be recycled through the twin piston feed into the gasifier. Steam raised in the methanol reactor, and in a heat recovery boiler atop the reformer, may be used, as in the demonstration plant, for space heating, or to generate electricity for powering the compressor and other auxiliaries. In the latter instance, net energy efficiency, raw biomass to fuel grade methanol, is calculated to be at least 70%.

Momentum is building to take seriously the need to move toward sustainable development through renewable energy. Biomass is, by far, the most versatile and widely distributed form of renewable energy, and environmentally attractive as well. In the present business climate, particularly here in the States, biomass to methanol would seem to be the best renewable energy venture.