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Introduction

Indirect liquefaction of biomass is accomplished by first gasifying it to produce a synthesis gas consisting of hydrogen and oxides of carbon, which in turn are converted to any one of a number of liquid fuels and/or chemicals by suitable choice of catalyst, synthesis gas composition and reaction conditions. This approach to producing synthetic fuels and chemicals has been extensively investigated where coal is the carbonaceous feed material, but less so for biomass or other feedstocks. It is generally recognized that the gasification to produce the synthesis gas posses one of the major technical and economic challenges to improving this technology. Herein, is reported a different slant on the indirect liquefaction that could lead to improvements in the efficiency and economics of the process.

Background

A variety of gaseous products are produced by gasifying biomass. The product composition depends upon the biomass composition and reaction conditions. A variety of gasification approaches have been investigated at rather small scale and reported in the literature(1,2). Many of these approaches have their roots in coal gasification. Noteworthy is the work on catalytic gasification by Baker et. al.(3) and Cox et. al.(4). The catalysts serve two primary functions: 1)to increase the yield of gases, at the expense of tar and char, at lower temperatures than are possible without catalysts, and 2) to catalyze secondary reactions to produce the specific product desired. Sufficiently high rates can be achieved to allow operation at lower temperatures so that oxygen is not needed as a co-reactant, thus eliminating the need for an oxygen plant.

Biomass Gasification - A New Approach

The advocated new approach to biomass gasification is predicated on the notion that it is better to gasify biomass to a CO_2-synthesis gas composed primarily of H_2 and CO_2, versus CO-synthesis gas composed primarily of H_2 and CO. The conversion to CO_2-synthesis gas and its subsequent utilization may be both technically and economically superior to the route through a CO- synthesis gas.

The carbon-steam(C-H_2O) gasification reaction is endothermic. A comparison of the stoichiometry of the respective routes is shown in equations 1 and 3, respectively. Both carbon-steam(C-H_2O)

$$C + H_2O = CO + H_2 \qquad (1)$$

$$CO + H_2O = CO_2 + H_2 \qquad (2)$$

$$C + 2H_2O = 2H_2 + CO_2 \qquad (3)$$

gasification reactions are endothermic. The enthalpy of the C-H_2O reaction to produce CO-syn gas is 31.4 kcal/g-mole while only 21.6 kcal/g-mole is require for the CO_2-syn gas reaction. The difference between reactions 1 and 3 is the exothermic(-9.8 kcal/g-mole) CO-shift reaction given in equation 2. Clearly, biomass is not carbon. Nevertheless, the conclusions are the same, except that the steam gasification of biomass is even more facile than carbon(i.e., graphite) and the thermodynamics more favorable.

By minimizing the energy requirements for the gasification portion of the overall sequence in the indirect conversion to fuels and chemicals, one has reduced the burden of the most costly and inefficient step in the overall process. Pinto and Rogerson(15) report cost of the reformer/gasmaking portion of a steam-reforming methanol plant as constituting 45% of the total capital cost. Henery and Louks (5) have shown that the economics of producing SNG(i.e., methane) from coal and lignite depend strongly on the cost of adding heat to the steam-carbon reaction. The amount of heat supplied and the method by which it is supplied to the gasification reactions are highly critical to the economics. In the case of SNG, Henery and Louks(5) estimate the cost of the gasification heat is 1/3 the cost of product(SNG). Any process that takes advantage of exothermic gasification reactions(e.g., $CO + H_2O = CO_2 + H_2$ and $C + H_2 = CH_4$) in the gasifier can reduce external heat requirements and substantially improve process economics and efficiency. Calculations based on equations 1 and 3 indicate that CO_2-syn gas requires 31% less energy to produce than CO-syn gas. Incidently the same argument applies to the manufacture of synthesis gas by steam reforming of other carbonaceous materials including natural gas.

It is general knowledge and well documented in experimental investigations that the reactivity of biomass can vary among the different types (6,7). The reactivity of biomass is such that sufficiently low temperatures (<750 °C) can be employed so that reaction enthalpy can be supplied indirectly by a tube still reactant heat exchanger. Hence, the need for pure oxygen and a plant for producing it is not necessary and a major expense and energy penalty to the gasification section of the plant is eliminated. Furthermore, reaction conditions can be selected to favor the production of CO_2-syn gas over CO-syn gas, including temperature, residence time, steam to biomass ratio and the use of catalysts. The predicted gasification product composition is particularly sensitive to temperature and steam to biomass feed ratios. This sensitivity is shown in the equilibrium data in Table I, which indicates that the optimum conditions for producing CO_2-syn gas are high steam:biomass ratio, low temperatures and low pressures. At 1 atm, 600 °C and a steam:biomass(i.e., H_2O:C) mole ratio of 10:1, the product gas composition is 65.4% H_2, 31.2% CO_2, 3.0% CO and 0.4% CH_4. Since biomass has about 30 wt.% oxygen, the amount of water required is predicted to be substantially less than 10:1.

While practically all gasification studies, irrespective of carbonaceous feedstock, have been conducted with the mind-set of producing CO-syn gas, there is sufficient experimental and theoretical evidence to suggest that through reaction engineering principles, high conversions of feedstocks can be achieved, producing high yields of CO_2-syn gas. Some of the predictions in Table I can be compared to experimental results under similar conditions shown in Table II.

CO- and CO_2- Synthesis Gas Chemistry

The use of synthesis gas to produce a broad range of products has been the subject of extensive research and development beginning about 70 years ago in Germany with the production of fuels using cobalt catalysts(10,11,12). While this chemistry is loosely referred to as Fischer-Tropsch in recognition to the pioneering and extensive contribution of these individuals, there has been literally hundreds of significant contributors. Interestingly, the use of CO-synthesis gas, i.e., synthesis gas composed primarily of H_2 and CO, has been the principle focus of this work, while CO_2-synthesis gas, i.e., synthesis gas composed primarily of H_2 and CO_2 has scarcely been considered.

Table III, illustrates the range of products that can be produced from CO-synthesis gas. Interestingly, optimum methanol synthesis over Cu-ZnO catalysts requires about 5% CO_2 in the inlet gas. If the CO_2 content is lower or higher, the methanol formation rate drops. Furthermore, the methanol formation apparently does not occur if the synthesis gas is free of CO_2 and H_2O. Russian investigators(13,14) have accounted for these observations by a mechanism where methanol formation is dominated by hydrogenation of CO_2 formed during reaction by the water gas shift reaction from CO:

$$CO + H_2O + 2H_2 \longrightarrow [3H_2 + CO_2] \longrightarrow CH_3OH + H_2O$$

It is tempting to extend this reasoning, to the feasibility of methanol synthesis with CO_2-synthesis gas. Kuechen et. al.(20) reported that a deactivated Cu/ZnO catalyst at 3-5 MPa(30-50 atm) and 483-543K gave maximum rates of methanol synthesis with H_2-CO-CO_2 syn gas ratio 70:0:30. The activation energy of methanol synthesis from CO_2 and H_2 was considerably lower than that from CO and H_2.

Cox, et. al., (4) reported the methanation of CO-free CO_2-synthesis gas($4H_2/CO_2$) in a packed bed reactor over supported nickel catalyst at 375 °C, 100 psig, and space velocities of up to 7,000 hr^{-1}.

The respective stoichiometries of aliphatic, olefin and alcohol hydrocarbon formation from CO- and CO_2-synthesis gases are shown in reactions 5-10. The thermochemistry of some of the simpler homologs of these series of compounds is shown in Tables IVA and IVB. The data show that each are exothermic with favorable free energy changes at low temperatures and high pressures.

$$(2n+1)H_2 + nCO = C_nH_{2n+2} + nH_2O \qquad (5)$$

$$2nH_2 + nCO = C_nH_{2n} + nH_2O \qquad (6)$$

$$2nH_2 + nCO = C_nH_{2n+1}OH + (n-1)H_2O \qquad (7)$$

$$(3n+1)H_2 + nCO_2 = C_nH_{2n+2} + 2nH_2O \qquad (8)$$

$$3nH_2 + nCO_2 = C_nH_{2n} + 2nH_2O \qquad (9)$$

$$3nH_2 + nCO_2 = C_nH_{2n+1}OH + (2n-1)H_2O \qquad (10)$$

A comparison of the enthalpies of the CO- and CO_2-syn gases at 300 °C shows the methanation to be about 18% less for the CO_2-syn gas(reaction 8, n=1) than for CO-syn gas(reaction 6, n=1), 35% less for the olefin formation(reaction 9, n=2), 39% less for methanol formation(reaction 10, n=1), and 29% less for ethanol formation(reaction 10, n=2). Both CO- and CO_2-syn gas reactions are favored by pressure, but the CO-syn gas reactions are more favored than CO_2-syn gas. Comparative volume contractions for CO-syn gas versus CO_2-syn gas reactions are 50% versus 40% for methanation, 50% versus 37.5% for olefin formation, 66.5% versus 40% for methanol formation, and 66.7% versus 50% for ethanol formation. Hence, pressure can be used to considerable advantage to increase equilibrium conversions. As expected form the enthalpies of reaction, the free energies are less for the respective CO_2-syn gas reactions. At 200 °C the respective free energy change(kcal/mole) for the CO- and CO_2-syn gas reactions are respectively -24.6 versus -19.5 for methanation, -13.46 versus -3.25 for olefin formation, 3.8 versus 8.9 for methanol formation, -9.9 versus 0.3 for ethanol formation. For those reaction conditions with positive free energy changes elevated pressures can be used to increase equilibrium yields, as is currently practiced in the commercial production of methanol from CO-syn gas. In the alcohol synthesis reactions, where free energy changes are not as favorable as for the other hydrocarbon synthesis reactions, higher pressures would be required to achieve equivalent equilibrium yields with the CO_2-syn gas.

The inference from these results is that many of the synthesis schemes that have used CO-synthesis gas in the past can also be accomplished with CO_2-synthesis gas. And while this may or may not prove to be a technical or economic breakthrough in its own right, that CO_2-synthesis gas can be used in place of CO-synthesis gas may have significant overall process implications and in some instances reaction specific benefits.

Other salient features of the CO_2-syn gas is that carbon deposition should not be the problem as it is for CO-syn gas since the CO_2 counters the Boudouard reaction. In addition, as can be

$$2CO = C + CO_2 \tag{11}$$

seen from the thermodynamic data in Table IVB, synthesis reactions with CO_2-syn gas are less exothermic, reducing the difficulty of temperature control while using CO-syn gas. Low concentrations of CO in the syn gas should also reduce saftey issues dealing with high concentrations of CO.

Conclusions

A new approach is advanced to indirect liquefaction of biomass. The crux of the process is based on the premise that it is easier to gasify the biomass to a CO_2-syn gas versus a CO-syn gas. Thermodynamic arguments are presented that show the energy savings that may be achieved in the gasification is about 30%. Some experimental data are presented that are consistent with the thermodynamic prediction that a CO_2-syn gas can be achieved through control of gasification conditions. Optimum gasification conditions are about 600 °C, atmospheric pressure, and steam:biomass ratio equal 10:1 in the presence of a gasification catalyst. The CO_2-syn gas under these conditions consists of 65.4% H_2, 31.2% CO_2, 3.0% CO, and 0.4% CH_4. Thermodynamic predictions have also been presented along with experimental results that indicate that a range of products may be produced by the catalytic conversion of CO_2-syn gas analogous to what has been achieved with CO-syn gas. Furthermore, carbon deposition and heat removal are predicted to be more easily controlled with CO_2-syn gas chemistry. Even if catalytic conversion diversity with CO_2-syn gas does not prove to have the versatility of CO-syn gas, the gasification to CO_2-syn gas still represents an improvement in gasification efficiency and the process can be used to produce fuel gas and hydrogen. While the discussion has focused on biomass, the ideas and concepts presented herein should hold for other carbonaceous materials such as coal and natural gas.

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Table I. Predicted Equilibrium Gasification Product Compositions(1 atm)

Product, mol. %	500°C	600°C	700°C	800°C
H_2O:C = 0.5				
H_2	38.1	49.3	50.9	49.8
CO_2	36.8	25.1	11.1	2.9
CO	4.9	16.8	34.9	46.2
CH_4	20.2	8.8	3.1	1.1
H_2O:C = 1.0				
H_2	38.1	49.3	50.9	49.8
CO_2	36.8	25.1	11.1	2.9
CO	4.9	16.8	34.9	46.2
CH_4	20.2	8.8	3.1	1.1
H_2O:C = 2.0				
H_2	38.1	50.7	57.1	57.1
CO_2	36.8	25.3	17.2	14.4
CO	4.9	16.0	24.7	28.4
CH_4	20.2	8.0	1.0	0.1
H_2O:C = 3.0				
H_2	46.2	58.8	60.9	60.0
CO_2	35.5	27.1	22.4	20.0
CO	3.9	10.9	16.4	20.0
CH_4	14.4	3.2	0.3	0.0
H_2O:C = 5.0				
H_2	56.9	63.8	63.2	62.6
CO_2	33.8	29.3	26.9	25.0
CO	2.7	4.5	6.3	8.0
CH_4	6.6	0.6	0.4	0.0
H_2O:C = 10.0				
H_2	64.6	65.4	65.1	64.7
CO_2	32.7	31.2	30.3	29.0
CO	1.5	3.0	4.6	6.3
CH_4	1.2	0.4	0.0	0.0

Table II. Experimental Gasification Results

Feed Material	coal char	Olive-husks	Biomass
Catalysts	K_2CO_3/Ni-Al_2O_3	none	Ni-Al_2O_3
Steam/feed, lb/lb	3.8	-	5.7
Pressure, psia	30	15	15
Temperature, °C	560	747	735
SCF H_2/ton feed	90,000	35,000	not reported
Product(mol%, H_2O free)			
CO	1.9	6	5.8
CO_2	36.6	25	29.9
H_2	61.4	67	64.1
CO	1.9	6	5.8
CH_4	0.0	2	0.2
Reference	4	8	9

Table III. Some Products Accessible through CO-Synthesis Gas

Product	Reaction Conditions	Ref.
CH_4	$3H_2$/CO, 350-400 °C, 50-100atm, 5,000-10,000 h^{-1} GSV, Ni/Al_2O_3 Catalyst	16
CH_3OH	$2H_2$/CO, 230-300 °C, 50-100atm, Cu-ZnO Catalyst	17
$C_nH_{2n+1}OH$ (n>1)	$1.1H_2$/CO, 260 °C, 130atm, 5,000-10,000 h^{-1} GSV, K-promoted MoS_2 Catalyst	18
C_nH_{2n} (n=2-4)	$1.4H_2$/CO, 280 °C, 10atm, 340 h-1 GSV, Fe-Mn Catalyst	18
C_{5+}	$2.1H_2$/CO, 200 °C, 20atm, Co/SiO_2, 360 h^{-1}	19

Table IVA. Comparative Thermochemistry of CO- and CO_2- Synthesis Gases(reactants and products in their normal states)

Reaction	Free Energy,kcal 25°C	200°C	250°C	300°C	350°C
5(n=1)	-36.04	-24.59	-21.78	-18.94	-16.06
6(n=2)	-31.48	-13.46	- 9.34	- 5.16	- 0.95
7(n=1)	- 6.97	3.76	6.64	9.56	12.50
7(n=2)	-32.89	- 9.90	- 4.17	1.60	7.40
8(n=1)	-31.26	-19.49	-17.15	-14.77	-12.34
9(n=2)	-21.92	- 3.25	- 0.07	3.18	6.49
10(n=1)	- 2.19	8.86	11.27	13.73	16.22
10(n=2)	-23.34	0.31	5.09	9.94	14.85

Table IVB. Comparative Thermochemistry of CO- and CO_2- Synthesis Gases(reactants and products in their normal states)

Reaction	25°C	Enthalpy,kcal 200°C	250°C	300°C	350°C
5(n=1)	-59.78	-50.96	-51.38	-51.77	-52.13
6(n=2)	-71.26	-52.24	-52.76	-53.25	-53.70
7(n=1)	-30.63	-23.38	-23.72	-24.03	-24.31
7(n=2)	-81.83	-63.85	-64.34	-64.76	-65.13
8(n=1)	-60.47	-41.35	-41.88	-42.38	-42.85
9(n=2)	-72.64	-33.03	-33.76	-34.46	-35.13
10(n=1)	-31.32	-13.77	-14.22	-14.64	-15.02
10(n=2)	-83.21	-44.64	-45.33	-45.97	-46.56