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Biomass Conversion to Fischer-Tropsch Liquids: Preliminary Energy Balances

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ABSTRACT

We present preliminary energy balances, based on a simplified calculation approach, for the production of Fischer-Tropsch (FT) liquids from biomass, coal, and natural gas. We make comparisons to results published by others in the case of coal and natural gas feedstocks in process configurations designed to maximize production of F-T liquids. With biomass feedstocks, we present results for two process configurations using an atmospheric-pressure indirectly-heated gasifier. In one case, production of F-T liquids is maximized. In the other case, F-T liquids are produced via one-pass of the synthesis gas through the F-T reactor, with unconverted syngas used to co-produce electricity in a gas turbine combined cycle. Additionally, we compare the energy efficiencies of "once-through" process configurations for five different biomass gasifier designs: indirectly-heated (two low-pressure designs), oxygen-blown (high-pressure), and air-blown (high-pressure and low-pressure).

1. INTRODUCTION

Fischer-Tropsch conversion involves the synthesis of hydrocarbons from carbon monoxide (CO) and hydrogen (H_2) over iron or cobalt catalysts. The CO and H_2 feed gas can be produced from a variety of carbon-containing feedstocks, for example by gasification of biomass or coal.

Fischer-Tropsch conversion was first used commercially in the 1930s, when Germany started producing F-T liquids from coal to fuel vehicles. A coal-to-fuels program has been operating in South Africa since the early 1950s. There is renewed interest globally today in F-T synthesis to produce liquids from remote natural gas that has little or no value because of its distance from markets (Fouda, 1998). Of particular interest is the production of middle distillate with an unusually high cetane number and with little or no sulfur or aromatics. Such a fuel can be blended with conventional diesel fuels to meet increasingly strict vehicle fuel specifications designed to reduce tailpipe emissions. Recent commercial efforts in "gas-to-liquids" (GTL) technology development include those at Exxon, Rentech, Sasol, Shell, and Syntroleum (Knott, 1997; Parkinson, 1997; Rentech, 1999). Because a large percentage of the world's gas fields are relatively small (Anonymous, 1998), one segment of the industry developing F-T synthesis processes is focussed on smaller-scale facilities (Knott, 1997; Tijm *et al.*, 1997; Rentech, 1999). Technological developments in this sector of the industry might be especially relevant to F-T synthesis using biomass as a feedstock.

We present energy balances using a simplified calculation approach for the production of F-T liquids from biomass, coal, and natural gas. We compare our results to other published results in the case of coal and natural gas feedstocks.

An important recent technological development in commercial F-T conversion is "liquid-phase" synthesis. In a liquid phase reactor, the feed gas is bubbled through a heavy oil (e.g., the waxy fraction of F-T liquids) in which catalyst particles are suspended. The vigorous mixing, the intimate gas-catalyst contact, and the uniform temperature distribution enable conversion of feed gas to F-T liquids in a single pass of about 80%, as measured by fraction of CO converted (Bechtel Group, 1990). This compares to less than 40% conversion with traditional fixed-bed F-T reactors, such as those used in the Shell Malaysia plant and in South Africa. Considerable recycling is required with fixed-bed reactors to achieve high overall yield. The higher gas throughput capacity per unit volume with liquid-phase synthesis reduces capital costs compared to a fixed-bed reactor, and catalyst consumption per unit of product is reduced dramatically (Jager, 1997). Liquid-phase reactors are now commercially available for F-T synthesis (Jager, 1997), and are being developed for synthesis of methanol and dimethylether (Tijm *et al.*, 1997).

2.2. F-T conversion of coal

The main difference between a process for producing F-T liquids from coal compared to production from natural gas is in the syngas production step. The reforming step is replaced by a pressurized oxygen-blown gasifier when using coal. The resulting syngas (after gas cooling and cleaning) consists almost entirely of CO and H_2. Depending on the gasifier design, the H_2/CO ratio in the syngas can be too low for F-T synthesis. The ratio is adjusted using the shift reaction, either in a shift reactor upstream of the F-T synthesis step, or by direct injection of steam into the F-T reactor, wherein the shift reaction occurs along with the F-T synthesis reactions.

2.3. F-T conversion of biomass

The process for converting biomass into F-T liquids (Fig. 2) is similar in many respects to that for coal conversion. However, some methane and other light hydrocarbons are found in the product gas from most biomass gasifiers, so a hydrocarbon reforming step is needed after gasification to maximize conversion to F-T liquids. Biomass is more reactive than coal, so lower temperatures can be used in the gasification step. This provides the possibility of using indirectly-heated gasifiers, which produce a gas undiluted by inert nitrogen without the use of costly oxygen. [Indirectly-heated gasifiers under development include the Brightstar Synfuels Company (BSC) design (Menville, 1998), the Battelle Columbus Laboratory (BCL) design (Anson *et al.*, 1999), the Thermochem design (MTCI, 1990), and the DMT design (Chughtai and Kubiak, 1998).] Air-blown gasification can also be used, though this requires larger downstream vessel sizes to handle the nitrogen-diluted syngas. Oxygen-blown gasification avoids nitrogen dilution, but the reduced vessel and piping costs must be evaluated against the added costs for oxygen supply.

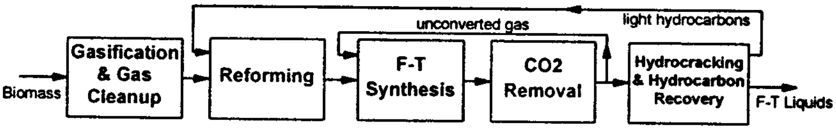

Figure 2. Simplified diagram for Fischer-Tropsch liquids production from biomass.

A simpler process design involves "once-through" F-T synthesis, wherein the reforming step is eliminated, and the syngas passes only once through the F-T synthesis reactor. Unconverted gas, rather than being recycled for further conversion, is used to fire a gas turbine to generate electricity as a co-product (Fig. 3).

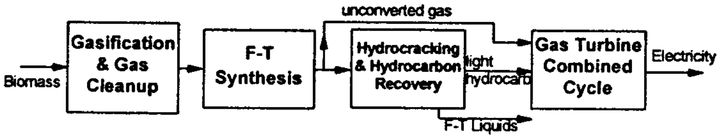

Figure 3. Simplified diagram of "once-through" co-production of electricity and F-T liquids from biomass.

Table 1. Energy balances for F-T liquids production from coal and from natural gas.

Feedstock ➪	Coal		Natural Gas	
	Bechtel[a]	Calcs.[b]	Bechtel	Calcs.[d]
	Gasifier		[c]Reformer	
mass % H_2	2.33		-	3.20
N_2	1.0		-	65.4
CO	90.5		-	24.2
CO_2	5.88		-	2.70
CH_4	0.013		-	0
H_2O	0.30		-	4.60
kg_{gas}/kg_{feed}	1.69		-	6.74
GJ_{gas}/GJ_{feed}	0.80		-	0.847
	Process energy demands (GJ/GJ_{feed})			
Electr. (GJ_e/GJ_{feed})	0.009[e]	0.0634[f]	not	0.054[g]
Butane (GJ/GJ_{feed})	0.0296	-	0.00356	-
	Products (GJ/GJ_{feed})[h]			
Electr. (GJ_e/GJ_{feed})	0	0.00151	not	0.0860
LPG (C_3-C_4)	0.016	0	0.0156	0
Naphtha (C_5-C_9)	0.274	0.608	0.209	0.553
Kerosene (C_{10}-C_{12})				
Diesel (C_{13}-C_{18})	0.298		0.337	
	Fraction of feedstock HHV converted to			
Net electricity	- 0.009	- 0.0619	0.00473	0.032
Net hydrocarbons	0.559	0.608	0.558	0.553
Overall Eff.	**0.550**	**0.546**	**0.563**	**0.585**

a. Based on Choi, *et al.* (1993) using a Shell gasifier with Illinois #6 coal. See also Bechtel (1991-1994).

b. Our calculations, with gasifier performance as for Bechtel and α=0.92 for F-T synthesis.

c. Based on Choi, *et al.* (1996). Reforming is primarily by partial oxidation, but the reformate is supplemented by reformate from a separate, smaller steam reformer to increase the sythesis feed-gas H_2:CO ratio.

d. Our calculations, assuming air-blown partial oxidation reformate composition from A.D. Little (1994), and α=0.92 for synthesis.

e. Bechtel study assumed use of steam-driven air separation unit, so process electricity requirement is relatively low.

f. Process electricity demands (GJ_e/GJ_{feed}) include 0.00437 for hydrogen separation using PSA, 0.055 for cryogenic oxygen production, and 0.004 for other uses.

g. Process electricity demands (GJ_e/GJ_{feed}) are 0.0457 for compressors, 0.0057 for H_2 separation with PSA, 0.003 for other.

h. Assumed higher heating values (MJ/kg): C_3-C_4, 50.0; C_5-C_9, 48.50; C_{10}-C_{12},47.94; C_{13}-C_{18}, 47.66; C_{19+}, 47.50; C_5-C_{12}, 48.36.

The elimination of recycle loops compared to the "full recycle" configuration reduces investment costs for the synthesis and refining steps. Also, CO_2 removal is not needed if a high-α synthesis step is used in combination with hydrocracking. In such a configuration, only liquid-phase material will go to the hydrocracker and all gases will be directed to the combined cycle.

3. PRELIMINARY ENERGY BALANCES

3.1. Calculation method

We estimate mass and energy balances for each major piece of process equipment as follows. For *coal and biomass gasifiers*, we adapt from the literature the mass and energy balances for different gasifier designs, as detailed in the notes to subsequent tables. Given the preliminary nature of the calculations in this paper, we have not sought to verify quoted gasifier performance. With one exception, we assume all *reformers* are steam reformers, with a fraction of the feed gas to the reformer diverted to a burner to provide heat to drive the endothermic reactions. The fraction of feed gas diverted varies with hydrocarbon content of the gas being reformed, and is based on work by Katofsky (1993). For the conversion of natural gas, we assume air-blown partial oxidation reforming, with performance based on A.D. Little (1994). Reforming converts all hydrocarbons to CO and H_2.

The *F-T synthesis* step is modeled assuming that a single pass of synthesis gas through the reactor results in 80% mass conversion of the [CO + H_2] in the feed gas. Hydrocarbons constitute between 24% and 44% of the mass of converted [CO + H_2], depending on the starting H_2:CO ratio. The balance of the converted [CO + H_2] forms H_2O and/or CO_2. The carbon-number distribution of the hydrocarbon products is given by a Schulz-Flory distribution. The F-T synthesis step assumes an α value between 0.92 and 0.95, and the product distribution from the *hydrocracker* is based on published empirical results. The hydrogen requirement for the hydrocracker is estimated based on discussions with industry experts. Hydrogen for the hydrocracker is assumed to be recovered from mixed gases using *pressure swing adsorption* (PSA). When a *gas turbine* is included in the overall process, the efficiency of converting fuel gases to electricity is assumed to be 50% on a higher heating value basis, representing a modern gas turbine/steam turbine combined cycle. *Process steam demands* are assumed to be met by waste heat recovery, e.g., from reformer furnace flue gases, F-T synthesis cooling flows, product streams, etc. *Process electricity demands* are estimated for the main compressors (assuming single-stage adiabatic efficiency of 80%, maximum single-stage pressure ratio of 3:1, and multiple stages with intercooling for larger overall pressure ratios); for oxygen production (assuming 480 kWh/tonne O_2); for PSA [based on Katofsy (1993)], and for the balance of demands (assuming the same kWh per unit of feedstock energy as given by Williams *et al.* (1995) for methanol production from the same feedstock).

Table 2. Calculated energy balances for F-T liquids from biomass with indirectly-heated gasifier, F-T reactor α=0.95, and with hydrocracker.

Process Design ⇨	Full Recycle	Once-through
Gasifier performance[a]		
mass % H_2	3.58	
CO	35.8	
CH_4	10.2	
CO_2	39.3	
C_2H_2	1.33	
H_2O	5.52	
N_2	4.29	
kg_{gas}/kg_{feed}	0.932	
GJ_{gas}/GJ_{feed}	0.727	
Process electricity demand		
GJ_e/GJ_{feed}	0.0373[b]	0.0251[c]
Products (GJ/GJ_{feed})		
Electr. (GJ_e/GJ_{feed})	0.0373	0.197
LPG (C_3-C_4)	0	0
Naphtha (C_5-C_9)	0.125	0.067
Kerosene (C_{10}-C_{12})	0.246	0.132
Diesel (C_{13}-C_{18})	0.123	0.0658
Waxes (C_{19+})	0	0
Fraction of feedstock HHV converted to		
Net electricity	0	0.172
Net hydrocarbons	0.494	0.265
Overall HHV eff.	**0.494**	**0.437**
Effective eff.[d]	**---**	**0.521**

a. Gasifier performance from Menville (1998), with input biomass moisture content of 40%.

b. Process electricity demands (GJ_e/GJ_{feed}) are 0.0220 for compressors, 0.0118 for PSA-H_2 separation, and 0.0036 for other uses.

c. Process electricity demands (GJ_e/GJ_{feed}) are 0.0194 for compressors, 0.0021 for PSA-H_2 separation, and 0.0036 for other uses.

d. Effective efficiency equals higher heating value of net hydrocarbons divided by HHV of biomass charged to hydrocarbon production. The latter is the total biomass input less the biomass that would be required for a stand-alone BIG/GTCC to generate the same amount of net electricity as generated at the F-T facility. Assuming a stand-alone generating efficiency of 35% (HHV), the Effective efficiency = NH/[1 - (NE/0.35)], where NH = net hydrocarbon fraction and NE = net electricity fraction.

3.2. Energy balances for coal and natural gas

Table 1 compares our estimates of overall process energy efficiency for F-T liquids production from fossil fuels with results published by others based on detailed process modeling. In all cases the process designs incorporate recycle loops to increase F-T liquids production. The overall efficiency for converting natural gas is higher than for converting coal, as expected. Our calculated efficiency with natural gas is higher than reported by Bechtel (Table 1), but is slightly lower than indicated in a study by Gray and Tomlinson (1997). Our coal conversion efficiency agrees reasonably well with Bechtel's result (Table 1), but is somewhat lower than indicated by Gray and Tomlinson. In any case, both of our calculated efficiencies are within one or two percentage points of other published results, providing some confidence in our simplified calculation approach.

3.3. Energy balances for biomass

Table 2 shows results of our calculations for biomass conversion using an indirectly-heated gasifier design. Results in the first column are for a "full recycle" process configuration, which maximizes F-T liquids production but generates no exportable electricity. (Just enough electricity is generated using diverted fuel gas to meet the process electricity demand.) The overall efficiency of producing F-T liquids in this case is about 49%. This is a few points lower than our calculated result for coal (Table 1), due primarily to the lower cold-gas efficiency for biomass gasification (73% versus 80% for coal) and the greater energy demand for reforming hydrocarbons in the biomass-gasifier product gas before F-T synthesis.

The second set of results in Table 2 is for a "once-through" configuration. The "once-through" biomass conversion case has an overall efficiency (counting both electricity and F-T liquids as products) about six percentage points lower than the "full recycle" case because a significant amount of syngas is converted to electricity rather than to F-T liquids, and the efficiency of

Table 3. Calculated energy balances for "once-through" co-production of F-T liquids and electricity from biomass for different gasifier designs. Alpha = 0.95 for the synthesis reaction, and hydrocracking is used to produce final products.

Gasifier Design ⇨	Indirect (BSC)[a]	Indirect (BCL)[b]	Oxygen (IGT)[c]	Air,low P (TPS)[b]	Air,high P (Bioflow)[b]
	Gasifier efficiency (HHV gas output/HHV biomass input)				
GJ_{gas}/GJ_{feed}	0.727	0.707	0.761	0.700	0.700
	Fraction of biomass HHV converted to				
Net electricity	0.172	0.183	0.038	0.082	0.142
Net hydrocarbons	0.265	0.231	0.473	0.318	0.264
Overall HHV eff.	**0.437**	**0.414**	**0.511**	**0.400**	**0.406**
Effective eff.[d]	**0.521**	**0.484**	**0.530**	**0.415**	**0.445**

a. Gasifier performance for the Brightstar Synfuels Company design, as reported by Menville (1998) with 40% feed biomass moisture.

b. Gasifier performance as reported by Consonni and Larson (1996) with 15% feed biomass moisture content. BCL = Battelle Columbus Laboratory design; TPS = TPS Studsvik design; Bioflow = Fosterwheeler's Bioflow design.

c. Gasifier performance as reported by Katofsky (1993) with 10% feed biomass moisture. IGT = Institute of Gas Technology gasifier design

d. See Table 2, note d.

converting syngas to electricity is lower than that for conversion to F-T liquids. Interestingly, however, the effective efficiency of producing F-T liquids in the "once-through" configuration is about the same (actually slightly higher) than the efficiency of the "full recycle" case.[2] The high effective efficiency achieved with the simpler "once-through" process configuration suggests improved economics of F-T liquids production compared to production from the "full recycle" configuration.

For different biomass gasifier designs, Table 3 shows calculated efficiencies for "once-through" process configurations that co-produce F-T liquids and electricity. Results are shown for two indirectly-heated, atmospheric pressure gasifiers, one pressurized, oxygen-blown gasifier, one pressurized air-blown gasifier, and one atmospheric-pressure air-blown design.

The total overall efficiency ranges from 40% to 51% among the five cases. Differences in efficiencies between cases can be explained in terms of either differences in efficiencies of the gasification step and/or differences in the ratio of C_xH_y:(CO + H_2) in the gasifier product gas. Higher gasification efficiency gives higher overall efficiency. A higher C_xH_y:(CO + H_2) ratio means that a larger fraction of the energy in the product gas is converted to electricity and less is converted to F-T liquids. Since syngas conversion to electricity is less efficient than conversion to liquids, overall efficiency is lower for larger ratios of C_xH_y:(CO + H_2). The case with pressurized oxygen-blown gasification gives the highest overall efficiency, followed by indirectly-heated gasifiers and then air-blown gasifiers. More detailed performance analysis, together with cost assessment are needed to determine which of the different process configurations would be most cost competitive in a given application.

4. CONCLUSIONS

A resurgence of interest in Fischer-Tropsch conversion technology is being driven by the goal of converting remote natural gas resources into marketable liquid products such as high-cetane number, low-aromatic, no-sulfur diesel blending stock for reducing diesel-engine vehicle tailpipe emissions. Because remote gas fields are typically small, much of the F-T technology development effort is aimed at making smaller scale facilities cost competitive. An important recent technology development in this regard is liquid-phase synthesis, which achieves much higher throughput per unit volume than synthesis using traditional fixed-bed reactors. Processes for converting biomass to F-T liquids can take advantage of such technological developments.

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[2] The effective efficiency is the higher heating value (HHV) of F-T liquids divided by the HHV of the biomass charged to F-T liquids production. The biomass charged to F-T liquids is the total biomass input less the amount of biomass that would be required with a stand-alone gasifier/combined cycle to generate the same amount of electricity as that exported from the co-producing facility. Assuming a stand-alone generating efficiency of 35% (HHV), and using the results in Table 2, the effective efficiency of producing F-T liquids with the once-through process is 0.265/[1.0 - (0.172/0.35)] = 0.521.

We have presented preliminary energy balances for the conversion of biomass to F-T liquids in "full-recycle" process configurations that maximize F-T liquids production and in "once-through" configurations that co-produce electricity and F-T liquids. A significant result is that the effective efficiency of producing F-T liquids using a "once-through" design is about the same as the efficiency of producing F-T liquids in a "full recycle" configuration. The simpler process configuration of the former should provide for better economics.

5. REFERENCES

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6. ACKNOWLEDGEMENTS

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