Techno-economic analysis of production of Fischer-Tropsch liquids via biomass gasification: the effects of Fischer-Tropsch catalysts and natural gas co-feeding

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Abstract

The effects of H₂/CO ratio in syngas from a biomass gasifier, the type of a Fischer-Tropsch (FT) catalyst, addition of a reformer in a recycle mode, efficiency of CO₂ removal, and co-feeding of biomass and natural gas on the overall thermal efficiency and costs for the production of FT liquid fuels from the biomass-derived syngas were analyzed using an Aspen Plus[®]-based process model. The overall thermal efficiency for biomass-fed processes was in a range of 41.3-45.5%. A

cobalt catalyst-based FT process achieved slightly higher efficiency than an iron-based FT process mainly owing to the absence of water-gas shift activity on a cobalt FT catalyst. A proper amount of CO₂ in the syngas can inhibit the amount of CO₂ generated via the water-gas shift reaction in a FT reactor with an iron-based catalyst which yields a similar efficiency to a cobalt-based FT process. The lowest production costs were around \$28.8 per GJ of FT liquids for the biomass fed processes with a reformer. However, the addition of a reformer in the gas recycle loop can improve the economics only when the operation of the plant is optimized for maximum fuel production rather than co-generation of fuels and power. A process with co-feeding of natural gas into the reformer can achieve more attractive economics than a solely biomass fed process. Co-feeding of biomass and natural gas at 50% of thermal total thermal energy input of 400 MWth for each feedstock reduced the costs of FT liquid production by about 30% to \$19-\$20 per GJ of FT liquids. However, production of FT biofuels would be economically viable only at very high oil price or if some premiums are considered for the production of green fuels and power. At an oil price of \$60/barrel, production of FT biofuels in the process configurations considered in this study wouldn't be economically feasible.

Keywords: Fischer-Tropsch, Biofuel, Biomass Gasification, Aspen Plus[®], Process modeling, Techno-economic analysis

1. Introduction

There is an increasing demand for the production of clean and renewable fuels and power due to the depletion of fossil fuel sources and global warming. In the US alone, Energy Independence and Security Act of 2007 called for annual production of 36 billion US gallons ($140 \times 10^6 \text{ m}^3$) of biofuels by 2022 [1]. The conversion of biomass to liquid fuels in an integrated gasification and FT process may be promising and carbon neutral [2, 3] without a need for CO_2 capture and storage. Fischer-Tropsch (FT) synthesis is an industrially proven technology for producing a variety of liquid transportation fuels such as diesel, gasoline, and kerosene from syngas in the presence of an iron or cobalt based catalyst. The syngas can be produced from coal gasification, biomass gasification and natural gas reforming. Currently, there are several commercial plants around the world that produce FT liquids from natural gas (gas-to-liquid process, GTL) [5, 6] and coal (coal-to-liquid process, CTL) [7, 8]. Production of FT liquids from biomass (biomass-to-liquid, BTL) is, however, still at a development stage, although pilot and demonstration facilities are being developed across the world [9]. The biggest obstacle for the commercialization of FT biofuels is their lack of economic competitiveness in today's energy market, especially owing to their high capital costs [10].

FT biofuels exhibit attractive advantages over available biofuels such as bioethanol and biodiesel from food grains, which include:

- i. Being compatible with non-food crops such as woody biomass, wood residue, and grasses;
- ii. Having similar characteristics to conventional petroleum-derived transportation fuels such as diesel and gasoline but having a near-zero sulfur content and no need for

- 63 blending with petroleum-based fuels; and
- 64 iii. Compatibility with available infrastructure for fuel transportation and storage as well as
- 65 vehicle engine designs.

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67 A FT synthetic process can catalytically convert syngas into a variety of fuels and chemicals

68 such as methanol, ethanol, gasoline, diesel, lubricant, and olefins [6, 11, 12]. The FT synthetic

69 process can be divided into four main steps: syngas production, syngas cleaning and

70 conditioning, FT synthesis, and FT product refining and upgrading. Syngas can be produced in

71 various ways depending on the feedstock used: reforming of natural gas or gasification of

72 biomass, coal, petroleum coke, and municipal solid waste. The syngas requires additional

73 processing to remove possible contaminants and impurities such as particulates, sulfur and

74 nitrogen containing compounds. The syngas for a FT process might require to adjust H_2/CO ratio

75 and reduce CO_2 content [13]. The cleaned and conditioned syngas, is then converted to

76 hydrocarbons in a FT synthesis reactor. The products of FT synthesis are then separated and

77 upgraded into different liquid fuels and chemicals using similar unit operations that can be found

78 in a petroleum refinery [14].

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80 The technical and economic aspects of BTL process have been extensively studied. Tijmensen et

81 al. reported that the overall thermal efficiency of a BTL process on a lower heating value (LHV)

82 was 33–40% for gasification systems operated at an atmospheric pressure and 42–50% for

83 pressurized gasification systems [15]. The CO_2 removal might not always be favorable for

84 maximum FT liquid production in a BTL process, which needed further investigation [15].

85 Hamelinck et al. reported that the thermal efficiency of a BTL process on a high heating value

(HHV) basis was 40-45% [16]. The production costs of FT liquids in a BTL process was found to be 2-4 times higher than those of petroleum-derived diesel [15,16]. FT synthesis requires syngas with a proper H_2/CO ratio. Leibbrandt et al. reported that a gasification process operated with a moderate steam-to-biomass ratio followed by a downstream shift reactor would achieve higher thermal efficiency than the use of only a gasifier operated at a high steam-to-biomass ratio to produce syngas with a proper H_2/CO ratio [17].

However, there was no information found in literature on the effects of CO_2 content of syngas on FT synthesis and the use of CO_2 in syngas as a part of carbon sources in a BTL process. An iron or cobalt based FT catalyst requires different syngas composition, particularly CO_2 content that was industrially reduced by an acid-gas removal (AGR) process. It is not clear how the choice of either an iron or cobalt based FT catalyst would affect the overall thermal efficiency of a BTL system. Carbon conversion efficiency of a BTL process strongly depends on the amount of H_2 in the system as CO_2 can be utilized through a reverse water-gas shift reaction to produce additional CO as a main carbon source for FT synthesis reaction. This work was thus to investigate the effects of several main operating parameters on the energy efficiency and economics of a BTL refinery using an Aspen Plus[®]-based process model. These parameters include the CO_2 removal efficiency in an AGR process, the choice of iron or cobalt based catalyst for FT synthesis, once-through operation versus reforming and recycling of off-gas from the FT process, and co-feeding of natural gas into the refinery.

2. Methodology

2.1 Process model development

Various refinery configurations for the conversion of biomass to FT liquid fuels can be designed depending on the choices of gasification technology, FT process and the gas cleaning process. It should be noted that the configurations in this study only include commercially available technologies that are thus ready for the deployment. Figure 1 shows a general scheme with the main process steps for producing FT fuels and power from biomass.

Figure 1. Schematic view of a plant for the production of FT fuels and electricity through biomass gasification

Biomass feedstock after proper pretreatment such as grinding and drying is gasified into a gaseous mixture called syngas with dominant amounts of H_2 , CO , CO_2 , and CH_4 . The syngas then undergoes several cleaning and conditioning steps to prepare it for the FT synthesis. Those steps would include but not be limited to the removal of particulates and sulfur containing compounds, removal and/or catalytic cracking of tar compounds, a water-gas shift (WGS) process for the adjustment of H_2/CO ratio, and CO_2 removal. The cleaned and conditioned syngas then enters the FT synthesis reactor which could include either an iron or cobalt based catalyst at various operating temperatures and pressures. After the synthesis, the effluent of the FT reactor is cooled down to separate a gaseous cut (unconverted reactants and C_1 - C_4 hydrocarbons) and liquid hydrocarbons (C_{5+}). Off-gas can be partly recycled and/or used to generate heat and/or electricity. The liquid products will be further upgraded and separated into diesel, gasoline and other fuel blends in the refining area.

The integrated process configuration consisted of gasification, water-gas shift (WGS), acid-gas removal (AGR), reforming, FT synthesis, and power generation units were modeled in Aspen Plus[®], as depicted in **Error! Reference source not found.a**. Previous studies suggested that a biomass loading capacity higher than 400 MW_{th} is required for favorable production economy [16, 17] and thus, the input biomass thermal capacity of all cases in this study was fixed at 400 MW_{th, LHV}. This corresponds to 1923.7 ton/day of dried biomass (with 15% moisture). The design and specifications of the plant unit operations are described below.

a. Overall process flow chart

b. Process sub flowsheet for fluidized bed biomass gasification using the SMS approach [18]

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c. Process sub-flowsheet for gas reforming area

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d. Process sub-flowsheet of heat recovery and power generation area

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Figure 2. Process flow chart developed in Aspen Plus[®] for the production of FT liquids and electricity through biomass gasification

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148 2.1.1 Gasification

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Figure 2b gives the sub-flow chart developed in Aspen Plus[®] for a fluidized bed biomass gasifier using the sequential modular-based model (SMS) in our previous study [18].

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Among available reactor configurations for biomass gasification, the fluidized bed is a promising technology. Most biomass fluidized bed gasifiers under development nowadays employ one of two types of configurations: bubbling and circulating fluidized beds. In a fluidized bed, vigorous solid-gas mixing and high reaction rates ensure the good heat and mass transfer throughout the reactor [19]. In addition, a catalytic material such as dolomite and spent FCC catalyst can be easily added to the bed medium to improve the tar cracking for producing syngas with a very low tar content which would eliminate the need of an external catalytic tar cracker [20]. Some of the

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successful demonstrated pilot and commercial scale fluidized bed gasifiers up to date are IGT, TPS, Stein, EPI, BCL, and Sydkraft gasifiers [19]. A pressurized oxygen-blown fluidized bed gasifier was chosen in this study. According to previous studies, the use of oxygen as the gasifying agent (as opposed to air) has the most promising economics and advantages of scale for downstream liquid fuel synthesis [16, 17]. Air gasification introduces a large amount of inert nitrogen into the system, which will reduce the yields of liquid hydrocarbons in the synthesis reactor and significantly increase the size of downstream equipment.

Aspen Plus[®] does not contain an intrinsic reactor model that can be used to simulate complicated kinetics and hydrodynamics phenomena in a fluidized bed reactor system. We have developed a sequential modular-based model to simulate a fluidized bed gasifier in Aspen Plus[®] in our previous work [18], which was used in this study. The model takes into account of the hydrodynamic and detailed kinetics of the biomass gasification in a bubbling fluidized bed. The model includes the kinetics of tar decomposition which profoundly affects the syngas composition. Raw biomass (assumed to have 30% moisture) is dried down to 15% moisture using available process steam (Table 1). For the biomass input of 400 MW, the thermal power needed to evaporate the required amount of water was about 26.2 MW. The biomass then undergoes devolatilization (primary pyrolysis) reactions and the products are then split between a series of continuous stirred tank reactor and plug flow reactor (CSTR/PFR) pairs, representing emulsion/bubble phases in a fluidized bed. Each CSTR and PFR contains a set of reaction kinetics for the chemical reactions taking place in the bed using separate FORTRAN subroutines. The output of the last sub-reactor pair goes into the freeboard zone of the gasifier which was modeled as a PFR and finally hot syngas exits the gasifier. The model was able to predict the

composition of syngas with varying operation conditions such as equivalence ratio (ER), steam to biomass ratio (SBR) and bed temperature [18].

Table 1. Proximate and Ultimate Analysis of Woody Biomass (dry, ash-free basis) [21]

Proximate analysis (mass %)	
Fixed carbon	16
Volatiles	84
Ultimate analysis (mass %)	
C	50.3
H	5.7
O	44.0

The predictions of the model were validated by experimental data from the IGT gasifier using similar design parameters [22]. The steam to biomass ratio (SBR) for the IGI gasifier was 0.34 kg steam/kg biomass [22]. Two SBRs of 0.35 and 0.05 kg steam/kg biomass at the gasifier inlet were used in this study to analyze the effects of SBR on the performance of the BTL refinery. The H₂/CO ratios of the syngas produced at the two SBRs were 1.43 and 0.89, respectively, denoted as model-1 and model-2 in Table 2. The increase of SBR increases the H₂ content of syngas mainly owing to the water-gas shift reaction. However, the excessive amount of steam would significantly decrease the thermal efficiency, which should thus be avoided.

Table 2. Operating conditions and syngas compositions of two typical gasifier runs used in the simulations

Gasifier	Feed rate (ton/day) ²	O ₂ (kg/kg- dry- wood)	SBR (kg/kg- wet- wood)	T _{bed} (°C)	Gas composition (wet-vol%)					tar content (mg/Nm ³)	H ₂ /CO	CGE %
					H ₂ O	H ₂	CO	CO ₂	C ₁ -C ₄			
IGT ¹	100.1	0.3	0.34	983 ³	31.8	20.8	15.0	23.9	8.5	-	1.39	80.7
Model-1	1923.7	0.3	0.35	950 ⁴	31.6	21.3	14.9	23.5	8.7	198	1.43	77.7
Model-2	1923.7	0.3	0.05	950 ⁴	28.5	19.9	22.4	20.6	8.9	235	0.89	77.9

¹Data from [22]

²On a dry basis (15% moisture)

198 ³ *Temperature at exit*
199 ⁴ *Average temperature of bed and splash zone*
200

201 2.1.2 *Gas cleaning*

202 The crude syngas may contain different types of contaminants such as particulates, tar
203 compounds, alkali compounds, H₂S, COS, HCN, NH₃ and HCl in various quantities depending
204 on the source of biomass and operating conditions of a gasification reactor. These contaminants
205 would deposit in downstream equipment and cause serious erosion and corrosion problems if not
206 removed effectively [23]. Some of these contaminants might also lower the activity of catalysts
207 in downstream processes such as WGS, FT, and reforming [24]. Sulfur is known to poison iron
208 and cobalt-based FT catalysts by strongly adsorbing on the active sites of catalysts [25, 26].
209 Syngas from a gasifier, thus, needs to undergo several cleaning steps to reduce the concentrations
210 of all contaminants to satisfy the requirements of downstream processes. Dry and wet gas
211 cleaning are the two methods that have been discussed in literature. The latter is an industrially
212 proven technology, while the former is still under development. The hot syngas cleaning might
213 be advantageous in terms of efficiency as it doesn't require the cooling of the hot syngas prior to
214 cleaning. However, it is not ready for commercial scale deployment. Therefore, wet syngas
215 cleaning, as described in the reference [27], was used in this study. In such a scheme, after the
216 removal of particulates in a cyclone, syngas is typically cooled-down to a temperature below
217 100°C and brought in contact with scrubbing liquids such as water or a water-NaOH solution to
218 remove a range of contaminants including particulate matter, nitrogen compounds (NH₃, HCN),
219 and tars [23]. The number and type of wet scrubbers and filters used in the wet gas cleaning can
220 be tailored according to the type and the quantity of contaminants as well as the extent of
221 cleaning required for downstream applications.

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2.1.3 Water-Gas Shift and CO₂ removal

The ratio of H₂/CO in the syngas is an important parameter that affects the performance of a FT process. The optimum values of H₂/CO are 2.15, 1.65, and 1.0 for low-temperature cobalt, low-temperature iron and high-temperature iron-based processes, respectively [28]. The H₂/CO ratio can be adjusted in a water-gas shift unit in which H₂O reacts with CO to produce more H₂ according to the following reaction:

For an iron-based FT process, this step might not be necessary as iron has significant WGS catalytic activity and is able to internally adjust H₂/CO [28]. In addition, iron can also convert CO₂ to CO through the reverse WGS and consequently to FT products. High temperatures and high concentrations of H₂ and CO₂ in the syngas promote the WGS reaction in the reverse direction although attainable CO₂ conversion especially at low-temperature FT conditions might be very low. In the case of an iron FT catalyst and the presence of CO₂ in syngas, the Ribblett ratio [H₂/(2CO+3CO₂)] is the preferred term to compare the relative amount of H₂ to the stoichiometric amount of H₂ for the complete conversion of CO and CO₂ to FT products (2 and 3 moles of H₂ per each mole of CO and CO₂, respectively). While the Ribblett ratio of 1 corresponds to the stoichiometric amount of H₂ required for the full conversion all CO and CO₂ in syngas, previous experimental work has shown the possibility of carrying out FT synthesis on an iron-based catalyst with CO₂-containing syngas that has a Ribblett ratio as low as 0.5 [29-33]. A Ribblett ratio higher than 1 is not recommended as it will shift the product distribution of FT synthesis toward shorter-chain hydrocarbons [34].

A sour water-gas shift process is proposed here. This process typically uses a cobalt-

molybdenum based catalyst which is resistant to sulfur poisoning as opposed to an iron-based sweet shift catalyst. The sour shift process also hydrolyzes the COS into H₂S which makes the downstream sulfur removal more facile [35, 36]. In Aspen Plus[®], the WGS reactor was modeled using an adiabatic Gibbs reactor under the restricted equilibrium option. The WGS reactor is placed on a side stream to reduce the size of the reactor. The split ratio of the side stream is adjusted using a Design Spec in Aspen Plus[®] to obtain the desirable H₂/CO ratio in the exit gas.

The syngas from the gasifier also contains a large amount of CO₂ that will further increase due to the water-gas shift reaction. The presence of CO₂ in the syngas would lower the yield of liquid hydrocarbons in the FT synthesis, especially when a cobalt FT catalyst is chosen. Iron and cobalt FT catalysts behave differently in the presence of CO₂. In the case of a cobalt catalyst, CO₂ is not a reactant in the FT reaction but high concentrations of CO₂ would negatively affect the activity and C₅₊ selectivity [37, 38]. For an FT iron catalyst, however, CO₂ does not affect the catalyst selectivity and can also be converted to hydrocarbons according to the equilibrium constraints of WGS reaction [30, 31, 33, 39-42]. A Rectisol process is proposed to remove CO₂ and other acid gases. This process has a lower energy consumption than CO₂ absorption processes such as Selexol and MDEA processes [43]. Although a Rectisol process can achieve almost complete sulfur removal (0.1 ppmv), it is selectively configured to remove the CO₂ at a desired level (up to 97%) [44]. If a cobalt FT catalyst is used, a ZnO guard bed can be placed prior to the FT reactor to remove the traceable amount of sulfur-compounds as the cobalt is more prone to sulfur poisoning than an iron based FT catalyst [26].

For the sake of simplification, a Sep1block is used to represent the AGR unit in Aspen Plus[®]. On

the flowsheet, two streams exit the AGR unit, representing CO₂ and other contaminants such as H₂S, water, and tar to be removed in syngas cleanup. The heating and cooling duties for Rectisol unit were 0.2238 and 0.5590 MJ/kg-CO₂, respectively [43] which were assumed to be provided by onsite generated electricity.

2.1.4 Fischer-Tropsch Synthesis

There are two main operating modes for FT synthesis: low-temperature (LTFT) mode (200-240 °C) for the production of mainly diesel and wax hydrocarbons and high-temperature (HTFT) mode (300-360 °C) for the production of mainly gasoline and middle distillate hydrocarbons. A cobalt-based FT process is only operated in the LTFT mode while an iron-based process is flexible and can be operated in both modes. Here, we chose a slurry bubble column FT reactor that enables a per-pass conversion efficiency of as high as 80%, compared to a conversion efficiency lower than 40% for traditional fixed-bed FT reactors. It is worth noting that although gas-solid fluidized bed reactors are typically used for a HTFT process, their economic data is scarce in the literature and therefore we used the economic data of slurry phase reactors for all cases.

Tables 4 and 5 list the kinetics and product distribution models that were taken from the literature to calculate the extent and the product distribution of a FT process in different operating modes. The kinetics of FT synthesis is different for iron and cobalt catalysts and is typically reported in term of the rate of CO in moles converted to products per unit mass of the catalyst. The reaction rate equations were converted on a reactor volume basis (kmol-CO/s·m³) using a catalyst loading of 600 kg-catalyst/m³-reactor, which was a typical amount of catalyst per

unit volume of the reactor in a slurry bubble column FT reactor [16]. In this form, the reaction rates were implemented into the reactor subroutine codes in Aspen Plus®.

The product distribution of FT synthesis varies depending on the type of a catalyst and operating conditions employed. The distribution of the hydrocarbon products on a cobalt-based FT catalyst can be assumed to follow the theoretical Anderson-Schulz-Flory (ASF) distribution based on the chain growth probability values [16]:

$$m_{C_n} = \alpha^{n-1}(1 - \alpha) \quad (Eq. 2)$$

where α is the probability of the chain growth and m_{C_n} is the mole fraction of hydrocarbon with n carbon atoms. Here, α is calculated using the empirical correlation developed by Song et al. [45]:

$$\alpha = \left(0.2332 \frac{y_{CO}}{y_{CO} + y_{H_2}} + 0.633 \right) [1 - 0.0039(T - 533)] \quad (Eq. 3)$$

Table 3. FT reaction kinetics on cobalt and iron catalysts

FT catalyst	Kinetic equation	Reference
Cobalt (220-240 °C)	$r_{FT, Co} = \frac{a P_{CO} P_{H_2}}{(1 + b P_{CO})^2}$ $a = 10^{10} \exp\left(\frac{-115}{RT}\right) \quad \text{mol}/(s.kg.bar^2)$ $b = 3.5 \times 10^{-23} \exp\left(\frac{192}{RT}\right) \quad \frac{1}{K.bar}$	[16]
Iron (240-250 °C)	$r_{FT, Fe} = k_{FT} \frac{P_{CO} P_{H_2}}{(1 + 0.125 P_{CO} + 7 P_{H_2O})^2}$ $k_{FT} = 5.56 \times 10^{-2} \left(\frac{\text{mole}}{kg.s.MPa^{1.5}} \right)$ $r_{WGS, Fe} = k_{sh} \frac{P_{CO} P_{H_2O} - P_{CO_2} P_{H_2} / K_{EQ}}{(1 + 2.1 P_{CO} + 24.19 P_{H_2O})^2}$ $\log K_{EQ} = \left(\frac{2073}{T} - 2.039 \right)$	[46]

Iron (300 °C)	$r_{FT, Fe} = k_{FT} \frac{P_{CO} P_{H_2}}{P_{CO} + 33P_{H_2O} + 2.7P_{CO_2}}$ $k_{0,FT} = 8.5 \times 10^{-4} \left(\frac{\text{mole}}{\text{g.s.MPa}} \right)$ $r_{WGS, Fe} = k_{sh} \frac{P_{CO_2} P_{H_2} - P_{CO} P_{H_2O} K_{EQ}}{P_{CO} + 65P_{H_2O} + 7.4P_{CO_2}}$ $k_{0,WGS} = 4.1 \times 10^{-4} \left(\frac{\text{mole}}{\text{g.s.MPa}} \right)$	[41]
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This correlation takes into the account of the effects of H₂/CO ratio at the reactor inlet and the temperature of the reactor, which are two main parameters affecting the probability of chain growth. At H₂/CO molar ratio of 2.15 and the reactor temperature of 220 °C, the α value equaled to 0.82. It is assumed that alkanes are the only products of FT synthesis on a cobalt catalyst. Unlike iron-based FT synthesis, the formation of olefins on a cobalt-based FT catalyst is negligible [47].

For iron-based FT synthesis, olefin-readsorption product distribution model (ORPDM) developed by Van Der Laan and Beenackers [48] was used, which is given in Table 5. This model is an extension to ASF distribution which includes readsorption of α -olefins. The ORPDM gives the mole fraction of alkanes and alkenes with various syngas compositions and pressures. For high temperature FT, the constants of parameters p and t_p ¹ were modified to match the product selectivity to the values obtained from our experimental work at 300 °C and 20 bar [29].

Table 4. Parameters of the ORPDM for determining products via iron catalyst-based FT synthesis [48]

Mole fractions of FT hydrocarbons	Model parameters
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$m_{CH_4} = t_p^1 \theta_1$ $m_{C_2H_4} = \frac{t_0^2}{1 + k_R^2} \theta_2$ $m_{C_2H_6} = t_p^2 \alpha_2 \theta_1$ $m_{C_{2n}H_{2n+2}} = \theta_1 \prod_{i=2}^n \alpha_i$ $m_{C_{2n}H_{2n}} = \frac{t_0}{1 + k_R e^{cn}} \theta_1 \prod_{i=2}^n \alpha_i$ $\sum_{i=1}^n m_i = 1$	$t_p^1 = 6.62 \pm 1.92,$ $t_0 = 6.1686 P_{H_2}^{-0.5}, k_R = 3.3210^{-4} \frac{P_{H_2}^{1.4} P_{CO}^{-0.49}}{\frac{\phi_{v,0}}{W}}$ $k_R^2 = (12.58 \pm 3.55) k_R e^{2c}, c = 0.29 \pm 0.07$ $t_p^2 = 1.59 \pm 0.29$ $\frac{\theta_2}{\theta_1} = \alpha_2 \quad \text{for } n=2$ $\frac{\theta_n}{\theta_{n-1}} = \alpha_n \quad \text{for } n>2$ $P = 13.8 P_{H_2}^{-0.47} P_{CO}^{0.43}$
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323 Three separate FORTRAN subroutines were written to nest the kinetic equations and product
324 selectivity model into cobalt and iron based FT processes. The model can be used to calculate the
325 syngas conversion efficiency for a given reactor volume and also the molar distribution of
326 hydrocarbon products up to C₂₀. The sum of all longer chain hydrocarbons was represented by
327 C₂₁₊.

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329 2.1.5 Autothermal reforming

330 The FT synthesis products exit the reactor and are cooled down to separate gaseous cut
331 (unconverted reactants and C₁-C₄ hydrocarbons) and liquid and waxes (C₅₊ and water). The
332 liquid products will be further separated and upgraded, while the gaseous effluent can be
333 recycled or used to generate heat and electricity. The off-gas typically contains a significant
334 amount of light hydrocarbons (C₁-C₄) which can be reformed to produce syngas for the
335 production of additional high-value FT liquids. In a reformer, hydrocarbons react with steam to
336 produce additional H₂ and CO according to the following reaction:

The reforming reactor is typically operated at a temperature higher than 800 °C in the presence of a nickel-based catalyst [49]. When CO₂ exists in the feed stream of a reformer, dry-reforming reaction also takes place:

WGS (Eq. 1) is another important reaction which takes place in a reformer.

In this study, an autothermal reformer (ATR) was proposed in which the heat for highly endothermic reforming reaction is provided by the partial oxidation of the methane in the feedstock as follows:

In Aspen Plus[®], a Gibbs reactor was used to represent an ATR as shown in **Error! Reference source not found.**2c. The restricted chemical equilibrium option was chosen in Aspen Plus[®] and reactions Eqs. 1 and 4-6 were specified. The oxygen required by the ATR and gasifier was provided by an onsite cryogenic air separation unit (ASU) at 99.5% purity. The amount of O₂ fed into the reformer was controlled by using a design spec form in Aspen Plus[®] to automatically set the gas outlet temperature to 950 °C. Although the theoretical molar ratio of steam to methane is 1:1, an excess of steam (H₂O:C = 1.2 :1) is used to avoid coke formation [50].

2.1.6 Heat Recovery and Power Generation

The heat integration scheme shown in Figure 2d was used to utilize available excess heat to adjust the temperature of other streams in the process and generate steam for power production. The syngas produced in the gasifier is cooled down in two consecutive heat exchangers. In the

first heat exchanger, syngas is cooled to 350°C in a vertical fire-tube syngas cooler. This type of heat exchanger will minimize the deposition of small particles in the gas and alkali species that condense during cooling. The remaining particulates after the cyclone separation can then be removed by a barrier filter (ceramic or sintered metal) at 350 °C [2]. In the second syngas cooler, shifted syngas and reformed process gas from the ATR are further cooled down to 40 °C. The heat from the first syngas heat exchanger and the exothermic FT synthesis are used to generate medium pressure steam (250 °C, 20 bar) for the gasification, ATR and power generation. A portion of FT off-gas is burned in a boiler to produce superheated steam (510 °C, 70 bar) for power generation in a steam cycle. Air in an excess of 20% is preheated to 300 °C by using a fraction of the heat recovered in the second syngas cooler and fed to the boiler. A three-stage steam turbine is modelled at expanding pressures of 23.6 bar, 2.4 bar, and 0.046 bar. The isentropic and mechanical efficiencies are set at 0.85 and 0.98, respectively [15]. The parasitic load is provided with onsite power generation and the excess power is exported to the grid. Designs proposed in this study are for maximum FT liquids production, which is achieved by adjusting the split ratio of the FT off-gas stream going to the boiler so that the net electricity export from the plant is about 2.5% of total input thermal power (~10 MW_e). If co-generation of fuels and electricity is demanded, this value can be adjusted to accommodate the desired ratio of each product.

2.1.7 Aspen Plus[®] simulation

The Aspen Plus[®] model was used to calculate mass and energy balances across all the block and stream in the flowsheet. Table 5 gives the input data for the model.

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Table 5. Input data for Aspen Plus[®] modeling

Process unit	Design parameters
Gasifier	P=22 bar, ΔP=-3 bar, T=950°C, O ₂ =0.3 kg/kg-dry-wood, MP Steam=0.05-0.35 kg/kg-wet wood, O ₂ @ 350 °C/20 bar
Water-gas shift reactor	ΔP = -0.5, T _{in} = 330 °C, H ₂ O/CO=1
Heat exchangers	ΔP=-0.3 bar [17]
FT reactor	P=22 bar, ΔP=-2 bar, T=220°C for Co, T=240°C for LTFT, T=300°C for HTFT
ATR	P=20 bar, T _{exit} =950 °C, ΔP=-1 bar, H ₂ O/C=1.2
Steam cycle/ HRSG	HP steam (510 °C/70 bar), MP steam (250 °C/20 bar), steam turbine expanding pressures: 23.6/2.4/0.046 bar, η _{isen} = 0.85, η _{mech} = 0.98

385 Surplus electricity and FT liquids are assumed to be the marketable products of the plant, which

386 are compared in various scenarios in terms of lower heating value (LHV) contents as follows:

$$387 \quad FT \text{ liquids } \% = \frac{LHV \text{ of FT liquids (MWth)}}{LHV \text{ of biomass feedstock (MWth)}} \times 100\% \quad (Eq. 7)$$

$$Surplus \text{ electricity } \% = \frac{net \text{ electricity surplus (MWe)}}{LHV \text{ of biomass feedstock (MWth)}} \times 100\% \quad (Eq. 8)$$

388 The LHV of streams were calculated using the API method (QVALNET property method)

389 available in the Aspen Plus[®] library. The FT liquid is the total FT hydrocarbons with a carbon

390 chain longer than 5. Net electricity is the amount of surplus electricity available for export to the

391 grid after subtracting the power required by oxygen plant, gas compression, and AGR unit from

392 the total turbine power output. The energy consumption of the air separation unit was assumed to

393 be 380 kWh/ton-O₂ [51].

394

395 **2.2 Economic model**

396 The total capital investment (TCI) and cost of FT liquids production are calculated for several

397 process configurations. TCI was calculated using the factored estimation method [52]. In this

398 method, the costs of major components of the plant for a known size is obtained as a reference

and an appropriate scaling factor is applied to calculate the cost for a desired equipment size using the following equation:

$$\text{Cost}_{\text{size B}} = \text{Cost}_{\text{size A}} (\text{Size B/Size A})^{\text{scale factor}} \quad (\text{Eq. 9})$$

All cost estimates listed in Table 6 were derived from the literature [2, 16, 17]. A conversion factor of 1 US\$₂₀₀₂=1.07 €₂₀₀₂ was used for the cost data in the reference [16]. Cost estimates in Table 7 are final installed costs, which include the balance of plant (BOP) costs (such as electrical connections, piping, insulation instrumentation and controls) and indirect costs (engineering, startup, and contingencies, etc.) according to the instructions in the references. To address the average cost escalations in plant materials, equipment, engineering, and construction over the past years, the Chemical Engineering Plant Cost Index (CEPCI) [53] was used to convert from original-year dollars to 2015 dollars. The CEPCI for 2002, 2007, and 2015 were 395.6, 525.4, and 562.9, respectively.

The levelized costs of FTL production are calculated based on the procedure recommended by EPRI's TAG report [54]:

$$\text{FTL production costs } (\$/\text{GJ}) = [(\text{LACCR} \times \text{TCI}) + (\text{O\&M costs}) + (\text{Feedstock costs}) - (\text{Electricity sales price})] / (\text{FT liquids production}) \quad (\text{Eq. 10})$$

where LACCR is the levelized annual capital charge rate, defined as the annual percentage of TCI that is charged against the final energy products sold each year. A value of 15.41%/yr was used for the LACCR, as discussed and calculated by Kreutz et al., which is calculated based on the real annual interest of 7%, construction period of 3 years and plant lifetime of 20 years [2]. Other parameters of the production cost equation are listed in Table 7. We did not carry out a

detailed calculation of operating and maintenance (O&M) costs in this work and instead assumed them to be 4% of TCI, which was also taken from the literature [2]. This method was used for economic analysis of similar CTL plants and has been originally taken from earlier work by the NETL on detailed O&M cost estimates made for a gasification-based facility [55].

Table 6. Basic costs for major equipment used with their maximum size

Unit	Base capacity	Base cost (Million US\$)	Scale factor	reference, \$ year
Air separation unit	tonne/hr O ₂	23	0.75	[17], 2002\$
Pretreatment and gasification				
Conveyers	200 MW _{th} LHV	0.77	0.8	[17], 2002\$
Grinding	200 MW _{th} LHV	0.81	0.6	[17], 2002\$
Storage	200 MW _{th} LHV	2.09	0.65	[17], 2002\$
Dryer	200 MW _{th} LHV	17.95	0.8	[17], 2002\$
Iron removal	200 MW _{th} LHV	0.69	0.7	[17], 2002\$
Feeding system	200 MW _{th} LHV	1.09	1	[17], 2002\$
IGT gasifier	200 MW _{th} LHV	19.8	0.7	[17], 2002\$
Gas cleaning				
Cyclone	9 m ³ gas/s	1.36	0.7	[16], 2002\$
Syngas cooler	110 MW _{th}	12.15	0.6	[16], 2002\$
Particulate filter	9 m ³ gas/s	2.64	0.65	[16], 2002\$
Scrubbers	9 m ³ gas/s	4.56	0.7	[16], 2002\$
Guard beds (ZnO & active C)	8 m ³ -NPTgas/s	0.07	1	[16], 2002\$
Syngas processing				
Recycle compressor	2 MWe	2.15	0.67	[2], 2007\$
Autothermal reformer	365 MMSCF/day	29.9	0.67	[2], 2007\$
Shift reactor	2,400 kmol CO+H ₂ /h	0.45	0.6	[17], 2002\$
PSA unit A+B	9,600 kmol feed/h	51.49	0.7	[16], 2002\$
Rectisol unit	200,000 Nm ³ /hr	28.8	0.67	[2], 2007\$
FT production and upgrading				
FT feed compressor	2 MWe	2.15	0.67	[2], 2007\$
Slurry phase FT reactor + HXs	2.5 MMSCF/hr	2.5	0.75	[2], 2007\$
FT product upgrading	m ³ FT/h	33.82	0.7	[16], 2002\$
Power Production				
Boiler steam generator, ductwork, stack	24 MW _{th} boiler duty	2.5	1	[2], 2007\$
Steam cycle	30 MWe	15.1	0.67	[2], 2007\$

Table 7. Main assumptions for calculating the overall production costs of FT liquids

Parameter	Value	Source
Plant capacity factor	90%	assumed
Total annual capital charges	15.41%/yr	[2]
Biomass cost	\$5/GJ, HHV	[2]
Natural gas cost	\$3.31/GJ, HHV	[56]
O&M costs	4% of TCI	[2]
Electricity sales price	66.7 \$/MWh	[56]

3. Results and Discussion

3.1 Comparison between iron and cobalt-based FT processes

Tables 9 and 10, and Figures 3 and 4 show the performance of different configurations of iron and cobalt-based FT processes using syngas with high and low H₂/CO ratios produced by biomass gasification. The acronyms used in the various process configurations are given in Table 8.

Table 8. Description of acronyms used in naming the various process configurations

B/BNG	feedstock: B=biomass, BNG= hybrid biomass-natural gas
Co	low temperature FT process with a cobalt catalyst at 220 °C
FeLT	low temperature FT process with an iron catalyst at 240 °C
FeHT:	high temperature FT process with an iron catalyst at 300 °C
OT	designs that pass syngas only once through (OT) synthesis reactor and use unconverted syngas to generate electricity
1, 2, 3	numerals: indicates varied CO ₂ removal efficiency

Table 9. Performance of different process configurations with iron and cobalt-based FT processes and $H_2/CO=0.89$ at the gasifier outlet (all cases use a reformer in the recycle loop to maximize the fuel production)

Case ¹	FT process (catalyst/ temp)	AGR CO ₂ removal efficiency (%) ²	FT liquids (barrel per day)	FT products selectivity (mole-C %)			%C in FT liquids ³	$H_2/(2CO + 3CO_2)$ ⁴	CO ₂ (ton/day) ⁵
				C ₅ -C ₁₂	C ₁₃ -C ₂₀	C ₂₁₊			
BCo	Co-220°C	97	2,984.6	64.7	26.9	9.4	30.8	1.05	2,320.3
BFeLT-1	Fe-240°C	97	2,821.8	58.2	27.7	14.2	29.9	0.87	2,355.8
BFeLT-2	Fe-240°C	91	2,835.0	57.3	28.1	14.6	30.1	0.75	2,346.1
BFeLT-3	Fe-240°C	75	2,890.1	56.0	28.9	15.2	30.6	0.51	2,328.9
BFeHT-1	Fe-300°C	97	2,898.6	66.3	27.6	6.1	30.6	0.68	2,329.2
BFeHT-2	Fe-300°C	85	2,927.6	64.8	29.1	6.1	30.9	0.52	2,319.3

¹ See Table 8 for the description of the acronyms used in case designations

² represents the fraction of total CO₂ in syngas removed in AGR prior to the synthesis reactor

³ total CO₂ vented from AGR unit and the boiler

⁴ fraction of total carbon in the biomass feedstock. The remainder of carbon in feedstock is vented as CO₂.

⁵ at the FT reactor inlet

Table 10. Performance of different process configurations with iron and cobalt-based FT processes and $H_2/CO=1.43$ at the gasifier outlet (all cases use a reformer in the recycle loop to maximize the fuel production)

Case ¹	FT process (catalyst /temp)	AGR CO ₂ removal efficiency (%)	FT liquids (barrel per day)	FT products selectivity (mole-C %)			%C in FT liquids	$H_2/(2CO + 3CO_2)$	CO ₂ (ton/day)
				C ₅ -C ₁₂	C ₁₃ -C ₂₀	C ₂₁₊			
BCo	Co-220°C	97	2,985.5	64.7	26.9	9.4	30.8	1.05	2,329.2
BFeLT-1	Fe-240°C	80	2,668.6	61.3	26.1	12.7	28.1	1.00	2,415.1
BFeLT-2	Fe-240°C	72	2,713.3	59.9	26.7	13.6	28.6	0.75	2,404.6
BFeLT-3	Fe-240°C	60	2,771.9	60.9	26.3	12.8	29.2	0.50	2,375.4
BFeHT-1	Fe-300°C	90	2,665.5	72.4	21.3	6.3	28.0	1.03	2,425.1
BFeHT-2	Fe-300°C	80	2,730.6	70.8	23.2	6.1	28.7	0.74	2,402.0
BFeHT-3	Fe-300°C	67	2,795.7	69.1	24.5	6.5	29.4	0.51	2,377.1

¹ see the footnotes of Table 9

Figure 3. Overall energy efficiencies of different process configurations listed in Table 9 with iron and cobalt-based FT processes and $H_2/CO=0.89$ at the gasifier outlet.

Figure 4. Overall energy efficiencies of different process configurations listed in Table 10 with iron and cobalt-based FT processes and $H_2/CO=1.43$ at the gasifier outlet.

As shown in Tables 9 and 10, in iron-based FT processes, the amount of CO₂ removed in the AGR unit was varied to yield the syngas with various Ribblett ratios between 0.5-1.0, while in the case of cobalt-based FT process, the ratio was fixed at 1.07 (H₂/CO~2.15). To better reflect the effect of various CO₂ removal efficiencies on the size and cost of an AGR unit, a varying split of syngas stream was sent to this unit to obtain the desired removal efficiency.

Overall, a total of the input biomass energy from 38.8% to 43% on a LHV basis was converted into FT liquids, depending on the FT catalyst and the process configuration (Figure and Figure). Taking into account of the electricity output, the overall thermal efficiency was in the 41.3-45.5% range which is similar to the values reported in the literature [15, 17]. The cobalt based FT process has the maximum energy conversion efficiency, yielding about 45.5% total energy of the input biomass as the FT liquids and power outputs. This was achieved regardless of H₂/CO ratio in the syngas coming from the gasifier. As it can be seen that the decrease of the amount of CO₂ removed from syngas in the AGR process increased the yield of FT fuels in iron-based FT processes. This was consistent with the previous experimental work that suggested the presence of CO₂ in the FT synthesis feed would inhibit the generation of additional CO₂ by the WGS reaction on an iron-based FT catalyst [31, 33]. For instance, if the CO₂ removal efficiency of an AGR unit was decreased from 97% to 75%, the yield of FT liquids was increased from 2821.8 to 2890.1 barrel/day for a refinery with 400 MW thermal biomass input (Table 9). Compared to complete removal of CO₂, the partial removal of CO₂ in the AGR unit will also reduce the power duty and energy consumption of the AGR unit, which would increase the overall energy efficiency as well. The amount of FT liquids and power generated by switching from a low H₂/CO to a high H₂/CO syngas were very similar. This is due to the fact that the ratio of H₂/CO

of syngas in a gasifier can be adjusted by varying the amount steam into the gasifier to displace the WGS reaction equilibrium in the gasifier. When low H_2/CO syngas is generated in a gasifier, the same mechanism is used in a subsequent water-gas shift reactor to increase the H_2 content, and thus the amounts of CO and CO_2 after the shift reactor remain identical in both cases.

It can be seen that low and high temperature modes of iron-based FT processes resulted in similar yields of liquid hydrocarbons. Although a low temperature FT process yields more liquid and waxy products, it also tends to produce more CO_2 byproduct at lower temperatures which favors the WGS reaction equilibrium in the forward direction. The combination of these effects results in similar overall carbon conversion efficiency for both high and low temperature iron-based FT processes. However, there was significant difference in the product distribution of these two processes (Tables 9 and 10). The low temperature FT process tends to produce more diesel and waxy hydrocarbons, while gasoline and middle distillates are main products of the high temperature FT process.

3.2 FT process off-gas reforming and recycling

When a slurry bubble column FT reactor is used, high CO conversion of up to 80% per pass can be attainable. At high syngas conversion levels, the resulting gaseous effluent contains very low amounts of reactants (CO and H_2), which makes it uneconomical to recycle. The effluent typically contains significant amounts of light hydrocarbons of C_1 - C_4 , CO_2 (in the case of an iron FT catalyst) and small amounts of H_2 and CO, which can be burned in a boiler or gas turbine to produce power or reformed to produce additional syngas. Addition of a reformer comes with significant investment and operating costs that should be economically justified [16]. Figure 8

shows the effect of adding a reformer on the efficiency of the energy conversion. The use of a reformer can recover some of the carbon to produce additional FT hydrocarbons which otherwise would be lost in the effluent gas. Improvement on carbon conversion to FT liquids was significant when a reformer was used as it increased the efficiencies by 78%, 97%, and 106% for BCo, BFeLT, and BFeHT processes, respectively. The total energy conversion of the plant also improved about 33% in all cases for which the FT liquids are main products. In general, when the off-gas is completely burned to produce power, electricity is a co-product of the process rather than a by-product. The co-generation slightly decreases the overall energy efficiency as the conversion of the syngas energy to FT products is more efficient than its conversion to power in a steam or gas turbine. This can be realized by comparing the BCo-OT, BCo-ATR, and BCo-ATR-P where the main products of the plants are fuel/electricity, fuel, and fuel/electricity, respectively.

Figure 5. Comparison of the energy efficiency for once-through and recycle configurations (OT: once-through mode with 80% CO conversion and power/fuel co-generation, ATR: recycle mode with 50% per pass CO conversion and maximum fuel production, ATR-P: recycle mode with 50% per pass CO conversion and power and fuel co-generation).

Figure 6. Comparison of the CO₂ emissions for once-through and recycle configurations, see Figure notes for the configuration definitions.

The use of a reformer also significantly reduced the CO₂ emissions of the plant per unit of products produced as shown in Figure 6. This was mostly because the production of more H₂ through the reforming reaction reduced the degree of shift-reaction required to adjust H₂/CO ratio as CO₂ is the main byproduct of the shift reaction. For iron-based FT synthesis, additional H₂ also promotes the occurrence of reverse WGS and conversion of CO₂ to FT hydrocarbons.

3.3 Hybrid biomass/natural gas to FT liquids process

It is known that the proper ratio of H₂ to CO in the syngas has a profound effect on the yield of FT hydrocarbons. Gasification of biomass typically yields syngas which requires additional processing through the water-gas shift reaction to achieve a proper H₂ to CO ratio for FT synthesis, which will inevitably lose some of carbon source in the form of CO₂. An alternative approach is to provide H₂ to the syngas from an external source such as natural gas reforming or water electrolysis and convert CO₂ to CO through reverse WGS and utilize CO in a FT process.

Although water electrolysis with renewable electricity would generate H_2 with zero CO_2 emission [57], it currently cannot economically compete with hydrogen produced using fossil-based sources such as natural gas and coal [58]. Reforming natural gas typically yields syngas rich in H_2 and CO , which might be ready for FT synthesis without a need for the additional shift reaction to adjust a H_2/CO ratio. This depends on the composition of natural gas source (more specifically its hydrocarbon content) and the type of reforming technology and operating conditions used. Reforming of natural gas with steam reforming, autothermal reforming, and partial oxidation technologies could yield syngas with H_2/CO ratios of 3, 2.3, and 1.7, respectively [50, 59]. Combining the syngas of high H_2/CO ratio from natural gas reforming with the syngas of low H_2/CO ratio from the biomass gasification could have some synergetic effects on carbon conversion and the yield of FT liquids. To study such a case, a plant with a total input of $400 \text{ MW}_{th,LHV}$ was considered. The total thermal input of the feedstock (biomass and natural gas) was split equally between the biomass and natural gas ($200 \text{ MW}_{th,LHV}$ each). Table 11 gives the composition of natural gas.

Table 11. Composition of natural gas used in the model [60]

Component	mole %
C_1	95.2
C_2	2.5
C_3	0.2
C_{4+}	0.1
CO_2	0.7
N_2	1.3

When the hybrid feedstock was used, more FT liquids were produced in all cases as shown in Table 12 than those from biomass only as shown in Table 9, even though the total energy content of the feedstock input remains the same ($400 \text{ MW}_{th,LHV}$).

Table 12. Performance of different process configurations with iron and cobalt-based FT processes and hybrid biomass/natural gas feedstock

Case ¹	FT process (catalyst/ temp)	AGR CO ₂ removal efficiency (%) ¹	FT liquids (barrel per day)	FT products selectivity (mole-C %)			%C in FT liquids ₂	H ₂ /(2 CO+3 CO ₂) ³	CO ₂ (ton/day) ⁴
				C ₅ -C ₁₂	C ₁₃ -C ₂₀	C ₂₁ +			
BNGCo	Co-220°C	97%	3,701.8	63.6	26.9	9.4	48.0	1.05	1,340.1
BNGFeLT-1	Fe-240°C	66%	3,274.1	62.2	25.8	12.2	44.0	1.07	1,470.5
BNGFeLT-2	Fe-240°C	42%	3,397.9	57.4	37.6	14.9	45.9	0.52	1,423.5
BNGFeHT-1	Fe-300°C	78%	3,461.1	66.6	27.5	5.9	46.5	1.05	1,410.0
BNGFeHT-2	Fe-300°C	48%	3,573.8	65.2	28.8	6.0	48.1	0.50	1,364.2

¹ see the footnotes of Table 9

It can be seen from Figure 7 that for low-temperature iron and cobalt based FT processes, the energy content of FT liquids produced were increased by about 20% and 22%, respectively. This was because the reforming of natural gas produces syngas with higher H₂/CO ratio for FT synthesis than the syngas derived from biomass gasification. When H₂/CO is not at its optimum level for FT synthesis, part of the CO needs to be converted to CO₂ through the shift reaction for producing more H₂ to adjust the H₂/CO ratio. This would decrease the available amount of CO for FT synthesis and reduce the final yield of liquid fuels.

Figure 7. Process energy efficiency for FT processing scenarios for iron and cobalt-based FT processes with and without natural gas co-feeding (all configurations use a gasifier with syngas of $H_2/CO=1.43$).

As shown in Figure 8, a hybrid NG/biomass process also produces about 23% less CO_2 per unit of FT products produced compared with similar processes using only biomass with the same amount of thermal input. However, without a life cycle assessment on both processes, it is not possible to compare the total CO_2 emission of the fuel from each configuration over its entire life cycle. A previous study shows that the BTL process is almost carbon neutral even without CCS option [2]. It is also worthy of note that in all cases, the CO_2 emissions are less than the average emissions of two separate biomass and natural gas fed processes. This is because the autothermal reforming of natural gas results in a syngas with a high H_2/CO ratio (~ 2.3), typically exceeding the FT requirement. The extra amount of hydrogen produced can make up for the hydrogen deficiency in the syngas from biomass gasification to some extent and improves the overall

589 carbon conversion.

590
591 *Figure 8. Comparison of the CO₂ emissions for biomass-fed and hybrid biomass/natural gas-fed*
592 *processes. Data for GTL process is derived from the reference [61].*

593
594 **3.4 Economic analysis**

595 The levelized cost of FT liquids production was calculated for the proposed process
596 configurations. As discussed before, the choice of a FT catalyst has an impact on the yields of FT
597 liquids and electricity, which are two main products. In addition, different CO₂ removal
598 efficiencies in an AGR system cause variation in the volume of the process gas and subsequently
599 the volume of the gas loop and downstream equipment, which has profound effects on the capital
600 costs of the plant.

601 *Table 13. Input parameters for process configuration considered in economic analysis (All configurations use a gasifier with syngas*
602 *of H₂/CO=1.43). See Table 8 for the definition of abbreviations.*

603

Designation	BCo		BCo-P	BFeLT1	BFeLT2	BFeHT1	BFeHT2	BCo-OT	BFeLT-OT	BFeHT-OT	BNGCo	BNGFeLT1	BNGFeLT2
Biomass input (MW _{th})	400		400	400	400	400	400	400	400	400	200	200	200
NG input (MW _{th})	0		0	0	0	0	0	0	0	0	200	200	200
CO ₂ removal (%)	97		97	97	91	97	85	97	97	97	97	66	42
Recycle (ATR)	Yes		Yes	Yes	Yes	Yes	Yes	No	No	No	Yes	Yes	Yes
FT catalyst	Co		Co	Fe	Fe	Fe	Fe	Co	Fe	Fe	Co	Fe	Fe
FT temp. (°C)	220		220	240	220	300	300	220	220	300	220	220	220
Main product	FTL		FTL/ electricity	FTL	FTL	FTL	FTL	FTL/ electricity	FTL/ electricity	FTL/ electricity	FTL	FTL	FTL

The total capital costs and production costs of FT liquids were calculated using the methodology described in section 2.2 and presented in Figures 9 and 10, respectively. It can be seen that the required capital cost to build a FT production plant with 400 MWth biomass input and once-through conversion operation is around 380 M\$. This will result in production costs of \$35.8 per GJ of FT liquids or \$4.3 per gallon of gasoline equivalent (GEG) for a cobalt-based FT process and around \$42 or \$5/GEG for iron-based FT processes. Interestingly, the recycle designs achieve lower cost of FT liquids production than the once-through designs, although the former requires slightly higher (6-9%) capital costs, mainly due to the addition of a reformer. This is in contrast to results of some previous studies that suggested the addition of a reformer would not decrease the cost of FT liquids production via biomass gasification [16, 17]. This can be explained by the fact that configurations proposed in this study aimed at maximizing the FT liquid production and only a small amount of power was exported to the grid (~2.5% of total thermal input), while in those studies, co-generation of FT liquids and power was considered. The results of this study show about 10-15% higher capital investment and production costs than those of previous studies on biomass gasification and Fischer–Tropsch synthesis. Taking into account more conservative equipment costs and higher biomass purchase costs, this was expected. In addition, all costs were adjusted to year 2015, and were affected by the steep escalation in plant construction costs seen in recent years.

Figure 9. Total capital investment for various configurations. Costs are in MUS\$₂₀₁₅

Figure 10. Cost of production of FT liquids per GJ and Gasoline-Equivalent Gallon (GEG) for various configurations.

The profitability of an additional reformer can be maximized by maximizing the recycle ratio

and thus the yields of FT liquids. This can be realized from Figures 9 and 10 by comparing BCo-OT, BCo, and BCo-P cases. It is worthy to note that the cost of iron-based FT processes is increased more by the addition of a reformer as it has a larger volume of the process gas due to the presence of a significant amount of CO₂ in the reactor effluent. Another interesting trend was that although the partial removal of CO₂ in an AGR system increased the volume of downstream units, it also had a positive impact on the yield of FT liquids. In all cases with iron-based FT process and partial CO₂ removal in AGR unit, the production costs of FT liquids are decreased compared to the similar configuration with full CO₂ removal, which means increased costs due to the larger gas volumes were reasonably offset by the increased yields of FT liquids. In addition, partial removal of CO₂ makes it possible to implement cheaper and less energy intense CO₂ removal processes such as membrane based and adsorption based processes, which could give significant costs advantages to iron-based FT processes. The most promising configuration was found to be BNG cases in which both biomass and natural gas were used as the feedstock. The hybrid process with 50% natural gas and 50% biomass thermal inputs significantly decreased the costs of FT liquids production down to \$19-\$22 range per GJ of FT liquids (\$2.2-\$2.6/GEG). For example, in the case of a cobalt-based FT process (BNGCo), the FT liquids costs were reduced by 32%, which was mainly the result of 36% increase in the yield of FT products accompanied by 20% and 13% decrease in feedstock and capital costs. It can be seen from Figure 11 that the biomass pretreatment and gasification is very expensive, adding up to 38% of the total capital costs for the BCo process. In the hybrid version of the same process (BNGCo), this cost was reduced by about 33% and was 26% of total capital costs.

Figure 1. Breakdown of capital costs for a biomass-fed (left, BCo) and a hybrid biomass/natural gas-fed (right, BNGCo) process.

4. Conclusions

The simulations on the BTL refinery based on biomass gasification and FT synthesis using n Aspen Plus[®]-based process model showed that the ratio of H₂ to CO in the syngas from a biomass gasifier had no significant effect on the overall plant efficiency when a downstream shift reactor was used. The overall thermal efficiency for biomass-fed processes was in a range of 41.3-45.5%. The BTL refinery configuration with a cobalt-based FT process achieved slightly higher overall efficiency than the configuration with an iron-based FT process mainly owing to the absence of water-gas shift activity on a cobalt FT catalyst. The adjustment of CO₂ removal efficiency in an AGR unit for an iron-based FT process can inhibit the generation of additional CO₂ in the FT reactor and thus improve the overall carbon conversion efficiency to FT products. The addition of a reformer in the gas recycle loop can improve the production economics only when the operation of the plant is optimized for maximum fuel production rather than co-generation of fuels and power. A natural gas/biomass co-fed process for producing FT liquids has more attractive economics than solely biomass fed process. Co-feeding of biomass and

natural gas at 50% of thermal total thermal energy input of 400 MWth for each feedstock reduced the costs of FT liquid production by about 30% to \$19-\$20 per GJ of FT liquids, compared to \$28.8 per GJ of FT liquids produced a solely biomass fed process. A hybrid process is a promising approach in the transition from a fossil-based energy economy toward production of green liquid fuels. Nevertheless, even at oil price of \$60/barrel, the production of FT liquids with none of process configurations in this study would be economically competitive. To make the FT biofuel production economically competitive with current fossil-based counterparts, an appropriate green energy and fuel premium is needed.

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Graphic Abstract

Process flowsheet developed in Aspen Plus® for the production of FT liquids and electricity through biomass gasification