Plant-Wide Modeling of an Indirect Coal-Biomass to Liquids (CBTL) Plant with CO₂ Capture & Storage (CCS)

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Abstract

The net greenhouse gases (GHG) emissions of conversional Fischer Tropsch (FT) synthetic fuels derived from coal are about double of those from petroleum fuels. Adding moderate amounts of biomass to coal can substantially reduce the carbon footprint of the indirect fuel production plant. The indirect coal-biomass to liquids (CBTL) technology with CO₂ capture and storage (CCS) is more environmental friendly than the conventional coal to liquids (CTL) processes. This paper focuses on the selection of CCS technologies and obtaining their optimal operating conditions for a CBTL plant. A detailed process model is developed in Aspen Plus V7.3.2 for this purpose. In this plant, syngas is produced in the biomass/coal-fed co-gasifier. Then, a sour water gas shift (WGS) reactor converts a portion of the CO in the syngas to CO₂ to obtain the desired H₂/CO ratio in the syngas feed to the FT unit. Substantial amount of CO₂ is captured before the FT reactor by using a dual-stage, selective physical solvent-based process. In the FT unit, the Fe-based catalyst is used in the low temperature FT (LTFT) slurry reactor to convert syngas to hydrocarbons. For selection of the post-FT CO₂ capture technology, three candidate technologies- Selexol, MEA and MDEA/PZ, are evaluated. The results show that the MDEA/PZ technology with intercooling has the lowest overall penalty. Impacts of two key design variables, H₂/CO ratio at the inlet of the FT unit and biomass/coal ratio of the feedstock, on the product yield and utility consumptions are investigated.

Key Words

Gasification, Water gas shift, Fischer-Tropsch, CO₂ capture and storage

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1. Introduction

Due to the increasing price of the petroleum-derived fuel, the insecurity of crude oil supply, global warming and climate change, various alternative technologies for fuel production are being investigated. Among the potential technologies, the Fischer-Tropsch (FT) process, first introduced in 1920s and commercialized later on, is one of the most popular and mature technologies. The FT process can produce fuels using the syngas derived from coal, biomass, natural gas, or a combination of those feedstocks. Several commercial coal-to-liquids (CTL) and gas-to-liquids (GTL) FT plants were built in the last century. Many of these plants are still producing significant amount of transportation fuel. (Dry, 2002; Kreutz et al., 2008) However, the life cycle CO₂ emission of fuels from a conventional CTL plant is roughly twice of that of fuels from petroleum. (Bartis et al., 2008; Edwards, 2011) Recently, wide interests in coal-biomass to liquids (CBTL) fuel process are being catalyzed by the relatively low prices of coal and carbon-neutrality of biomass. (Larson and Jin, 1999; Wang et al., 2009) Adding moderate amounts of biomass to coal for liquids production can substantially reduce the carbon footprint of CBTL processes. (Liu et al., 2011; NETL, 2009)

While there are numerous models reported for CTL plants, not many detailed computational models are available in the open literature for CBTL plants with carbon capture and storage (CCS). With this motivation, this paper focuses on selection of CCS technologies and obtaining their optimal operating conditions for CBTL plants by evaluating utility consumptions, fuel yield, and carbon emission from the indirect CBTL plant that produces syncrude.

Typically two separated gasifiers are considered for the CBTL plant- one for coal, and the other for biomass. (Liu et al., 2011; Baliban et al., 2011) However, both large-scale slurry-fed (GEE-Texaco type) and dry-fed (Shell-type) entrained-flow gasifiers and some fluidized bed gasifiers (IGT-type) have successfully handled coal mixed with moderate amount of biomass. Because biomass gasification technology is limited to smaller scale application (Long and Wang, 2011), applying a co-gasification technology can utilize biomass in large scale gasification plants with less number of trains, making the CBTL process more compact and economical. In this paper, we have developed and validated a yield model for coal-biomass co-gasification process. A study is also conducted to demonstrate the effect of biomass/coal ratio on the syngas composition and downstream processes.

Most of the CTL pilot and commercialized plants built in last century do not consider CCS. Deployment of suitable CCS technologies can reduce the carbon footprint of CTL/CBTL processes significantly. (Edwards, 2011) In the CBTL process, CO₂ is generated not only in the gasification unit but

1 also in the FT unit, as shown in Fig. 1. CO₂ produced by the Fe-based FT catalyst is quite high because of
2 the higher water gas shift (WGS) reaction activity of the Fe-based catalysts in comparison to the Co-based
3 catalysts. Even for H₂/CO ratio as high as 2.1, the CO₂ selectivity is still around 10-15 mol% of total
4 carbon on Fe-based catalysts. (Warzel, 2006) To reduce the overall CO₂ emission and recover the
5 valuable products, CO₂ must be removed both before and after the FT unit. In the acid gas removal (AGR)
6 unit before the FT unit, H₂S is also captured in addition to CO₂ to protect the downstream catalysts. The
7 CO₂ capture unit after the FT unit removes CO₂ from the FT reactor effluent.

8 In the AGR unit, physical absorption can be feasible if the partial pressure of CO₂ is high. Physical
9 absorption is preferred because of lower penalty for CO₂ capture in comparison to the chemical solvents.
10 For example, the heating requirement in the stripper when the physical solvent Selexol is used for CO₂
11 capture is only 25% of that when the chemical solvent MEA (30 wt%) is used. (Bechtel, 1992b) If a
12 physical solvent is used, CO₂ can be released simply by pressure swing at different pressure levels.
13 Therefore, the CO₂ compression penalty can be greatly reduced. (Bhattacharyya, 2011) Selexol and
14 Rectisol (chilled methanol) are two widely-used physical solvents. Rectisol has been considered in the
15 work of Liu et al. (Liu et al., 2011), while a dual-stage Selexol unit has been considered in a study
16 published by the National Energy Technology Laboratory (Reed et al., 2007). In this work, the Selexol
17 technology is selected for the AGR unit before the FT process.

18 For CO₂ capture after the FT process, typically a chemical solvent is used. The chemical solvents such
19 as the amines offer higher selectivity and therefore result in negligible loss of hydrocarbons. (Bechtel,
20 1992b) The secondary and tertiary amines are more suitable where the partial pressure of CO₂ is high. In
21 addition, the secondary and tertiary amines have lower solvent loss, lower heating requirement, and lesser
22 corrosivity than the primary amines. (Kohl and Nielsen, 1997) On the other hand, the physical solvents
23 have significantly higher solubility of hydrocarbons that can lead to loss of valuable products. However,
24 the utility requirement is much less in comparison to the chemical solvents. Even though the amine-based
25 technologies are usually used for post-FT CO₂ capture (Bechtel, 1992b), the appropriate technology,
26 physical or chemical, should be selected by comparing the combined energy penalty due to loss of
27 hydrocarbons and utility of each candidate technology for the same extent of CO₂ capture. For a fair
28 comparison, each capture technology should be appropriately designed to minimize the loss of energy.
29 For example, intercooling of the solvent in the absorber can be considered to reduce the energy penalty.
30 (Kohl and Nielsen, 1997; Xu et al., 1998) In this study, hydrocarbon loss and utility consumptions of three
31 solvents, one physical solvent and two chemical solvents with and without intercooling, are evaluated.
32 Studies on the effect of the lean solvent loading for CO₂ capture after the FT process are scarce in the

open literature. To this end, a study is presented on the effect of the lean solvent loading for the MDEA/PZ based CO₂ removal system with intercooling.

Most of the existing works in the open literature consider that the syngas produced in the gasifier is sent to the FT reactor without adjusting the H₂/CO ratio mainly because the typical Fe-based FT catalyst catalyzes the WGS reaction. (Bechtel, 1992a) This strategy needs to be revisited if CO₂ compression is considered for storage. If the H₂/CO ratio is optimally adjusted by using WGS reactor(s) before the FT reactor, then a significant portion of CO₂ can be captured by using a physical solvent such as Selexol before the FT unit due to higher partial pressure of CO₂. This can not only reduce the penalty for CO₂ capture, but can also reduce the duty for CO₂ compression as CO₂ can be flashed off by pressure swing at relatively higher pressure than the chemical processes. In the work of Liu et al. (Liu et al., 2011), a WGS reactor is used to increase the H₂/CO ratio from 0.67, which is the typical composition of coal-derived syngas, to about 1. According to Dry (Dry, 2002), the composition of syngas should match the overall usage ratio of H₂/CO in the FT reactors for increasing the plant efficiency. It can be noted that the typical inlet H₂/CO ratio of Sasol's low-temperature FT (LTFT) process is about 1.7. (Dry, 2002) Other studies show that syngas with H₂/CO ratio greater than 2 can greatly reduce the WGS (James et al., 2013) reaction on the Fe-based FT catalyst. However, a higher H₂/CO ratio at the inlet of the FT reactor can result in more methane formation in the FT reactor decreasing the overall fuel yield. (Dry, 2002) Thus, the WGS reactor and the pre-FT CO₂ capture process should be optimally designed by considering the tradeoffs between fuel yield and penalty due to CO₂ capture and compression. (Reed, 2007; Larson et al., 2010) With this motivation, sensitivity studies are presented by evaluating the impact of H₂/CO ratio.

In summary, following works are presented in this paper.

- A detailed process model of an indirect CBTL plant with CCS that produces raw syncrude has been developed. The focus is on technologies, configurations, and process operation that can produce higher amount of syncrude with less utility consumptions and low greenhouse gas (GHG) emission.
- Studies are conducted on the impact of the biomass/coal feed ratio on the syngas composition and steam generation.
- The Selexol based CO₂ capture process is optimally designed for CO₂ capture before the FT process to obtain about 90% carbon capture in the CBTL plant producing raw syncrude.
- A comparison of the CO₂ removal technologies applied after the FT synthesis block is done to select the most economical technology for removing CO₂ from the FT product. The three solvents considered are Selexol, MEA, and MDEA/PZ. Intercooling is considered for the amine-based

processes. A sensitivity study is conducted to determine the optimal pressure level of flash vessels in the Selexol unit. A sensitivity study is conducted to evaluate the effect of the lean solvent loading on the performance of the MDEA/PZ based CO₂ removal process with intercooling.

- The impact of changes in the H₂/CO ratio on the utilities consumption, carbon efficiency, and product selectivity is evaluated.

2. Process design and modeling

Fig. 1 shows the block flow diagram (BFD) of the indirect CBTL plant with CCS. In this work, it is assumed that the syncrude and light gases produced in this CBTL facility are sent to a crude oil refinery for product upgrading. In the CBTL facility, syngas is produced in a fluidized bed gasifier which is co-fed with coal and biomass slurry. Oxygen produced in an air separation unit (ASU) is compressed and fed to the gasifier. (Jones et al., 2011) After scrubbing, the syngas is split between a single stage sour WGS reactor and a carbonyl sulfide (COS) hydrolysis unit such that a desired H₂/CO ratio of the clean syngas is achieved at the inlet of the FT reactor. Due to presence of the gasifier and availability of the syngas at high pressure, the authors considered it appropriate to set the environmental targets at par with the integrated gasification combined cycle (IGCC) plants. (NETL, 2010) Therefore, the SO₂ emissions target was set at 0.0055 kg/ GJ. The shift catalyst causes almost complete hydrolysis of COS to form H₂S that is then captured in the AGR unit. A separate COS hydrolysis unit is considered for the stream that bypasses the WGS reactor for satisfying the overall SO₂ emissions target. The dual-stage Selexol technology is used in the AGR unit to remove H₂S and CO₂ selectively. H₂S is separated in the first stage of the Selexol unit and sent to the Claus unit for converting it to elemental sulfur. (Bhattacharyya, et al., 2011; Jones et al., 2012) In the second stage, CO₂ is separated and sent to the compression unit before sending it for sequestration. (Bhattacharyya, et al., 2011) In the FT reactor, the clean syngas is converted to syncrude. The Fe-based slurry-phase LTFT process is selected because it could produce higher amount of hydrocarbons that can be upgraded to transportation fuel in comparison to the typical HTFT processes, which produces more light gases. The vapor phase product is sent to the post-FT CO₂ removal unit. Captured CO₂ is sent to the CO₂ compression unit for sequestration. The sour water and black water produced in the process are treated and recycled back to the coal-slurry preparation section and to the scrubber for quench (NETL, 2010). The sour water stripper (SWS) is a major consumer of the stripping steam.

Fig. 1. Block flow diagram of the CBTL plant with CCS (utility streams not shown)

2.1. Steady-state modeling and simulation approach

In this section, the steady-state modeling and simulation of the indirect CBTL plant with CCS is discussed. The entire CBTL plant is divided into a number of well-defined sections, including gasification, syngas cooling and shift, Selexol unit, Claus unit, FT synthesis unit, post-FT CO₂ removal unit, and CO₂ compression unit. The plant-wide model is built in Aspen Plus V7.3.2. Yield models of the gasification and FT synthesis units are developed in Excel based on the experimental/operational data available in the open literature while the remaining unit operations are modeled by using the appropriate Aspen Plus blocks. Aspen User2 Blocks are used to connect the models developed in Excel with the Aspen Plus models.

2.2. Gasification

The technology for co-gasifying coal and moderate amount of biomass is nearing commercialization. (Liu et al., 2011) In the base case, the feed to the gasifier contains 92 wt% of Illinois No. 6 coal and 8 wt% of bagasse (dry basis). The proximate and ultimate analyses are shown in Table 1. (Bhattacharyya, et al., 2011; Bain, 1992)

Table 1

Proximate and ultimate analysis of coal and biomass feedstock.

Coal	Biomass
Proximate Analysis (dry basis)	

Moisture	11.12	10.6
Fixed Carbon	49.72	14.8
Volatile Material	39.37	82.1
Ash	10.91	3.1
Ultimate Analysis (dry basis)		
Ash	10.91	3.10
Carbon	71.72	47.90
Hydrogen	5.06	6.20
Nitrogen	1.74	0.60
Sulfur	2.82	0.01
Oxygen	7.75	42.19

The coal-biomass co-gasifier is simulated by combining a reactor model for coal gasification based on minimization of the Gibbs free energy with a yield model for biomass gasification, with the assumption that the interaction between coal and biomass is negligible due to the low biomass to coal ratio and the yield of the co-gasifier is a linear combination of these two model. This assumption is consistent with experiment done by Andre (Andre et al., 2005), which shows an approximate linear correlation between syngas composition and biomass to coal ratio. The reactor model for coal gasification has been developed by considering restricted equilibrium and has been reported by our group previously (Bhattacharyya, et al., 2011) since the WGS reaction catalyzed by the ash as well as the uncatalyzed WGS reaction continue till the reaction is quenched. (Kasule et al., 2012) The yield of each species for biomass gasification is generated by the following correlation, $y = A + BT + CT^2$, that has been developed for the fluidized bed IGT gasifier. (Bain, 1992) In the work of Bain, the values of the parameters A , B , and C have been determined from the regression analysis of the experimental data available for a biomass gasifier operating between 754-982 °C at 2300 kPa. In this work, for satisfying the elemental balance the MGAS model of Syamlal and Bisset (Kasule et al., 2012; Syamlal and Bisset, 1992) is used to obtain the final yield of major gas components from the proximate and ultimate assays, tar and char compositions, and preliminary prediction of product distribution from temperature correlation shown above. Table 2 compares the results from our model for biomass gasification with the experimental data (Bain, 1992) obtained at 830 °C. As seen in Table 2, the model is satisfactory.

Table 2

Comparison between the experimental data and the yield model developed in this work for biomass gasification.

Gas (mol%)	Experimental	Our Model	error%
CO	8.73	9.26	-6.14
CO ₂	21.31	20.35	4.50
CH ₄	8.41	7.69	8.56
H ₂	17.07	15.91	6.77
H ₂ O	43.20	45.72	-5.82
NH ₃	0.48	0.48	0

2.3. Syngas Cooling and Shift

The syngas from the gasifier goes to the radiant syngas cooler (RSC) to generate high pressure (HP) steam, which can be sent to the heat recovery steam generation (HRSG) section for superheating for power generation. As shown in Fig. 2, syngas is then sent to the scrubber where quench water is used to decrease the temperature of the syngas to the desired value. (Bhattacharyya, 2011) After scrubbing, a portion of the syngas enters an adiabatic sour WGS reactor, while the remaining portion enters a COS hydrolysis unit. The reversible WGS reaction is shown in Reaction 1 with the kinetics given by Eq. (2) for a cobalt molybdenum-based catalyst, which is a sour shift catalyst. (Bhattacharyya, 2011; Overstreet, 1974; Berispek, 1975) The equilibrium constant is given by Eq. (3) (Bhattacharyya, 2011). The WGS reactor is modeled as an adiabatic plug flow reactor (PFR) in ASPEN Plus.

$$-r_f = 2.6 \times 10^4 \exp\left(-\frac{E_f}{RT}\right) [CO] \frac{kmol}{m^3s} \quad (2)$$

$$K_{eq} = \exp\left(-4.33 + \frac{8240}{T}\right) \text{ for } 1060 \leq T \leq 1360 \quad (3)$$

where $E_f = 53127 \text{ kJ/kmol}$, CO in kmol/m^3 , and T in $^{\circ}\text{R}$.

The Langmuir-Hinshelwood Hougen-Watson (LHHW) kinetics, Eq (5), is used to simulate the COS hydrolysis reaction shown in Reaction 4. The kinetics captures the inhibiting effect of water and provides good agreement with the experimental data. (Williams et al., 1999) The kinetic parameters are obtained from the open literature. (Svorones and Bruno, 2002; Williams et al., 1999)

$$r = \frac{kP_{COS}}{1 + KP_{H_2O}} \quad (5)$$

where $k = 6.4322 \exp \left[\frac{11,144}{R} \left(\frac{1}{T} - \frac{1}{373.73} \right) \right]$, $K = 1.3 \times 10^{-7} \exp \left(\frac{10010}{T} \right)$, T in K, P in kPa, r in kmol/kg-hr.

A design spec is used in Aspen Plus to manipulate the split fraction of the syngas sent to the WGS reactor to obtain the desired H_2/CO ratio.

The syngas from the WGS and the COS hydrolysis reactors is combined and then sent to the heat recovery section where a series of heat exchangers is used to cool down the syngas by generating intermediate pressure (IP) steam, low temperature (LP) steam and heating boiler feed water (BFW). The hot side outlet temperatures of the IP steam generator, the LP steam generator and the BFW heater are set to 191 °C, 138 °C, and 121 °C, respectively. The condensate from the heat recovery section contains very high amount of NH_3 and is sent to a sour water stripper (SWS). The NH_3 -rich gas from the SWS is sent to the Claus furnace while the clean water from the bottom of the SWS is recycled to the gasification section. The SWS column is simulated in ASPEN Plus by using 'RadFrac' block. For the thermodynamic model, 'ELECNRTL' is used for liquid phase and 'SRK' is used for the vapor phase.

Fig. 2. Configuration of the syngas production section and water treatment units

2.4. Selexol Unit

1 In this work, the dual-stage Selexol unit, as shown in Fig. 3, is used for selectively removing H₂S in the
2 first stage followed by removal of bulk CO₂ in the second stage from the sour syngas by using
3 dimethylether of polyethylene glycol (DEPG) as the solvent. (Bhattacharyya et al., 2011) This
4 configuration is similar to the work of Bhattacharyya et al. The tail gas from the Claus unit is recycled to
5 the first stage of the H₂S absorber. The off-gas from the top of the H₂S absorber is sent to the CO₂
6 absorber. A portion of the loaded solvent from the CO₂ absorber is sent to the H₂S absorber. The
7 remaining portion of the loaded solvent is heated and sent to a series of flash vessels to recover H₂ and
8 flash off CO₂. The CO₂ is flashed off in a series of three separators operating at decreasing pressure levels.
9 The semi-lean solvent from the last separator is cooled by exchanging heat with the loaded solvent and
10 then chilled to 2°C using NH₃ as the refrigerant before returning it to the CO₂ absorber. The flow rate of
11 the refrigerant in the vapor-compression cycle is determined by a design specification considering a
12 minimum temperature approach of 5.5 °C. Equilibrium stage models are developed for all the columns by
13 using the RadFrac block in Aspen Plus. The PC-SAFT EOS is used for calculating the thermodynamic
14 properties. (Bhattacharyya et al., 2011; Gross and Sadowski, 2001) Detailed information on the modeling
15 approach of the AGR unit for the IGCC power plant can be found in Bhattacharyya et al. (Bhattacharyya
16 et al., 2011) Due to the considerable difference in the operating pressure of the gasifier between the IGCC
17 power plant and CBTL plant, the operating pressure of the AGR unit in this work is different than the
18 previous work. (Bhattacharyya et al., 2011) The operating pressures of the main equipment are
19 summarized in Section 3.4 Table 7. The solvent circulation rate in the AGR unit as part of the CBTL
20 plant is expected to be higher, because of the lower CO₂ partial pressure in the CBTL plant than that in
21 the IGCC plant. The solvent circulation rate is manipulated by a ‘design spec’ in Aspen Plus to achieve
22 90% CO₂ capture.

Fig. 3. Configuration of the Selexol unit and the CO₂ compression section (Bhattacharyya et al., 2011)

2.5. Claus Unit

The Claus unit is a gas desulfurizing process recovering elemental sulfur from the acid gas stream generated from the gasifier and the SWS column. It includes one thermal stage and two catalytic stages. More details about this unit can be found in the work of Bhattacharyya et al. and the plant configuration is the same as Fig. 5 in that paper. (Bhattacharyya et al., 2011)

2.6. Fischer-Tropsch Synthesis

The model of the FT Synthesis section has been developed in Excel and connected to Aspen Plus via a User2 block, where total mass and atom conservations are satisfied by using a VBA solver code. As mentioned before, a Fe-catalyzed slurry phase low temperature FT (LTFT) technology is considered in this study because of its high efficiency and flexibility. It has been reported that the capital cost of a slurry reactor is only 25% of a multi-tubular system. The slurry reactor has also lesser temperature gradient resulting in higher conversion. Removal and addition of catalyst while the reactor is running result in longer reactor runs for slurry reactor. (Dry, 2002; Espinoza, et al., 1999). In the Fe-catalyzed slurry phase FT reactors, following main reactions take place.

A yield model is developed for obtaining the product distributions of a LTFT reactor based on the information available in the open literature. (Bechtel, 1992a; Kuo, 1985; Kuo, 1983; Fox and Tam, 1995; Bechtel, June 1990) Anderson-Schulz-Flory (ASF) theory is often used to estimate the FT product distribution. As increasing wax yield is the key objective of LTFT process, the wax selectivity (S_{wax} , wt%) is often used as the indicator to calculate the ASF parameters. (Dry, 2002; Bechtel, 1992a) The correlations for wax yield vs. operating conditions were reported in the open literature. (Bechtel, 1992a; Kuo, 1985; Bechtel, 1998) It is modified in this study to generate more accurate estimations of the FT product distribution from operating temperature (T), pressure (P) and superficial velocity ($S.V.$) in the low operating temperature range shown in Eq. (7) and Eq. (8). The coefficients determined via linear regression of 12 sets of experimental data obtained from the Mobil's pilot plant data (Kuo, 1985) are as follows: $a=-0.1306$, $b=121.0773$, $c=271.6$, $d=-112.21$, where all the terms are in SI unit. The selectivity of CO_2 is calculated by WGS ratio (K_{WGS}) defined in Eq. (9), with a value of 2.69 for LTFT reactors when a low CO_2 -selective Fe-based catalyst is used. (James et al., 2013; Fox and Tam, 1995; Bai et al., 2002)

$$S_{wax} = aT + \frac{bP}{S.V.} \quad (7)$$

$$\text{Syngas Conversion (\%)} = c \left(\frac{k \cdot P}{S.V.} \right) + d \quad \text{where } k = \exp \left(-\frac{100}{RT} \right) \quad (8)$$

$$K_{WGS} = \frac{(H_2)(CO_2)}{(H_2O)(CO)} \quad (9)$$

Because the H_2/CO ratio in the syngas has a strong effect on the product distribution from the FT process, another correlation is developed to estimate the wax selectivity at different inlet H_2/CO ratios at a constant temperature, shown in Eq. (10). It has been reported that the slurry reactors tend to produce more wax than the fixed bed reactors with Fe-based catalysts at similar operating conditions, the product selectivity of the fixed bed reactors is more sensitive to H_2/CO ratio in comparison to the slurry bed reactors, and the wax selectivity could be correlated to the inlet H_2/CO ratio. (Jager and Espinoza, 1995; Dry, 1981; Espinoza and Steynberg, 1999; Steynberg and Dry, 2004) For regressing the parameters a and b in Eq. (10), experimental data for wax selectivity in slurry bed reactors due to changes in the H_2/CO ratio are needed. However, there are very few experimental data in the open literature for wax selectivity in the Fe-catalyst based LTFT reactors for low H_2/CO ratio. (Kuo, 1985; Kuo, 1983) Therefore, it was decided to regress the parameters with the data for low H_2/CO ratio, extrapolate the correlation for high H_2/CO ratio, and compare with the data available for the fixed bed reactors at high H_2/CO ratio to see if the trends are similar. Fig. 4 shows that the trend of wax selectivity estimated by the correlation for the

slurry bed reactors is similar to that for the fixed bed reactors. It should be noted that the wax selectivity for the fixed bed reactor has been reported by Dry. (Dry, 2002; Steynberg and Dry, 2004)

$$S_{wax} = 33.6 + \frac{13.1}{H_2/CO} \quad (10)$$

Fig. 4. Effect of syngas composition on wax selectivity

By using the calculated wax yield, the chain growth probabilities (α) in the ASF theory can be calculated by the polynomial $\alpha - S_{wax}$ correlations shown in Eq. (11a) – (11c). (Bechtel, 1992a) Then Eq. (11 d) – (11f) are used for predicting the carbon number distribution in the hydrocarbon products. In these equations, W_n denotes the weight fraction of hydrocarbon with n carbon atoms and M is the methane factor, which is applied for methane selectivity estimation and defined as the actual methane yield divided by what would be predicted from the observed value of α_2 . (Fox and Tam, 1995) This model has been proven to match the LTFT experimental data. (Bechtel, 1992a) Triple values of α are used to explain the high methane yield and change in the chain growth probability at certain point due to the vapor-liquid equilibrium in the reactor, which cannot be accounted for by the conversional single α value method. The two break point is set to be $n_1=1$, and $n_2=21$. It should be noted that n_2 is also set to be the starting carbon number for wax.

$$S_{wax} = 1401 - 4427(\alpha_2) + 3375(\alpha_2)^2 \quad (11a)$$

$$S_{wax} = -36687 + 125834(\alpha_3) + 1439067(\alpha_3)^2 + 54888(\alpha_3)^3 \quad (11b)$$

$$M = \frac{(1 - \alpha_1)^2}{(1 - \alpha_2)^2} = 6.413 - 0.0580(S_{wax}) + 0.00165(S_{wax})^2 + 7.986 \times 10^{-6}(S_{wax})^3 \quad (11c)$$

$$W_1 = (1 - \alpha_1)^2 x \quad (11d)$$

$$W_n = n(1 - \alpha_2)^2 \alpha_2^{n-1} y \quad n = 2, 3, 4, \dots, 20 \quad (11e)$$

$$W_n = n(1 - \alpha_3)^2 \alpha_3^{n-1} z \quad n = 21, 22, \dots \quad (11f)$$

where x, y, z are given by:

$$x/y = \alpha_2 / (M \alpha_1)$$

$$z/y = [(1 - \alpha_2)^2 \alpha_2^{20}] / [(1 - \alpha_3)^2 \alpha_3^{20}]$$

$$y = 1 / (\sum_{n=2}^{20} W_n + \sum_{n=21}^{\infty} W_n z/y + W_1 x/y)$$

For the same carbon number, components in the FT liquid are not only normal paraffin, but also olefin, and oxygenates. (Kuo, 1985) The olefin components have to be hydrotreated before sending them to the upgrading blocks. Since the olefin content in the FT crude can be high, the olefins fraction γ is an important variable that should be satisfactorily estimated. The olefins fraction will decrease with an increase in the carbon number, and the value finally settles down to 0.7 when the carbon number is larger than 6. (Fox and Tam, 1995) Table 3 lists the typical value of γ obtained experimentally. (Kuo, 1985)

Table 3

Olefins fraction versus carbon number in FT hydrocarbons (Kuo, 1985).

C _n	2	3	4	5	6	7+
olefins%	0.72	0.82	0.72	0.72	0.72	0.7

The wax obtained from the FT reactor can be treated as a single lumped C₂₀₊ wax pseudo component. From the modified ASF theory, the average carbon number of the C₂₀₊ wax can be calculated using the following equation (Fox and Tam, 1995):

$$C_{avg} = n + \alpha_3 / (1 - \alpha_3) \quad (12)$$

Besides alkenes, oxygenates produced at the FT reaction also need to be hydrogenated for stability of final products. Hence, it is also important to predict the oxygenate yield correctly. The total oxygenate yield in our model is obtained by using a polynomial correlation, given by Eq. (13), published in the open literature (Bechtel, 1992a; Fox and Tam, 1995). The species distributions for oxygenates are the average value of the reported pilot data. (Kuo, 1983; Kuo, 1985) It can be noted that the species distributions for oxygenates are not strong function of operating condition. (Bechtel, 1992a; Kuo, 1983; Kuo, 1985)

$$S_{OxyV} = 0.39 \quad (13a)$$

$$S_{OxyW} = 1.128(S_{wax}) + 0.05558(S_{wax})^2 \quad (13b)$$

$$S_{OxyHC} = 1.351(S_{wax}) + 0.1331(S_{wax})^2 + 0.1105(S_{wax})^3 \quad (13c)$$

where S_{OxyV} , S_{OxyW} , S_{OxyHC} denote oxygenate weight percent in vapor, water, and oil phase.

16 sets of experimental data from Run 256-7 conducted by Mobil in 1985 (Kuo, 1985) are used for validating the model at several different operating conditions. Fig. 5 shows a comparison, between the results of the modified model and the experimental data to check the model accuracy, where HC and Oxy denote hydrocarbons (no including wax), and oxygenates, respectively.

Fig. 5. Comparison between the model results and experimental data

2.7. Post-FT CO₂ removal unit

The products from the FT reactor, especially when Fe-based FT catalyst is used, can contain high amount of CO₂ that must be removed. In this study, we have considered CCS where the captured CO₂ is sent to the CO₂ compression unit for sequestration. Solvent-based and other technologies, such as high concentration MEA, inhibited MDEA, Benfield hot K₂CO₃, Rectisol, Ryan-Holmes cryogenic distillation, membrane, and PSA, have been compared by Bechtel for post-FT CO₂ removal. (Bechtel, 1992b) It was observed that the chemical absorption and the Ryan-Holmes process were the most likely candidates for FT application because of very little loss of valuable components, such as H₂, CO, and light hydrocarbons.

1 The chemical absorption process was selected for the baseline design because of its lower capital cost.
2 (Bechtel, 1992b) Out of the chemical absorption processes in Bechtel's study, the inhibited MDEA is
3 preferred over the MEA process because of its less corrosiveness and about 13.8% lesser steam
4 consumption. (Bechtel, 1992b)

5 Three solvents are evaluated in this study, one physical solvent, Selexol, and two chemical solvents,
6 methyl diethanolamine (MDEA)/ piperazine (PZ) and monoethanolamine (MEA). The advantages of
7 chemical solvents over physical solvents are that the hydrocarbon loss is very low due to lower selectivity
8 towards hydrocarbons, and the process could be operated at low pressure. In addition, a high level of CO₂
9 removal can be achieved in order to avoid CO₂ accumulation in downstream equipment. However, the
10 chemical solvents suffer a higher parasitic loss, mainly due to the considerable amount of steam required
11 for solvent regeneration (Bechtel, 1992b), in comparison to the physical solvents. Another disadvantage
12 of most chemical solvents is the relatively lower operating pressure for solvent regeneration than that of
13 the most physical solvents in order to avoid solvent degradation. This results in more power consumption
14 for CO₂ compression section. It should be noted that 98% of CO₂ removal is specified for baseline design
15 of the chemical absorption processes in this work.

16 2.7.1. MDEA/PZ

17 The PZ activated MDEA is a chemical solvent with high potential for CO₂ capture at reduced energy
18 consumption in comparison to MEA. The stripper reboiler duty for the MDEA/PZ system is expected to
19 be lower than the MEA system (Kohl and Nielsen, 1997; Neveux, et al., 2013) PZ, a cyclic amine, is
20 added to MDEA to improve solvent performance. (Xu et al., 1998; Puxty and Rowland, 2011; Plaza, 2012)

21 The process flow diagram is shown in Fig. 6. Three packed columns are considered in the CO₂ removal
22 unit, one for absorption, two for solvent regeneration. The FT vapor stream enters at the bottom of the
23 absorption column while the recycled lean solvent enters at the top of absorption column. The rich solvent
24 leaving the bottom of the absorber is heated by the lean solvent out of the stripper bottoms and sent to the
25 strippers to remove CO₂. In the CBTL process, the operating pressure of the absorber is much higher than
26 those of the strippers as shown in Table 7. For satisfactory vapor velocity in the stripper, two strippers are
27 used for one absorber. This is also consistent with the open literature. (Bechtel, 1992b; Bechtel, 1992c)

Fig. 6. Amine-based CO₂ removal unit

The lean solvent at the base case condition constitutes of 21 wt% MDEA and 5 wt% PZ aqueous solution with loading of 0.06 mol of CO₂/mol of amine group. Reactions considered in the rate-based model of the column are shown below, where reactions 14 a-e are assumed to be at equilibrium. Reactions 14 f-m are modeled using power law kinetics as shown in Eq. (15). The reactions listed, kinetic model, thermodynamic model and related constants are obtained from recent works. (Austgen et al., 1991; Hilliard, 2008; Bishnoi and Rochelle, 2000; Bishnoi and Rochelle, 2002)

$$r = k \left(\frac{T}{T_0} \right)^n \exp \left[-\frac{E}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \prod_{i=1}^N C_i^{a_i} \quad (15)$$

Intercooling of the solvent in the absorber is considered in the baseline design for decreasing the utility consumptions. In the Aspen Plus environment, the intercooling is modeled by the pumparound option in the RadFrac block. The pumparound flow rate is set to be the lean solvent flow rate. The cooling temperature is set to be 40°C.

Norton IMTP 1.5in, metal packing is used. The electrolyte NRTL properties package in Aspen Plus V7.3 is used. Column design carried out with the following objectives:

(1) The CO₂ stream concentration should meet the recommended design basis for the CO₂-sequestration gas for a remote, deep, geological storage site;

(2) The stripper column temperature should be chosen in a way that prevents solvent degradation;

(3) The CO₂-lean FT product must be free of solvent.

A design spec is used for capturing 98% CO₂ by manipulating the solvent recycle rate.

2.7.2. MEA

MEA is another popular chemical solvent for CO₂ capture. The plant configuration and modeling approach are similar to Section 2.7.1. Reactions considered are shown below. Reactions 16 a-c are considered to be equilibrium-limited. Reactions 16 d-g are simulated by using power law kinetics as shown in Eq. (15). (Zhang et al., 2009) The kinetic model and the pilot plant data for model validation are available in the open literature. (Dugas, 2006; Hikita et al., 2006) In agreement with the existing studies (Bechtel, 1992b; Dugas, 2006), the lean solvent is 30 wt% aqueous solution of MEA with CO₂ loading of 0.27 mol of CO₂/mol of amine group. The system design is subjected to the same constraints and operating conditions mentioned in Section 2.7.1.

2.7.3. Single-stage Selexol unit

The single-stage Selexol technology is considered here as another potential technology to remove CO₂ from the FT product due to its low utility consumption of the capture process itself and the downstream CO₂. The drawback of the Selexol technology is hydrocarbon loss. Hydrocarbon loss and utility saving for Selexol are compared with the previous two chemical solvents. The modeling approach is similar to that mentioned in Section 2.4. The rich solvent from the bottom of the absorber is sent to a H₂ recovery vessel to recover 70% of H₂ and then to a series of flash vessels to remove CO₂ from the solvent. Lean solvent out of the flash vessel again is chilled and sent back to the absorber. The configuration is shown in Fig. 7. The temperature of the chilled lean solvent is 2 °C, and the operating pressure of the absorber is 1965 kPa. The operating pressures of HP, MP and LP flash drums are determined by an optimization study discussed in Section 3.2. The percentage of CO₂ captured is set to be 93% in this case. It can be noted that the extent of CO₂ capture is lower than the chemical solvents due to the relatively low operating pressure of the post-FT CO₂ capture unit that limits the extent capture for the physical solvent.

Fig. 7. Configuration of the single-stage Selexol unit

2.8. CO₂ compression

The CO₂ captured from the pre-FT (Selexol unit) and post-FT CO₂ removal units is compressed by a split-shaft multistage compressor. A separate CO₂ compression unit is considered for post-FT CO₂ capture while selecting the post-FT CO₂ removal technology. Once the most suitable technology is

selected, one integrated CO₂ compression section is considered for the entire plant. It should be noted that the CO₂ stream from the post-FT CO₂ removal unit can be mixed with the CO₂ stream from the LP flash drum in the pre-FT unit as both these streams have similar pressure, if the amine-based CO₂ capture technology is selected for post-FT CO₂ removal. If the single-stage Selexol technology is selected for post-FT CO₂ removal, then the CO₂ streams from the post-FT CO₂ removal unit are available at three pressure levels and can be mixed with the CO₂ streams from the pre-FT unit depending on the pressure level. The final pressure of the sequestration-ready CO₂ is 15.16 MPa. Impurity limits in the CO₂ to be sequestered (Bhattacharyya et al., 2011) should be satisfied. The limits on H₂S, CH₄, and SO₂ are automatically satisfied, but the H₂O content in the stream out of the LP flash vessel is higher than the limit, i.e. 0.015 vol %. 90% of the incoming water in the CO₂ stream is removed by cooling and flashing. The remaining amount of water that needs to be removed to satisfy the limits is removed in an absorber using triethylene glycol (TEG) as the solvent. The modeling approach for this section can be found in the work of Bhattacharyya et al. (Bhattacharyya et al., 2011)

3. Results and discussions

The following studies are conducted for technology selection and obtaining the optimal operating conditions. To obtain the base case design, the optimal technology for post-FT CO₂ capture is selected in Section 3.3. Since the candidate technologies should first be optimally designed for a fair comparison, the optimal lean solvent loadings for the MEA and MDEA/PZ systems with intercooling and the optimal pressure levels for the Selexol unit are first obtained in Section 3.1 and Section 3.2. For brevity, the effect of the lean solvent loading for only the MDEA/PZ system is presented. This is followed by a study that helps selecting the optimal post-FT CO₂ capture technology for the base case. Studies shown in Section 3.4 to Section 3.7 are conducted with the most suitable post-FT CO₂ capture technology selected. Briefly, a study on the impact of the biomass/coal ratio on syngas composition and utility generation in the heat recovery section is presented. The effect of the H₂/CO ratio at the inlet of the FT reactor is evaluated by studying its impact on the fuel yield and major utility consumptions including electric power and steam.

3.1. Effect of the lean solvent loading on MDEA/PZ CO₂ removal unit with intercooling

Lean solvent loading is one of the key operating conditions for amine-based CO₂ removal systems. A decrease in the lean solvent loading can reduce the solvent circulation rate required for the same extent of CO₂ removal. However, it can result in an increase in the heat requirement for solvent regeneration. Six values of lean solvent loading are investigated. Table 4 shows the variations in the key performance variables as the lean solvent loading is changed. It should be noted that the solvent circulation rate is manipulated to achieve 98% of CO₂ removal for these studies. The inlet FT stream composition can be

found in Section 3.4 Table 8 Stream 12. In these studies, the lean solvent loading is calculated in terms of moles of CO₂ per moles of amine groups. The costs of cooling water, LP steam, and power are taken as \$0.354/GJ, \$13.28/GJ, and \$16.8/GJ, respectively. (Turton et al., 2012) Table 4 shows that the utility cost first decreases as the lean solvent loading is increased. But with further increase in the lean solvent loading, the utility cost increases. The optimum lean solvent loading is found to be about 0.06 mol CO₂/mol amine group for the FT product. It can be noted that the optimum value of lean loading can change if the gas composition, operating pressure and/or extent of CO₂ removal change. In this study, the solvent circulation rate and utility consumption do not change significantly with the lean solvent loading mainly because of relatively low range of lean solvent loading and high operating pressure that are considered in this study. These results are in agreement with other studies available in the open literature (Seagraves and Weiland, 2009; Salkuyeh and Mofarahi, 2013) for MDEA-based systems.

Table 4

Effect of lean solvent loading in the MDEA/PZ based CO₂ capture unit (not including CO₂ compressing).

<u>Lean loading</u> (mol CO ₂ /mol amines)	Solvent/CO ₂ (mol/mol)	Cooling Water (GJ/hr)	Reboiler Duty (GJ/hr)	Pumping Power (kW)	Utility Cost (\$/hr)
0.03	19.00	118.93	120.33	876.94	1694
0.05	19.47	118.64	120.18	888.87	1692
0.06	19.71	118.56	120.05	895.55	1690
0.08	20.22	118.82	120.27	909.78	1694
0.09	20.49	119.25	120.68	918.17	1700
0.10	20.77	119.30	120.88	924.25	1703

3.2. Effect of the operating pressure of the flash drums on the single-stage Selexol unit

In the single-stage Selexol unit for post-FT CO₂ capture, 93% CO₂ capture is achieved in the absorber and released in a series of flash drums at decreasing pressure levels. The reduction of the power consumption of this unit with the CO₂ compression can be achieved by operating the HP, MP and LP flash drums at optimum pressures. With different operating pressures of the LP flash drum, the CO₂ loading in the lean solvent recycled back to the absorber becomes different, which will significantly affect the solvent circulation rate of the system with the same extent of CO₂ removal. If the operating pressure of the LP flash drum is fixed, the solvent circulation rate does not change much with change in the pressures of MP and HP flash drums, but the relative distribution of CO₂ obtained from the three flash drums will change, which will affect the power consumption of the CO₂ compression system. In this

study, first the MP and HP drum pressures are fixed at 414 kPa and 690 kPa, respectively to study the effect of the operating pressure of the LP flash drum. Once the optimum LP drum pressure is obtained, the effect of the MP and HP flash drum pressures are obtained.

Fig. 8 shows, as expected, that the solvent circulation rate increases with the increasing pressure of the LP flash vessel. With the increasing solvent circulation rate, the total power consumption increases mainly due to the increase in the refrigeration load and power consumption by the solvent circulation pump. An increase in the solvent circulation rate also results in higher loss of hydrocarbons. The optimal pressure of the LP drum is found to be 138 kPa. Once this pressure is fixed, Fig. 9 shows the effect of the change in the pressure of the MP and HP flash drums. From Fig. 9, the optimal pressures of the MP and HP flash drums are 310 kPa and 621 kPa, respectively. Fig. 9 shows that the total power consumption does not change significantly in the pressure range studied. It should be noted that the pressures of the HP and MP drums were not changed widely as these pressures are constrained by the operating pressure of the H₂ flash drum (1.1 MPa). Furthermore, the CO₂ compressor consumes about 33% power in the Selexol unit, while the remaining power is consumed for solvent chilling and circulation.

Fig. 8. Effect of LP Flashdrum Pressure

Fig. 9. Effect of Pressures of MP and HP Flashdrums

3.3. Selection of the post- FT CO₂ removal technology

In this section, three solvents, MEA, MDEA/PZ, and Selexol, are evaluated for removing CO₂ from the FT hydrocarbons. As mentioned before, the selectivity of Selexol, a physical solvent, is poor, and as a result significant amount of hydrocarbons can be lost. The lower heating value (LHV) of total hydrocarbon lost in the Selexol unit is calculated and converted to equivalent utility consumption for a fair comparison with the amine-based CO₂ removal technologies. The hydrocarbon loss and corresponding LHV loss in the Selexol unit are shown in Table 5. The loss is found to be about 15 wt% of total hydrocarbon produced. Table 6 indicates that the Selexol technology is not suitable for removing CO₂ from the FT product because of the considerable hydrocarbon loss. It also shows that the intercooling can significantly reduce the total utility cost of MEA and MDEA/PZ based CO₂ removal units. The MDEA/PZ CO₂ removal unit with intercooling gives the lowest utility cost and is therefore considered to be the desired technology for the following base case studies. It is also observed that the steam consumption of MDEA/PZ system is 14.4% less than that the MEA system, which might be more economic than the inhibited MDEA system (13.8% less than the MEA system) selected by Bechtel (Bechtel, 1992b) as their base case. Additionally, it can be noted that the MDEA/PZ as a solvent is also advantageous due to its lower corrosion and lower vapor pressure in comparison to MEA.

Table 5

Hydrocarbon loss in the single-stage Selexol unit.

HC Loss (kg/hr)	Heat Loss (GJ/hr)
-----------------	-------------------

C ₁	267	13.3
C ₂₌	1393	66.5
C ₂	533	25.1
C ₃₌	1825	83.4
C ₃	396	18.2
C ₄₌	1544	69.7
C ₄	581	27.0
C ₅₌	1156	52.3
C ₅	414	18.6
C ₆₌	630	28.1
C ₆	217	9.6
Total		411.8

Table 6

Comparison of the three CO₂ removal technologies (including CO₂ compressing).*

	Selexol	MEA w/o	MEA w/	MDEA/PZ w/o	MDEA/PZ w/**
Power (MW)	13.92	6.20	6.13	6.03	5.88
Cooling Water (GJ/hr)	30.84	175.65	167.32	164.81	147.33
Reboiler Duty (GJ/hr)		146.23	137.94	136.81	120.05
Heat Lost (GJ/hr)	411.8				
Utility Cost (\$/hr)	6322	2379	2262	2240	2001

* w/o denotes without intercooling, and w/ denotes with intercooling; the lean solvent loading of MEA units is 0.27 mol CO₂/ mol amine (Dugas, 2006).

** the technology selected for all following base case studies

3.4. Material and utility summaries of the CBTL plant with CCS (base case)

The operating conditions of the key units for the base case are summarized in Table 7. In the base case, the H₂/CO ratio and the biomass/coal weight ratio are set to 2 and 8/92 (dry); the total feed flowrate of coal and biomass is 246.6 ton/hr and the MDEA/PZ with intercooling process is used for post-FT CO₂ removal. Considering the valid range for the available correlations and the economic analysis available in the open literature (Bechtel, 1992a; Kou, 1985; Fox and Tam, 1995), the operating condition of the FT reactor for the base case is decided to be 257°C and 2 MPa. In our base case design, the inlet H₂/CO ratio is set to 2 to decrease the selectivity of main byproduct CO₂ and the utilities consumption in the CCS facilities. Further discussion on the impact of H₂/CO ratio is provided in Section 3.6 and 3.7. After the operating pressure of the FT unit is decided, the operating pressure of other units is calculated by

considering pressure drop in all equipment. The operating temperature of each unit is decided based on the optimization studies available in the open literature (Bhattacharyya et al., 2011; Bechtel, 1992a; Bain, 1992).

Table 7

Summary of the operating condition of key units.

	Pressure (kPa)	Temperature (°C)
Syngas Production		
ASU Air Compressor	1310	
Oxygen Compressor	2400	
Gasifier	2380	850
Fischer-Tropsch		
FT Reactor	2000	257
Selexol		
H ₂ S Absorber	2048	2
CO ₂ Absorber	2013	2
H ₂ S Concentrator	1930	117
<u>Selexol Stripper*</u>	<u>600</u>	<u>41/153</u>
H ₂ Recovery Drum	1620	
LP Flash Vessel	241	
Post-FT CO ₂ Removal		
Absorber	1965	38
<u>Stripper*</u>	<u>172</u>	<u>38/116</u>

*For strippers, the temperatures of condensers and reboilers are listed.

Table 8 lists the flow rate of the key species in the main streams numbered in Fig. 1 for the base case conditions. In the base case, 6% of carbon in the coal and biomass is vented to the atmosphere in form of CO₂, 53% of carbon is stored in the captured CO₂, while the remaining carbon is converted to the FT syncrude and fuel gas. To simplify the results and discussion of the plant utility consumptions, the plant shown in Fig. 1 is divided into four sections for showing the results and discussion. They are syngas production section, CO₂ capture and storage (CCS) section, FT synthesis section and others. Table 9 lists the main utility consumptions for the base case. The syngas production and the CCS sections are the two main consumers of the electric power, consuming about 54% and 36%, respectively, of total power demand. The production of purified syngas has been reported to cost 60-70% of the total capital and running cost in conventional CTL plants without CCS facilities. (Dry, 2002) The HP, IP and LP steam are generated from the syngas production and cleanup section, Claus unit, and the FTS section. The strippers

and heaters in the CBTL plant consume IP and LP steam. It can be noted that the HP steam generated in the radiant syngas cooler can be used to produce electricity. The power consumptions in the remaining units are calculated based on the utility summary available in the open literature (Reed et al., 2007; NETL, 2010; Bechtel, 1998) by scaling up with respect to the coal and biomass flowrate (dry).

Table 8

Stream summary of the CBTL plant with CCS.

Stream	1	2	3	4	5	6	7	8
Name	Air	O ₂	Coal & Biomass	Raw syngas	Raw syngas	Raw syngas	Shifted syngas	Cooled syngas
Temperature (°C)	15	32	16	850	208	208	301	21
Pressure (kPa)	103	2,380	2,380	2,380	2,324	2,324	2,289	2,082
Flowrate (kg/hr)								
H ₂ O	5,792			74,468	105,675	132,678	186,570	467
CO ₂	386			162,520	72,014	90,412	288,921	288,830
O ₂	197,602	184,434						
N ₂	643,327	2,794		5,988				
CH ₄				2,436	1,080	1,356	2,436	2,431
CO				239,229	106,056	133,159	158,774	158,769
COS				272	118	150	14	14
H ₂				16,402	7,271	9,131	22,190	22,190
H ₂ S				5,897	2,604	3,266	5,947	5,919
Coal			226,972					
Biomass			19,623					
Slag				24,916				
C ₂ -C ₄				231	104	127	231	231
C ₅ -C ₁₀								
C ₁₁ -C ₂₀								
Wax								
Oxygenates								
Stream	9	10	11	12	13	14	15	16
	Clean syngas	Make-up water	CO ₂	FT vapor	FT liquid	Light gases	CO ₂	CO ₂
Temperature (°C)	3	16	37	38	38	39	38	89
Pressure (kPa)	2,013	1,014	203	1,979	1,979	1,965	172	15,272
Flow Rate (kg/hr)								
H ₂ O	535	173,089	5	272	109	272	73	78
CO ₂	28,550		260,280	58,846	1,538	1,175	57,671	317,951

O ₂							
N ₂							
CH ₄	2,350	73	3,211	27	3,211		73
CO	153,834	4,940	12,211	41	12,193	18	4,958
COS							
H ₂	22,136	64	5,135	5	5,126	9	73
H ₂ S							
Coal							
Biomass							
Slag							
C ₂ -C ₄	27	204	6,446	1,021	6,446		204
C ₅ -C ₁₀			3,012	13,531	3,012		
C ₁₁ -C ₂₀			9	12,760	9		
Wax				27,189			
Oxygenates			689		689		

Table 9

Summary of the utilities in the CBTL plant with CCS.

Power Consumptions (MW)			%	Steam Generation (GJ/hr)	
Syngas Production	88.2		53.58	Syngas Production	
Syngas Generation	77.1		46.84	Radiant Syngas Cooler (HPSTM)	-240.6
Steam Generation	0.5		0.3	Heat Recovery (IPSTM)	-113.2
Black and Sour Water Treatment	10.6		6.44	Heat Recovery (LPSTM)	-348.1
CO₂ Capture and Storage	59.5		36.15	SWS Reboiler (IPSTM)	79.6
Selexol	33.1		20.11	Fischer-Tropsch Synthesis	
MDEA/PZ	0.9		0.55	IP Steam Generator (IPSTM)	-369.1
CO ₂ Compression	25.5		15.49	CO₂ Capture and Storage	
Fischer-Tropsch Synthesis	0.9		0.55	Selexol Striper Reboiler (IPSTM)	197.9
Others	16		9.72	MDEA/PZ Striper Reboiler (LPSTM)	120.1
Total	164.6		100	Others (IPSTM)	4.5

3.5. Effect of biomass/coal ratio in the feedstock

As mentioned before, an increase in the biomass content in the gasifier feed can significantly decrease the carbon footprint of the indirect CBTL plant. In this study, impact of the biomass content on the syngas composition and the utility generation in the syngas production and cleanup sections is investigated. Four

biomass concentrations are studied here, 5 wt%, 8 wt%, 15 wt%, and 20 wt% (dry), with the same dry feed flowrate. The results are listed in Table 10. When the biomass content in the feedstock is increased, the H_2/CO ratio of the raw syngas from the gasifier increases. This results in a decrease in the extent of the WGS reaction in the WGS reactors. Therefore, the heat that can be recovered after the WGS reactor also decreases because the WGS reaction is exothermic. Considering the total energy balance, this would be expected as the heating value of biomass is lower than the coal.

Table 10

Effect of biomass/coal ratio on the syngas composition and steam generation*.

Biomass/Coal	Syngas Composition (mol %)					H_2/CO	$\frac{\text{Syngas to WGS}}{\text{Syngas produced}}$	Heat to HRSG (GJ/hr)	
	H_2	CO	CO_2	H_2O	Others			RSC	Heat Recovery
5/95	32	33.8	14.2	15.5	4.5	0.947	0.447	240.9	541.0
8/92	31.7	33.2	14.4	16.1	4.6	0.955	0.443	240.6	532.8
15/85	30.9	31.9	14.7	17.6	4.9	0.969	0.433	239.9	513.8
20/80	30.3	30.9	15	18.7	5.1	0.981	0.429	239.5	500.5

* the heat recovery section includes IP, LP steam generators and BFW heater shown in Fig. 2 Section 2.3.

3.6. Effect of the H_2/CO ratio at the FT inlet on the utility consumption of CCS facilities

H_2/CO ratio in the coal derived syngas is always lower than the stoichiometric ratio needed in the FT reactor. However, the H_2/CO ratio in the coal derived syngas can be increased in the WGS unit. The effect of the H_2/CO ratio on the utility consumption in the CBTL process with CCS is evaluated. From Table 9, it can be noted that the units for CCS, i.e. the Selexol unit for pre-FT CO_2 capture, the MEDEA/PZ unit for post-FT CO_2 capture, and the CO_2 compression unit, use about 36% of the total electricity consumed in the plant. The range of H_2/CO ratio investigated is from 1 to 2. The lower bound is decided based on the composition of the raw syngas that is generated from the gasifier assuming that the WGS reactor is not available. The upper bound is set to match with the stoichiometric ratio of the FTS reaction shown in Reaction 6a. Table 11 presents the results from this study. With the increase in the H_2/CO ratio from 1 to 2 at the FT reactor inlet, the utility consumption keeps decreasing; however, the net heat recovery does not change appreciably. The decrease in power, IP steam and LP steam consumption results from the decrease in solvent circulation rates in both the Selexol and MDEA/PZ units as shown in Table 12. In summary, the power consumption in the CCS section (the Selexol, MDEA/PZ, and CO_2 compression units) and the entire CBTL plant (excluding the product upgrading section) can be reduced by 8.5% and 3.6% if the inlet H_2/CO ratio increases from 1 to 2. Fig. 10 shows that about \$3800/hr in utility costs can be saved using the H_2/CO ratio of 2 in comparison to the H_2/CO ratio of 1.

Table 11
Effect of H₂/CO ratio on the plant utility.

H ₂ /CO	2	1.7	1.5	1.3	1
Total Power Consumption (MW)	164.6	165.9	167.0	169.0	170.8
Syngas Production (MW)	88.2	88.4	88.5	88.5	88.7
CO ₂ Capture and Storage (MW)	59.5	60.6	61.6	63.5	65.0
FTS & Others (MW)	16.9	16.9	16.9	17.0	17.1
Heat Recovery (HPSTM) (GJ/hr)	-240.6	-240.6	-240.6	-240.6	-240.6
Heat Recovery (IPSTM) (GJ/hr)	-482.3	-499.4	-496.9	-493.5	-487.6
Heat Recovery (LPSTM) (GJ/hr)	-348.1	-354.3	-377.8	-405.7	-453.3
IPSTM Consumption (GJ/hr)	282.0	329.2	390.4	426.1	517.9
LPSTM Consumption (GJ/hr)	120.1	142.2	156.9	176.1	227.0

Fig. 10. Decrease in utility costs due to change in the H₂/CO ratio

Table 12
Effect of the H₂/CO ratio on the solvent circulation rates

H ₂ /CO	2	1.7	1.5	1.3	1
SELEXOL					
CO ₂ Captured (kmol/hr)	5914	5328	4865	4317	3380
Partial Pressure of CO ₂ (kPa)	564	523	488	445	366
Solvent Circulation Rate (kmol/hr)	9979	11340	12474	13971	16556
Solvent/CO ₂ (kmol/kmol)	1.69	2.13	2.56	3.24	4.90

MDEA/PZ

CO ₂ Captured (kmol/hr)	1311	1678	1967	2320	2954
Solvent Circulation Rate (kmol/hr)	25998	32487	37588	43587	54266
Solvent/CO ₂ (kmol/kmol)	19.83	19.36	19.11	18.79	18.37

1

2 In the Selexol process, the main power consumption is due to the compressors in the NH₃ vapor-
3 compression cycle. This is a strong function of the solvent circulation rate. The partial pressure of the acid
4 gases is the main driving force for mass transfer as Selexol is a physical solvent. The higher the CO₂
5 partial pressure (P_{CO_2}) is, the more efficient the Selexol process will be. In the CBTL plant, the operating
6 pressure of the absorbers in the Selexol unit is constrained by the pressure of the gasification section.
7 Hence, the only way to increase the inlet P_{CO_2} is to increase the H₂/CO ratio in the syngas sent to the
8 Selexol unit. Obviously, as the higher mole fraction of H₂ is achieved by converting CO to CO₂ through
9 the WGS reaction, the mole fraction of CO₂ increases. Fig. 11 shows that the circulation rates of Selexol
10 decreases considerably as the H₂/CO ratio is increased, even though the amount of CO₂ that needs to be
11 captured increases simultaneously. Fig. 12 shows that an increase in the H₂/CO ratio decreases the power
12 consumption in the Selexol unit significantly mainly due to the lower solvent circulation rate.

13 Another effect of the H₂/CO ratio on the Selexol unit is in the loss of syngas. The solubility of CO₂ in
14 Selexol is about 36 times of the solubility of CO. (Kohl and Nielsen, 1997) Since CO partial pressure is
15 still high in the syngas to the Selexol unit, still a considerable CO loss occurs. Table 13 shows that the CO
16 loss decreases from 5.29% to 3.21% when the H₂/CO ratio increases from 1 to 2.

17 Since MDEA/PZ is a chemical solvent, its performance does not get affected by the pressure significantly.
18 High H₂/CO ratio in the Fe-catalyzed FTS unit decreases the formation of CO₂. The solvent required in
19 the MDEA/PZ unit decreases with an increase in the H₂/CO ratio because of the decrease in the CO₂
20 selectivity in the FTS unit as shown in Fig. 13.

Fig. 11. Effect of H_2/CO on the solvent circulation rate in the Selexol unit

Fig. 12. Effect of the H_2/CO ratio on power consumption in the Selexol unit

Fig. 13. Effect of the H₂/CO ratio in the post-FT CO₂ capture unit

Table 13

Effect of the H₂/CO ratio on CO loss in the Selexol unit.

H ₂ /CO	2	1.7	1.5	1.3	1
CO loss (kg/hr)	4940	6518	7852	9512	2555
CO loss%	3.21	3.69	4.11	4.57	5.29

3.7. Effect of the H₂/CO ratio at the FT inlet on the carbon efficiency and product selectivity

As shown before, the high H₂/CO ratio results in a decrease in the utilities consumption in the CCS units. However, an increase in the H₂/CO ratio raises the light gas selectivity and reduces the fuel yield of the CBTL plant. Fig. 14 shows the carbon number distribution in light hydrocarbons from C₁ to C₂₀ (weight basis) for different H₂/CO ratios. The summary of product selectivity and carbon efficiency of the entire CBTL plant can be found in Table 14. The figure shows a high yield of CH₄ in comparison to other hydrocarbons, which is consistent with the experimental results available in the open literature. (Bechtel, 1992a; Kuo, 1985; Kuo, 1983; Steynberg and Dry, 2004) The higher the H₂/CO ratio is, the higher the selectivity of light hydrocarbons is. However, the H₂/CO ratio is not expected to affect the overall syngas conversion significantly. According to Fig. 13, the CO₂ selectivity increases with a decrease in the inlet H₂/CO ratio. However, when H₂/CO ratio increases, more CO in the raw syngas is converted to CO₂ in the WGS unit and captured in the Selexol unit. As a result, lower amount of syngas enters the FTS unit. In summary, the overall carbon efficiency, defined as fraction of carbon in feed converted to hydrocarbon, of the CBTL plant does not change much with the change in the H₂/CO ratio, but the utilities consumption in the CCS unit and CH₄ production does. This study suggests that an optimal H₂/CO ratio exists. The optimum can be determined by conducting a techno-economic analysis. To evaluate the impact of the H₂/CO ratio on the plant economics, the product upgrading section needs to be considered.

Fig. 14. Carbon number distribution

Table 14

Effect of the H₂/CO ratio on the product selectivity and carbon efficiency.

H ₂ /CO	2	1.7	1.5	1.3	1
Carbon Efficiency (%)	34.7	35.1	35.4	35.5	35.6
C ₁ -C ₄ (wt%)	16.48	16.16	15.88	15.51	14.68
C ₅ -C ₁₀ (wt%)	27.53	27.00	26.52	25.91	24.51
C ₁₁ -C ₂₀ (wt%)	15.80	15.49	15.22	14.86	14.07
Wax (wt%)	40.19	41.35	42.38	43.72	46.74

4. Conclusions

A plant-wide model of a coal biomass to liquids (CBTL) plant with CCS has been developed in Aspen Plus 7.3.2. The comparison between the three post-FT CO₂ removal technologies shows that the MDEA/PZ CO₂ removal technology has lesser overall penalty than the Selexol and MEA CO₂ removal technologies. Intercooling of the solvent in the absorber is found to decrease the solvent circulation rate and utility consumption for both MDEA/PZ and MEA cases. The optimum lean solvent loading for CO₂ removal from the FT product stream is found to be 0.06 mol CO₂/ mol amine when MDEA/PZ is used as the solvent.

For the current design, the carbon efficiency is about 35%. 53% of carbon in the feed is stored in the captured CO₂ while 6% is vented to the atmosphere as CO₂. When the biomass content in the feedstock is increased, steam production in the syngas heat recovery section decreases. The simulation results show

that high H_2/CO ratio at the inlet of the FT reactor can reduce the utility consumption of the entire plant significantly but at the cost of higher light gas yield. The power consumption of the CCS section and the entire CBTL plant could be reduced by 8.5% and 3.6% when the H_2/CO ratio is increased from 1 to 2. Another advantage of the high H_2/CO ratio is a reduction in the CO loss in the Selexol unit.

It must be noted that the optima found in this paper for the CCS technologies and their optimal operating conditions can be different if the product upgrading section is included in the analysis.

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