Process Modeling of Direct Coal-Biomass to Liquids (CBTL) Plants with Shale Gas Utilization and CO₂ Capture and Storage (CCS)

Yuan Jiang, Debangsu Bhattacharyya*

Department of Chemical Engineering, West Virginia University, Morgantown, WV 26505, USA

Abstract

Direct coal liquefaction (DCL) technologies have been commercially demonstrated for producing transportation fuels from non-petroleum sources. However, significant amount of hydrogen is required in the DCL process due to the low H/C ratio in coal. As a result, DCL processes are usually associated with a high level CO₂ emission from hydrogen production units. Hence, direct coal biomass to liquids (CBTL) processes with CO₂ capture and storage (CCS) and shale gas utilization are proposed in this work as an option for reducing CO₂ emission. In this study, the focus is on process simulation and calculation of material and energy balances of novel direct CBTL plants, which can be used as a basis for further studies, such as optimization, techno-economic analysis and life-cycle analysis. In this process, coal with moderate amount of biomass is converted into syncrude through reaction with the hydrogen-donor solvent and gaseous hydrogen in a catalytic two-stage liquefaction unit. Hydrogen required for the liquefaction and product upgrading unit is produced from the liquefaction residue partial oxidation unit and the shale gas steam reforming unit or from the coal/biomass/residue co-gasification unit. Different CCS technologies are evaluated to achieve 90% overall carbon capture if high extent of CO₂ capture is considered. Results of individual plant sections are validated with the existing data, if available. Sensitivity studies have been conducted to analyze the effects of key operating parameters and design parameters, such as the sources of hydrogen, CCS technologies, extent of CCS, and biomass/coal ratio. Key measures studied in this work include the fuel yield, thermal efficiency, CCS penalty and CO₂ emission.

Key Words

Coal, Biomass, Shale gas, Direct liquefaction, CO₂ capture and storage

* Corresponding author.

Tel: 1-304-293-9335, E-mail: Debangsu.Bhattacharyya@mail.wvu.edu

1. Introduction

Due to the worldwide insecurity of crude oil supply, and volatile crude oil price, studies on production of liquid fuels from coal are being conducted especially in those countries that have lack of petroleum resources but abundant coal reserves. Indirect coal liquefaction (ICL) and direct coal liquefaction (DCL) technologies have already been commercialized. In the ICL process, coal is first sent to the gasification unit to be converted into syngas [1]. Then the clean syngas from the acid gas removal unit is sent to the Fischer-Tropsch reactor to be converted into syncrude [2-5]. The Fischer-Tropsch technology is the key of the ICL process, which is first introduced in 1920s, and still under commercial operation in South Africa [6]. In the DCL technology, coal is converted to liquid by adding hydrogen at high pressure and temperature. Various DCL technologies have been developed in last hundred years such as Solvent Refined Coal (SRC)-I and SRC-II, Exxon Donor Solvent (EDS), H-Coal and catalytic two-stage liquefaction (CTSL) [7-10]. One big issue with both the ICL and DCL processes is the high life-cycle greenhouse gas (GHG) emissions. Adding biomass and/or shale gas into the feedstock and applying carbon capture and storage (CCS) are possible solutions to the GHG emission problem [5,9,11-15]. Therefore, locations with adequate coal, biomass and shale gas resources, such as the Appalachian region, are potential candidates for siting these plants [16,17].

Even though the DCL technology is claimed to have higher thermal efficiency than the ICL technology [1], most published studies on the process systems analysis, including process synthesis, optimization, and economic analysis, of coal liquefaction processes have focused on the ICL technology, mainly because the ICL technology is more mature and has adequate industrial experience [18-20]. In the area of the DCL technology, the focus in the existing literature is on design and optimization of liquefaction reactor and separation system individually rather than process systems analysis. Instead of the earlier single-stage liquefaction reactors, the two-stage liquefaction technology has been developed to achieve higher solid conversion and liquid yield as well as lower heteroatom content and hydrogen consumption [7, 8]. In the two-stage technology, operating conditions in two reactors in series are optimized for coal dissolution in the first-stage and hydrotreating/hydrocracking in the second stage [8]. The Shenhua DCL plant in Inner Mongolia, China, which is the only operating commercial scale DCL plant after World War II, has been developed based on the NEDOL process developed in Japan and the CTSL process developed by the Hydrocarbon Technologies Inc. (HTI) in the United States [9]. Other than that, the Residual Oil Supercritical Extraction-Solids Rejection (ROSE-SR) process can be combined with the traditional vacuum distillation technology to increase the oil recovery in the separation system with lower utility consumption leading to higher process efficiency [21,22]. Separation of ash and unreacted coal from heavy liquids is difficult because of the small size of solid particles, the small difference in densities

between solids and liquids, and the high viscosity and melting point of the liquids. In the ROSE-SR unit, benzene, toluene, xylene or their mixtures can be used as a solvent near their critical temperature and pressure because of their high solubility for direct liquefaction liquids [23]. The ROSE-SR process can recover 85-93% of the solvent as a supercritical fluid in the second stage settler saving about 40-50% of the utility in comparison to evaporation-based processes [22]. Furthermore, partial oxidation (POX) of liquefaction residues, an ash containing carbonaceous solid, can be used for producing hydrogen and reducing the need for external hydrogen requirement [24-26]. Since 1970's, Texaco Inc. has conducted a series of studies on the suitability of using coal liquefaction residues as feedstocks to entrained flow gasifiers where the liquefaction residues were fed into the gasifier as a molten fluid or water slurry [27,28].

Despite several efforts to increase the process efficiency of the DCL processes, the life cycle GHG emission for producing the DCL liquids is about double of that for producing them from the petroleum source [7]. In order to convert coal ($H/C \approx 0.8$) to transportation fuels ($H/C \geq 1.8$), either carbon needs to be rejected in the form of CO_2 (as in the ICL technology) or hydrogen needs to be added from external sources (as in the DCL technology) [2-4,6,7]. In DCL plants, the H/C ratio is increased by adding gaseous hydrogen to a slurry mixture of coal and recycled coal-derived liquids, so-called H-donor solvent, at high temperature and pressure in presence of catalysts. Coal gasification has been used in the Shenhua DCL plant for producing make-up hydrogen because of the relatively low cost and sufficient supply of coal in China. Mixtures of coal, biomass, and liquefaction residues can also be converted to syngas by co-gasification (CG) [2,12,29]. If natural gas or shale gas is available locally with reasonable price, hydrogen can also be produced by steam methane reforming (SMR) with less GHG emission in comparison to coal gasification [1,14]. Even though the conventional feedstock for the SMR unit is natural gas, due to abundant and cheap shale gas that is now available in the United States, shale gas is a potential feedstock in the SMR unit. However, because of the higher ethane and propane content in the shale gas in comparison to the natural gas, an adiabatic pre-reformer is preferred to convert ethane and propane before the main steam reforming reactor to prevent coke formation on reformer walls and catalyst surfaces [30-32]. It has been reported that current commercial hydrogen production technologies, either gasification or SMR, are usually associated with a large amount of CO_2 emission. A recent study shows that about 0.48 tonne of CO_2 is released per barrel of transportation fuels produced in the Shenhua DCL plant, where about 80% of that CO_2 is produced in the gasification-based hydrogen production unit [7]. In order to reduce GHG emissions, a small amount of biomass can be co-fed with the coal to the direct liquefaction reactors [33-35]. CCS technologies can also be applied in order to further reduce the overall carbon footprint of the liquefaction processes. [15]

Biomass is considered to be a carbon-neutral feedstock, because the CO_2 released to the atmosphere is reutilized by biomass. [13] Several experimental studies have been conducted on coal-biomass co-liquefaction [8,11,34-36]. Some researchers have reported that co-liquefaction of biomass and coal under mild condition (about 350°C) has higher conversion and oil yield than those that would be predicted based on a simple linear combination of the conversion and oil yield of liquefaction of biomass and coal independently [11,37]. This could be a result of the difference in the thermal cleavage temperature between coal and biomass. Biomass has a higher conversion and lower thermal cleavage temperature than coal, and can produce free radicals at lower temperature to promote the reaction of coal [36]. However, the synergistic effect reduces with the increasing temperature and pressure, as the reactivity of coal increases [36,38]. Ai performed a series of preliminary studies on co-processing of Shenhua coal and Sawdust at 450°C , which is similar to the operating conditions in the commercial DCL reactors, and observed that presence of sawdust resulted in apparent improvement of coal conversion [39]. Their study also shows that because of the higher H/C ratio of biomass compared to that of coal, the hydrogen consumption in the direct liquefaction plant and CO_2 emission associated with hydrogen production can be reduced by increasing the biomass content in the system [39]. Even though several efforts have been made to understand the kinetics and thermal behavior of DCL reactions and the hydrodynamics of DCL reactors [40-43], the direct coal-biomass to liquids (CBTL) process has been hardly modeled in details at the equipment-level or at the system-level especially with a focus on reduction of GHG emission from this process. Process modeling and simulation of the liquefaction section and the hydrogen production section simultaneously can help to accurately estimate the throughput of the hydrogen production section and associated CO_2 emission with different types and ratios of coal, biomass and shale gas. This would, in turn, help to obtain a more accurate estimate of the thermal efficiency and operating and capital costs of the CCS technologies for a given level of CO_2 capture.

As mentioned before, significant amount of CO_2 is generated for producing H_2 irrespective of whether the gasification or SMR route is used. The CO_2 present in the product stream from these processes has to be removed to produce high-purity hydrogen even if CCS is not considered. Additional CO_2 might need to be captured if high extent of CCS is considered. In most commercial plants, CO_2 is typically captured by physical or chemical absorption. [39] In the chemical absorption processes, the main utility consumption is in the reboiler of the solvent stripper. In the physical absorption process, the solvent can be simply regenerated by pressure swing or thermal regeneration of only a portion of the solvent, but solvent chilling may be necessary leading to significant utility consumption. The selection of the appropriate technology mainly depends on the CO_2 partial pressure (P_{CO_2}), extent of CO_2 capture and other components present in the stream. If P_{CO_2} is high enough to provide sufficient driving force and

concentration of hydrocarbons (or other components with high solubility in physical solvents) are low, physical absorption is preferred because it is typically more energy-efficient than the chemical absorption and the captured CO₂ is released at relatively high pressure (HP) resulting in lower power consumption in the downstream CO₂ compressor. [44] Otherwise, chemical absorption is preferred for CO₂ removal. In chemical absorption, CO₂ is typically released at low pressure (LP) adding to the cost of compression, because the stripper pressure is limited by the solvent decomposition temperature [45]. For example, the physical absorption technologies (i.e. Selexol, Rectisol) are preferred for pre-combustion CO₂ capture from the syngas generated by coal gasification mainly because of high P_{CO_2} and lack of hydrocarbons, while chemical absorption technologies (i.e. MEA, MDEA) are preferred for the post-combustion CO₂ capture from the low pressure flue gas [46-48]. Even though, large number of studies have been conducted on selection of CCS technologies for different CO₂-producing technologies, such as the Fischer-Tropsch technology [20,47], integrated gasification combined cycle [46,48], pulverized coal combustion and natural gas combined cycle [46], not much studies have been conducted on selection of technologies for CCS in the direct liquefaction technology.

To summarize, the existing literature lacks systems level analysis of the DCL process that can greatly benefit from the cheap and abundant shale gas (especially in the continental US) and biomass as well as the novel CCS technologies due to potential improvement in its thermal efficiency, fuel yield, and environmental performance. With this motivation, four novel plant configurations are proposed and plant-wide models are developed for these configurations. The configurations are SMR_CCS (base case), SMR_VT, CG_CCS, and CG_VT, where the first acronym before the underscore denotes whether hydrogen is produced from shale gas steam methane reforming (SMR) or coal/biomass/residue co-gasification (CG), while the second acronym denotes whether CO₂ is stored (CCS) or vented (VT). Our focus in this paper is on process synthesis, technology selection and performance analysis, which provides the basis for further studies, such as optimization, life cycle analysis, and techno-economic analysis [1]. In particular, contributions of this work can be summarized as follows:

(1) proposed four novel configurations for direct CBTL processes and developed high-fidelity plant-wide models for each of them, (2) utilized shale gas as a novel sources for H₂ in the direct CBTL process, (3) designed the CCS units for all configurations, (4) investigated the plant performance in terms of productivity, efficiency and CO₂ emission for different hydrogen sources, CCS solvent, extent of CCS and biomass to coal ratio, and (5) compared the direct CBTL plant with indirect CBTL plant for various process configurations.

2. Process design and modeling

Block flow diagrams (BFD) of direct CBTL plants are shown in Fig. 1 and Fig. 2. Liquefaction technology is the core technology for all different configurations. Coal and biomass with a low biomass/coal ratio (8/92 weight basis, base case) are mixed with the recycled oil in the slurry tank, and then pressurized and preheated before being fed to CTSL reactors along with make-up and recycled H_2 . The product from the second liquefaction reactor is sent to a hot HP separator. The vapor product from the hot HP separator is then sent to the inline hydrotreater for stabilization. Hydrotreated liquids from the inline hydrotreater and the liquid product from the hot separator are sent to the hydrocarbon recovery and solid/liquid separation unit to be separated into H_2 -rich gases, light gases (C_1 - C_4), light naphtha (C_5 , C_6), heavy naphtha (C_7 -177°C), distillate/gas oil (177-376°C), solvent oil (376-524°C) and liquefaction residues (more than 524°C). H_2 -rich gases and solvent oil are recycled back to the CTSL unit. A portion of the light gases is used in the process furnaces, while the remaining is sent to the power island for electricity generation. Naphtha and gas oil are sent to the product upgrading unit for generating on-spec gasoline and diesel as main products. The liquefaction residue is sent to the POX unit for H_2 production.

Because considerable amount of H_2 is consumed in the CTSL unit, hydrogen production is also critical for direct CBTL plants. Considering different H_2 sources and CO_2 control targets, four different configurations are considered in our study. In the SMR_CCS (base case) and SMR_VT processes as shown in Fig. 1, a portion of the required H_2 is generated from partial oxidation of the liquefaction residue, while the remaining is generated by shale gas steam reforming. Alternatively, the required H_2 is supplied from coal/biomass/liquefaction residue co-gasification. In the CG_CCS and CG_VT processes as shown in Fig. 2, pre-processed coal and biomass are fed to the liquefaction unit and the POX unit along with liquefaction residues, while other blocks remain the same as the SMR_CCS and SMR_VT processes. In all configurations, the syngas from the POX/CG unit and/or the SMR unit is sent to the acid gas removal (AGR) unit for CO_2 and H_2S removal, and then to pressure swing adsorption (PSA) unit for H_2 purification. Three different CO_2 capture technologies are considered for the AGR unit- Selexol, monoethanolamine (MEA), piperazine- activated methyl diethanolamine (MDEA/PZ). H_2S produced in the POX/CG unit via gasification is removed in the H_2S absorber of the dual-stage Selexol unit, while H_2S produced in the liquefaction and hydrotreating units is removed by chemical absorption using MDEA as solvent. The removed H_2S is then sent to the Claus unit to be recovered as elemental sulfur. In the SMR_VT and CG_VT processes, CO_2 captured from the syngas is directly vented to the atmosphere. In the SMR_CCS and CG_CCS processes considering high extent of CCS, a portion of the flue gas produced from the gas turbine or process furnaces also needs to be sent to the AGR unit for post-combustion CO_2 removal, and all CO_2 streams from the AGR unit are sent to the CO_2 compression section for sequestration.

Fig. 1. BFD of the direct CBTL plant with H₂ from shale gas (SMR_CCS/SMR_VT).

Fig. 2. BFD of the direct CBTL plant with H₂ from coal and biomass (CG_CCS/CG_VT).

2.1 Steady-state modeling approach

In this section, the steady-state modeling approach of the direct CBTL plants is discussed. The plant is divided into five well-defined sections - the liquefaction and product recovery section, the product upgrading section, the syngas production section, the acid gas removal and hydrogen recovery section,

and the combined cycle power island. Most of the unit operations are modeled as standard equipment items in Aspen Plus, while yield models are developed in Excel for liquefaction reactors and upgrading units based on the experimental or operational data available in the open literature. Aspen User2 blocks are used to connect Excel with Aspen Plus. In the process model, coal and biomass are specified as unconventional component, while syncrude are specified as either pseudo-components or petroleum assays defined by boiling point ranges. The compositions of Illinois No.6 coal, wood chip and Marcellus shale gas are given in Table 1 and Table 2 [48-50].

For all case studies, hydrogen, carbon and utility balances have to be satisfied and constrained by Eq. (1) to (3). In the liquefaction plant, H_2 is consumed due to liquefaction and hydrotreating while it is produced from gasification, steam reforming and catalytic reforming. The make-up H_2 requirement and purge rate of H_2 -rich recycle stream from the liquefaction and hydrotreating units are determined by the required H_2 partial pressure (P_{H_2}) and H_2 /solid or H_2 /oil ratio. Feed flowrates of shale gas and coal/biomass mixture to the syngas production section are determined by the hydrogen balance, as shown in Eq. (1). The entire gas oil column bottom produced in the product upgrading unit and a portion of the fuel gas (FG) produced in the entire plant are utilized as heating utilities in the furnaces. Eq. (2) is used to determine the percentage of the remaining fuel sent to the power island based on the utility balance. Eq. (3) is used to determine the amount of CO_2 to be captured.

$$H_{2,produced \text{ from SMR,POX,catalytic reforming}} = H_{2,consumed \text{ in liquefaction,hydrotreating}} \quad (1)$$

$$\frac{FG \times LHV_{FG} + Gas \text{ oil} \times LHV_{Gas \text{ oil}} - Q_{Process \text{ furnaces}}}{LHV_{FG}} = FG \text{ to gas turbine} \quad (2)$$

$$\frac{Carbon \text{ in products} + Carbon \text{ in captured } CO_2}{Total \text{ Carbon in the feedstock}} = Extent \text{ of CCS (90\%, base case)} \quad (3)$$

Table 1

Proximate and ultimate analysis of coal and biomass feedstock.

	Proximate analysis (dry basis)				Ultimate analysis (dry basis)					
	M	FC	VM	A	A	C	H	N	S	O
Coal	3.08	50.65	37.85	11.50	11.50	71.00	4.80	1.40	3.20	8.00
Biomass	9.58	16.55	82.51	0.94	0.94	48.51	6.17	0.12	0.04	44.22

Table 2

Composition of Marcellus shale gas (well 3).

Component	C ₁	C ₂	C ₃	CO ₂	N ₂
vol%	83.8	12.0	3.0	0.9	0.2

2.2. Liquefaction and product recovery

2.2.1. Catalytic two-stage liquefaction (CTSL) unit

In the CTSL unit, coal and biomass are mixed with hot recycle solvents in the slurry tank, preheated and then sent to two ebullated bed reactors in a close-coupled mode with recycled and make-up H₂ stream. [51-53] Because the heavy oil produced from the 2nd stage is recycled to form feed slurry and is fed back to the 1st stage, two stages are interrelated and treated as a single unit in this study [54]. A yield model is developed for the CTSL unit fed with coal and small amount of biomass. As mentioned in Section 1, biomass can promote DCL process under mild condition, while the synergistic effect gets reduced with the increasing temperature being comparatively negligible under the normal operating temperature of the DCL reactors [11,36-39]. Hence, in this study the interaction between coal and biomass is ignored because of the low percentage of biomass in the feedstock and high operating temperature and pressure, and therefore the yield of the coal biomass co-liquefaction reaction is considered to be a linear combination of the yields from the coal and biomass liquefaction reactions. The yield of liquids and their hydrocarbon distribution from the coal liquefaction reactors are estimated based on the operating data from the DCL proof-of-concept (POC) facility reported by HTI in 1995 [21]. Operating conditions in POC-01 Period 26, shown in Table 3, were recommended by HTI's study because of its higher efficiency and better operability, and therefore, are considered in our baseline study [21,51]. There is limited information in the open literature on direct biomass liquefaction using oil as the slurry medium and H₂ as the reduction gas. In this work, data from the Pittsburgh Energy Research Center (PERC) are used as baseline. In the process reported by the PERC, wood chips were fed to the reactor with the recycle oil serving as the solvent. The oil yield was about 45-55% of the dry wood with about 100% conversion of the wood [55-57]. It is also assumed that the elimination of oxygen from wood can occur by producing H₂O, CO and CO₂ [58]. Therefore, the yield of bio-oil and gases can be estimated by atom balance with the elemental analysis of bio-oil to be 81 wt% carbon, 10.2 wt% hydrogen and 8.8 wt% of oxygen as reported in the open literature [56,59]. These assumptions result in an estimated oil yield of 47% from the biomass liquefaction, which is consistent with the experimental data [56]. In order to simplify atom balance calculation in the yield model of coal/biomass co-liquefaction, syncrude is specified as pseudo-components in Aspen Plus, with the elemental composition of each crude cut calculated by a linear combination of the corresponding data of coal liquids reported by HTI and biomass liquids reported by PERC [21,56,59]. The yield model of the coal-biomass co-liquefaction process is developed in MS Excel

by applying atom balance for calculating H₂ consumption and the yield of gases (i.e. CO, CO₂, NH₃, H₂S, H₂O), since the heteroatoms in the coal and biomass are either converted into gases or contained in the liquids. For the base case with a biomass/coal weight ratio of 8/92, the calculated elemental composition of syncrude and the results from the reactor model are shown in Table 4 and Table 5.

Table 3

Operating conditions of the CTSL unit.

Variable	Value	Variable	Value
Reactor inlet pressure (MPa)	22.1	1 st stage temperature (°C)	407
Reactor outlet pressure (MPa)	20.7	2 nd stage temperature (°C)	432
Hydrogen partial pressure (P_{H_2} , MPa)	13.4	Solvent/feed ratio (wt/wt)	1.82

Table 4

Element analysis of raw syncrude (base case).

Crude cut	Average NBP (°C)	Specific gravity	Elemental composition (wt%)				
			C	H	O	N	S
IBP-177 °C	93	0.799	84.75	14.09	0.99	0.16	0.01
177-288 °C	232	0.924	86.92	11.33	1.54	0.20	0.02
288 -344 °C	315	0.975	87.89	10.05	1.84	0.20	0.02
344 -454 °C	399	1.012	88.63	9.93	1.17	0.21	0.04
454-FBP	540	1.097	88.78	8.11	1.10	0.52	1.45

Table 5

Outlet stream distribution of the coal/biomass CSTL reactors (base case).

Component	wt%	Component	wt%	Component	wt%
Coal	1.14	C ₁	0.57	288 - 344 °C	8.86
H ₂ O	4.06	C ₂	0.45	344 - 454 °C	45.92
H ₂ S	0.94	C ₃	0.47	454 °C - FBP	17.36
CO	0.18	C ₄	0.76	Char	0.03
CO ₂	0.69	IBP - 177 °C	5.57	Ash	3.45
NH ₃	0.43	177 - 288 °C	9.1		

2.2.2. Product recovery and inline hydrotreating

As shown in Fig. 3, the product from the CTSL reactors is first sent to the hot HP separator. The vapor product from the hot HP separator, consisting of H₂-rich light gases, most of the naphtha (IBP-177°C) and

a portion of the gas oil and solvent oil (177-454°C), is then sent to the inline hydrotreater for stabilization. The hydrotreated syncrude is sent to warm and cold HP flash vessels. The vapor product from the cold HP flash separation contains about 80-85% H₂ and therefore most of this H₂-rich stream is recycled back to the liquefaction reactor, while a portion of it is purged to maintain the P_{H_2} in liquefaction reactors. Liquid products from the warm and cold HP flash vessels are sent to the warm and cold LP flash vessels, respectively. The bottom product from the hot HP separator is de-pressurized and sent to the LP reactor liquid flash vessel where small amount of N₂ is used for stripping. The top product from the LP reactor liquid flash vessel is sent to the warm LP flash vessel while the top product from the warm LP flash vessel is sent to the cold LP flash vessel. Liquid products from the warm and cold LP flash vessels, mainly IBP-454°C syncrude, are sent to the atmospheric distillation column to be separated into light gases, light naphtha, heavy naphtha, gas oil, and liquefaction solvent. The bottom product from the LP reactor liquid flash vessel, a mixture of heavy oil and solid residues, is sent to the vacuum distillation column and the ROSE-SR unit for solid/liquid separation. The bottom product from the atmospheric distillation column, heavy vacuum gas oil (HVGO) from the vacuum distillation column and the deashed oil (DAO) from the ROSE-SR unit are sent to the recycle solvent tank for preparing coal/biomass slurry. Light naphtha, heavy naphtha, and gas oil from the atmospheric distillation column and light vacuum gas oil (LVGO) from the vacuum distillation column are sent to product upgrading units to produce gasoline, diesel and gas oil column bottom.

Fig. 3. Plant configuration of the liquefaction and product recovery section.

and then fed into the 1st stage settler with a solvent to vacuum column bottom weight ratio of 3 [60, 61]. The heavy phase from the 1st stage settler, containing 10-20 wt% of the liquefaction liquids along with deashing solvent and essentially all of the solids, is “let down” to the deashing solvent separator operated at atmospheric pressure [22,61]. The light phase from the 1st stage settler, which contains 80-90 wt% of the liquefaction liquids and deashing solvent, is heated and sent to the 2nd stage settler. In the 2nd stage settler, most of the solvent is recovered under supercritical condition as the decrease in density and solubility of the supercritical fluid with the increasing temperature is exploited for solvent separation in the 2nd stage settler. The light phase from the 2nd stage settler, containing mainly supercritical solvent, is cooled in a heat exchanger and then sent to the HP solvent tank for preparing recycle solvent. The heavy phase from the 2nd stage, containing mainly deashed oil and small amount of deashing solvent, is “let down” to another deashing solvent separator. A small portion of the deashing solvent is recovered from the two deashing solvent separators, which is cooled and condensed and sent to the deashing solvent feed tank and then pumped to the HP solvent tank. The DAO is recycled to the liquefaction reactor serving as H-donor solvent and is hydrocracked to improve the performance of liquefaction unit, while the residues is partially oxidized to syngas and shifted to hydrogen in order to reduce the external hydrogen demand of the whole liquefaction system. More information about the POX unit is provided in Section 2.4.2.

Fig. 4. Plant configuration of the ROSE-SR unit.

The approach to modeling the inline hydrotreater is the same as the liquefaction reactor [3]. With the elemental analysis of raw syncrude calculated from Section 2.2.1 and known elemental analysis of hydrotreated syncrude reported by HTI [21,51], the H₂ consumption of the inline hydrotreater is estimated by atom balance, assuming O, N and S in the syncrude are rejected by producing H₂O, H₂S and NH₃. Table 6 lists the elemental analysis of the hydrotreated syncrude obtained from the open literature. [21,51]. For the inline hydrotreater, the syncrude is specified as pseudo-components for the sake of

applying atom balance, while syncrude is specified as petroleum assay for other equipment items in the product recovery unit for better estimate of vapor-liquid equilibrium (VLE). For each cut specified in Table 4 and Table 6, true boiling point distillation curves are available in the open literature [21,56]. Peng-Robinson equation of state (EOS) is used as the thermodynamic model for the system [62]. Both atmospheric and vacuum distillation columns are modeled using PetroFrac block in Aspen Plus. The 1st stage and 2nd stage settlers in the ROSE-SR unit are modeled as component separators, using solids rejection efficiency and energy balance reported by HTI and assuming 88% and 80% solvent recovery in the light phases from the 1st and 2nd stage settlers, respectively [21,63]. Deashing solvent separators are modeled as flash separators. Table 7 and Table 8 summarize the operating conditions and design specifications of the key equipment items in the product recovery unit. Detailed specifications of the distillation columns can be found in the Appendix A.

Table 6

Elemental analysis of hydrotreated syncrude.

wt%	C	H	O	N	S
IBP-177 °C	85.54	14.05	0.01	0.01	0.00
177-288 °C	87.90	12.55	0.01	0.01	0.01
288-344 °C	88.30	11.97	0.01	0.02	0.01
344-454 °C	88.10	11.28	0.01	0.03	0.05

Table 7

Operating conditions of the product recovery unit.

Equipment	Pressure ⁽¹⁾ (bar)	Temperature ⁽²⁾ (°C)	Equipment	Pressure ⁽¹⁾ (bar)	Temperature ⁽²⁾ (°C)
Warm HP flash drum	172	232	Cold HP flash drum	170	40
LP reactor liquid flash drum	7.9	405	Warm LP flash drum	7.8	232
Atmospheric distillation tower	2.8	40/320	Cold LP flash drum	7.6	40
Vacuum distillation tower	0.1	65/305	1 st stage settler	55	300
Deashing solvent separator	1.0	325/270	2 nd stage settler	54.5	370

(1) Top pressure for all towers

(2) Top/bottom temperature for all towers

Table 8

Design specifications of the product recovery unit.

Equipment	Manipulated variable	Target	Value
Hot HP separator	Operating temperature	ASTM D86 FBP of the vapor product	370 °C
LP reactor liquid flash drum	Stripping N ₂ flowrate	Recovery of the 288-344°C syncrude in vapor	50%
Atmospheric distillation tower	Bottom flow rate of heavy naphtha stripper	ASTM D86 95vol% temperature of light naphtha	107 °C
	Bottom flow rate of distillate stripper	ASTM D86 95vol% temperature of heavy naphtha	187 °C
	Bottom flow rate of main column	ASTM D86 95vol% temperature of gas oil	376 °C
Vacuum distillation tower	Duty of top pump-around	First stage temperature	65 °C
	Sidestream flow rate of LVGO	ASTM D86 95vol% temperature of LVGO	376 °C
	Sidestream flow rate of HVGO	Recovery of 890-975°F crude in bottom	77.3%
ROSE-SR unit	Operating temperature of deashing solvent separators	Solvent recovery of deashing solvent separators	98%
	Heat duty of the heat exchanger between settlers	Inlet temperature of the first stage settler	300 °C

2.2.3. Heat integration in the liquefaction and product recovery section

In the direct CBTL plant, the coal/biomass slurry and recycled H₂ need to be pre-heated to a high temperature before being fed to the CTSL reactors, which results a considerable fuel consumption in the pre-heating furnaces. The product from the liquefaction reactor has to be cooled for separation. In the DCL baseline design reported by Bechtel/Amoco [51], the recycle H₂ is pre-heated by exchanging heat with the hot stream from the top of the hot and warm HP flash vessels. Even though exchange of heat between cold slurry feed and downstream fluid is not considered by Bechtel/Amoco, it is considered to reduce the duty of the preheat furnaces in the SRC-I, SRC-II and NEDOL processes [64-66]. In this study, a global heat integration analysis is considered for increasing the overall thermal efficiency. Aspen Energy Analyzer is used to design and optimize the heat exchanger network. The minimum temperature approach is set to be 10 °C. The forbidden matches between streams are specified to avoid operability problem such as that caused by large differential pressure and unexpected leakage during operation.

2.3. Product upgrading

One advantage of DCL process is that the products can be processed similar to traditional petroleum products without extensive renewal of current infrastructures [7]. Compared with typical petroleum oils, the DCL syncrude obtained from the two-stage liquefaction of bituminous coals is usually low in boiling range, low in hydrogen and high in oxygen, low in heteroatom contents and high in contents of cyclic compounds, and mainly composed of paraffins, naphthenes, and aromatics [7,9,67]. On the other hand,

bio-liquids usually contain high amount of oxygenates, such as cyclic ketones, alkyl-phenols, methoxy-phenols, naphthols, which can be converted to cyclohexane, alkyl-cyclohexane by hydrotreating [55,56,59]. Despite these differences, the syncrude produced in the direct liquefaction plant with low biomass/coal ratio is very similar to petroleum and can be processed through petroleum refining technologies, where hydroprocessing is a major technology [68].

In this study, a significant portion of the aromatics and heteroatom in the low boiling range oil is converted in the inline hydrotreating unit. The hydrotreated naphtha cut from the atmospheric distillation column is low in sulfur and nitrogen and has an octane number of about 70, which is an excellent feed for gasoline production [21]. Isomerization and catalytic reforming technologies are applied to increase the octane number of this naphtha cut. Because the entire gas oil cut from the CTSL reactors is not sent to the inline hydrotreater considering the operating flexibility and product quality [68], the gas oil recovered from the atmospheric distillation column needs to be sent to the gas oil hydrotreating unit for further upgrading. In this study, the yields of the upgrading units are obtained from correlations due to the limited information on the detailed feed composition. Utility consumptions in the isomerization and catalytic reforming units are estimated based on the plant throughput using the correlations available from Bechtel Corp. [69], while detailed models of the key equipment items are developed to estimate the utility consumption in the gas oil hydrotreating unit, as shown in Fig. 5.

In the isomerization unit, n-paraffins in the light straight run naphtha with low octane number are transformed on Pt catalyst into branched chains with the same carbon number but high octane number. The typical yield of isomerization unit used in this study is 0.35 wt% C₃, 2.39 wt% C₄ and 97.26 wt% C₅₊ with a research octane number (RON) of 83 [62]. The H₂/oil ratio in the feed is specified to be 0.14 wt% as reported by Bechtel Corp. [69]. Our study only considers low biomass/coal mix ratio, and most of the oxygenates is hydrotreated and converted to paraffins and naphthenes in the hydrotreater unit. Hence, the distribution of components in the hydrotreated naphtha from biomass/coal co-liquefaction is assumed to be 15 vol% paraffins, 65 vol% naphthenes and 20 vol% aromatics, which are similar to that of DCL naphtha [7,9,51]. A yield model, shown in Eq. (4) and (5), is used in this study to estimate the yield of H₂ and C₅₊ reformat from the feed composition (N+2A)_F and severity of catalytic reforming (RON_R), where N, A, and RON_R denote naphthenes (vol%), aromatics (vol%) and reformat RON, respectively [62,70,71]. Eq. (6) gives the relation between RON_R and aromatic vol% in the reformat (A_R vol%). Table 9 shows this model can provide a reasonable estimation of DCL liquid catalytic reforming process [72]. The motor octane number (MON) of reformat can be estimated by Eq. (7) [71,73,74].

$$C_{5+} (vol\%) = 142.7912 - 0.77033 \times RON_R + 0.219122 \times (N + 2A)_F \quad (4)$$

$$H_2 \text{ (wt\%)} = -12.1641 + 0.06134 \times C_{5+} \text{ (vol\%)} + 0.099482 \times RON_R \quad (5)$$

$$A_R \text{ (vol\%)} = 1.6857 \times RON_R - 92.994 \quad (6)$$

$$MON_R = 22.5 + 0.83RON_R - 20.0SG \quad (7)$$

Table 9

Validation of the yield model of the catalytic reforming unit.

Feed composition		Cases	RON _R = 94.2		RON _R = 97.7	
			Experimental	Model	Experimental	Model
N (vol%)	64.4	C ₅₊ (vol%)	92.5	91.4	91.1	88.7
A (vol%)	16.0	H ₂ (wt%)	2.50	2.81	3.00	3.00
		A _R (vol%)	65.8	65.8	71.7	71.7

Fig. 5. Plant configuration of the gas oil hydrotreating unit.

The main purpose of the inline hydrotreater is to stabilize the liquefaction product, while the diesel cut from the inline hydrotreater does not necessarily satisfy the diesel specification [75]. Hence, the gas oil hydrotreating unit is required to produce on-spec diesel. In the gas oil hydrotreating unit, the raw gas oil is pre-heated by the hot hydrotreated gas oil and then sent to hydrotreater with heated H₂ stream. H₂-rich stream is recovered from the HP flash drum and recycled back to the reactor. The liquid from the LP flash vessel is sent to a distillation column followed by a diesel stabilizer to separate the hydrotreated product into light gas, heavy naphtha, diesel (177-343°C), and gas oil column bottom (343-454°C). The approach

to modeling the gas oil hydrotreating reactor is the same as the inline hydrotreating reactor as described in Section 2.2.2. The gas oil hydrotreater is operated at 180 bar and 350 °C with a pressure drop of 7 bar, a temperature increase of 83 °C, P_{H_2} of 124 bar, and a liquid hourly space velocity of 1 h⁻¹. It can be noted that these specifications are similar to that reported by Bechtel/Amoco [51]. PetroFrac model in Aspen Plus is used to simulate the distillation column and the diesel stabilizer. Peng-Robinson EOS is used as the thermodynamic model. A ‘design spec’ in Aspen Plus is set up to satisfy the ASTM D86 90 vol% specification of diesel (ASTM D975) by manipulating the bottom flowrate of the gas oil distillation column.

2.4. Syngas production

Significant amount of H₂ is required in the direct CBTL plant. The first step to H₂ production is to generate the syngas from fuels, such as natural gas, shale gas, coal, biomass and liquefaction residues. Then the raw syngas is sent to a high temperature shift (HTS) reactor and a low temperature shift (LTS) reactor, where H₂ concentration in the syngas is increased by the water gas shift reaction. In order to reduce H₂ production from external fuels, liquefaction residues from the ROSE-SR unit is used to produce syngas in the POX unit by gasification. Additional H₂ is produced by shale gas steam reforming in the SMR_CCS and SMR_VT processes, or by coal/biomass/residue co-gasification in the CG_CCS and CG_VT processes. Throughput of the SMR or CG unit is determined by the overall hydrogen balance, as shown in Eq. (1).

2.4.1. Shale gas steam methane reforming (SMR)

In the SMR unit, as shown in Fig. 6, the shale gas is compressed, heated by the steam reformer outlet stream and sent to an adiabatic pre-reformer, where heavier hydrocarbons are converted to methane and syngas through Reactions 8-10. The outlet stream of the pre-reformer is reheated by exchanging heat with the steam reformer outlet stream and then sent to the steam reformer, where most of the methane is converted to syngas by Reactions 9-11. The heat required by the highly endothermic in the steam reformer is produced in the reformer furnace by burning fuel gas taken from the plant fuel gas header. The product from the steam reformer is cooled and sent to HTS and LTS reactors. The syngas from the shift reactors is cooled by generating HP, intermediate pressure (IP), and LP steams. The syngas from the LP steam generator is sent to a condenser to remove most of the water. The hot flue gas from the reformer furnace is sent to a series of heat exchangers to generate super-heated HP steam used for steam reforming. In this study, the pre-reformer and steam reformer are modeled as equilibrium reactors [76]. The HTS and LTS reactors are modeled as plug flow reactors (PFRs) with kinetics obtained from the open literature [48]. The reformer furnace is modeled as ‘RStoic’ reactor in Aspen Plus with specified combustion

reactions. The Peng-Robinson EOS is used as the thermodynamic model of the syngas side, while IAPWS-95 is used for the steam side. Operating conditions of all reactors and heat exchangers can be found in Table 10.

Table 10

Operating conditions of the shale gas SMR unit.

Flowsheet element	Parameter	Value
Shale gas feed	Temperature/pressure	20 °C/20 bar
Compressor	Pressure	30 bar
Steam feed	Temperature/pressure	510 °C/30 bar
Preheaters	Cold stream outlet temperature	510 °C/650 °C
Adiabatic pre-reformer	Pressure drop	1.7 bar
Steam reformer	Temperature/pressure drop	815 °C/1.7 bar
HP/IP/LP steam evaporator	Hot stream outlet temperature	350 °C/215 °C/143 °C
Cooler	Hot stream outlet temperature	40 °C
Feed water heater/economizer	Cold stream outlet temperature	120 °C/227 °C

Fig. 6. Plant configuration of the shale gas SMR unit.

2.4.2. Residue partial oxidation (POX) and coal/biomass/residue co-gasification (CG)

In the SMR_CCS and SMR_VT processes, the hot liquefaction residue from the ROSE-SR unit is gasified in the POX unit as shown in Fig. 7. The residue containing mainly 510 °C plus solid, ash and unconverted coal/biomass is sent to an entrained flow gasifier with O₂ obtained from the air separation unit (ASU) and steam obtained from the heat recovery and steam generation (HRSG) section. In the CG_CCS and CG_VT processes, the liquefaction residue is grinded and mixed with pre-processed coal/biomass and slurry water before being fed to the entrained-flow gasifier. In all cases, the raw syngas from the gasifier is cooled and then sent to the HTS and LTS reactors to convert CO into H₂ similar to the SMR unit. Flow rate of the shift steam to the HTS reactor is manipulated to achieve 95% of overall syngas CO conversion in the two stage water gas shift unit.

Here the gasifier is modeled as an equilibrium reactor, while the HTS and LTS reactors are modeled as PFR reactors. More details about the water gas shift reactors and co-gasifier can be found in our previous publications [2,39]. The entrained-flow gasifier fed only with the liquefaction residue is operated at 56 bar and 1315 °C with a steam to residue ratio of 0.4 and a carbon conversion of 99% similar to the data available in the open literature [23,27,28,77-79]. The amount of oxygen fed into the gasifier is manipulated to satisfy the energy balance. Simulation results from the residue gasification show that the H₂ yield of the residue POX unit is about 10.2 wt% of the liquefaction residue [21,27].

Fig. 7. Plant configuration of the POX unit.

2.5. Acid gas removal (AGR), H_2 recovery, and CO_2 compression units

The fuel gas released from the liquefaction, product recovery, and upgrading units contains H_2S , which needs to be removed before being utilized in process furnaces or gas turbines. MDEA is considered to be the desired solvent for removing H_2S from fuel gas in presence of CO_2 [75]. The general configuration of

a chemical absorption process is shown in Fig. 8. The absorber is operated at 38 °C and 20 bar [75]. The ‘RadFrac’ model in Aspen Plus with rate-based calculations is used to simulate the absorber and stripper using the kinetics and thermal model available in the open literature [80,81].

Fig. 8. Schematic of the amine-based chemical absorption process.

For all four process configurations, the gas oil column bottom and fuel gas produced in the process are sent to either process furnaces or a gas turbine, which eventually get converted to CO₂, as discussed in Section 2.1. The major CO₂ emission of the system is from H₂ production units, process furnaces, and the gas turbine. The H₂-rich syngas stream from the POX/CG unit contains not only a significant amount of CO₂, but also a small amount of H₂S. In order to recover pure H₂, those streams are sent to the AGR unit to selectively remove CO₂ and H₂S, no matter if CCS is considered or not. The removed CO₂ is vented or sent to the CO₂ compression unit, depending on whether CCS is considered and the targeted extent of CCS. If high extent of CCS is considered, additional CO₂ needs to be captured from the gas turbine flue gas using post-combustion CO₂ capture technologies, and the amount is determined by carbon balance as shown in Eq. (3). In this study, physical absorption is considered for streams with high P_{CO_2} , while chemical absorption is considered for streams with intermediate or low P_{CO_2} .

For the physical absorption process, the acid gas partial pressure is the main driving force for absorption and has a significant effect on the process efficiency [2]. For the chemical absorption process, the acid gas partial pressure does not have much effect. For all four configurations, the dual-stage Selexol technology is applied to selectively remove H₂S and the majority of CO₂ from the HP syngas obtained from the POX/CG unit. In the SMR_CCS and SMR_VT processes, the extent of CO₂ capture is decided to make the P_{CO_2} of the clean syngas from the HP CO₂ absorber in the Selexol unit to be the same as P_{CO_2} of the IP syngas from the shale gas SMR unit. Then the syngas from the HP CO₂ absorber is mixed with the syngas from the SMR unit, and sent to an IP CO₂ absorber unit using chemical solvent to further remove CO₂. If high extent of CCS is considered, the amount of CO₂ removed in the IP CO₂ absorber unit is determined such that the treated gas P_{CO_2} is the same as the flue gas P_{CO_2} , and this treated gas is mixed with the gas

turbine flue gas and sent to a LP CO₂ absorber using chemical solvent to achieve the targeted extent of CCS. In the CG_CCS and CG_VT processes, the dual-stage Selexol technology is considered to treat the raw syngas obtained from the POX/CG unit, while an additional chemical absorption unit is required to treat the flue gas obtained from the CG_CCS process.

The plant configuration of the dual-stage Selexol unit can be found in our previous publication [48]. The configuration of the chemical absorption unit is similar to Fig. 8, where multiple absorption columns operating at different pressure is considered, since the syngas and flue gas are available at different pressures and cannot be mixed. Rich solvents from different absorbers are mixed first, and then sent to the lean/rich exchanger and then to the strippers for solvent regeneration. Absorbers in the Selexol unit are modeled by the 'RadFrac' block with equilibrium-stage modeling using the PC-SAFT EOS. MDEA/PZ and MEA are the two chemical solvents considered in this study. All absorbers and strippers in the chemical absorption unit are modeled and sized by the 'RadFrac' block with rate-based modeling using ELECNRTL EOS. Parallel trains are considered if the column diameter exceeds 10 meter. The modeling approach and reaction kinetics of the MDEA/PZ/CO₂ system and the MEA/CO₂ system are described in our previous publications [2].

Removed H₂S stream from the Selexol unit is mixed with the H₂S stream from the MDEA unit and then sent to the Claus unit for conversion to elemental sulfur. The extent of H₂S removal is computed by comparing the gas turbine sulfur tolerance and the SO₂ emission regulation (40 CFR 60.42b) and selecting the lower value. CO₂-rich streams at different pressure levels are vented or sent to different stages in a split-shaft multistage CO₂ compressor, determined by the targeted extent of CCS. The clean syngas from the AGR unit is sent to the PSA unit for producing pure H₂. The number of beds required for PSA units has been approximated by using the study from Bechtel [70]. Plant configuration and modeling approach of the Claus and CO₂ compression units can be found in our previous publications [2,48]. The PSA unit is modeled as a component separator in Aspen Plus while designing it using the approach detailed in our previous publication [3].

2.6. Combined cycle power island

Most of the flue gas and waste heat produced in the product recovery and upgrading unit, the POX/CG unit and the SMR unit are utilized in the combined cycle power island. The steam generator in the combined cycle power island operates at three pressure levels and not only produces steam to generate electricity but also provides IP and LP steams needed in the POX/CG, product upgrading, and AGR units, as shown in Table 11. The modeling approach of the combined cycle plant and its pressure levels is the same as our previous study [3,48].

Table 11

Configuration of the HRSG section and steam header.

Steams	Pressure (bar)	Temperature (°C)	From	To
HP steam to ST	114	510	POX, GT, SMR	ST HP section
IP steam to ST	25	510	POX, SMR, HCR (through reheater)	ST IP section
LP steam to ST	4	140	GTFG, HCR, SMR POX, HCU	ST LP section
HP steam to header	57		ST HP section	POX, HCU
IP steam to header	9		ST IP section	AGR
LP steam to header	4		ST LP section	AGR, HCU

3. Results and discussions

For the base case conditions, the biomass/coal weight ratio, the plant capacity and the extent of CCS are set to be 8/92 (dry basis), 10000 bbl/day, and 90% (for SMR_CCS and CG_CCS). Here, the extent of CCS is defined by Eq. (3). The following studies are conducted for analyzing the feasibility of applying CCS and introducing shale gas and biomass into the traditional DCL processes. First, heat integration is applied to reduce the utility consumption, and the AGR unit is designed depending on the carbon balance. Then the material and energy balance of the direct CBTL processes is obtained based on the process model of the entire system and compared with the data reported in the open literature for validation. Based on the validated process model, sensitivity studies are conducted by changing the biomass/coal ratio, CCS solvent and the extent of CCS with different hydrogen sources. Finally, the direct CBTL process is compared with the indirect CBTL processes.

3.1. Heat integration in the liquefaction and product recovery section

Temperature changes in key streams in the liquefaction and product recovery section are shown in Fig. 9, where the cold streams are shown as bars filled with upward diagonals and the hot streams are shown as bars filled with downward diagonals. 25 heat exchangers, steam generators, heaters and coolers are designed by Aspen Energy Analyzer using pinch analysis. Table 12 lists the forbidden and matched hot and cold streams in the heat exchanger network design. Stream numbers mentioned in Fig. 9 and Table 12 are shown in Fig. 3. With the new design, the coal/biomass slurry is heated to about 350 °C by hot liquefaction product before entering the preheat furnace, while the heat duty of the preheat furnace is reduced by about 52%. These results are similar to the NEDO's DCL experience, where the coal slurry is

preheated to 340 °C in the heat exchangers and the heat duty of the furnace is reduced by about 60% [82,83].

Table 12

Forbidden and matched hot and cold streams in the heat integration.

	4	5	6	7	8	9	10
1	✓	✓	✓	✗	✗	✓	
2			✓	✓	✓	✗	✗
3	✗	✓	✗				✓

✗ - the hot and cold streams are not allowed to exchange heat

✓ - recommended match of hot and cold streams by Aspen Energy Analyzer

Fig. 9. Temperature chart of the liquefaction and product recovery section.

3.2. Carbon balance and design of the CO₂ removal system

Based on the models developed for the liquefaction and product recovery section and the syngas production section, carbon balances of the direct CBTL plants are computed and shown in Table 13. In the SMR_CCS and SMR_VT processes, 53.9 % of the carbon in the feedstock is converted to gasoline and diesel. In the CG_CCS and CG_VT processes, it is only 43.5 % because the H/C ratio in coal and biomass is less than that in shale gas or natural gas, resulting in less efficiency in the H₂ plant. In order to achieve 90% carbon capture (considered to be high level CCS in this study), another 36.1 % of carbon in the feedstock (78.3 % of CO₂ generated) needs to be captured by the CO₂ capture process in the SMR_CCS process, and another 46.5 % of carbon in the feedstock (82.3 % of CO₂ generated) needs to be

captured in the CG_CCS process. Based on the design procedure described in Section 2.5, Table 14 through Table 16 list the main CO₂ sources ordered by P_{CO_2} and flowrate, preliminary selection of absorption technologies, operating conditions and targeted extent of CO₂ removal for each stream.

Table 13

Carbon balance of the direct CBTL plants⁽¹⁾.

Carbon in (%)	SMR	CG	Carbon out (w/o utility, %)	SMR	CG	Carbon out (w/ utility, %)	SMR	CG
Coal	77.4	94.6	Gasoline	11.4	9.4	Fuel	53.9	43.5
Biomass	4.6	5.4	Diesel	41.2	34.1	POX/CG	10.7	38.8
Shale gas	18.0		Fuel oil	7.0	5.8	SMR	19.2	
			Fuel gas	10.5	11.9	Gas turbine	9.5	12.1
			H ₂ plants	29.9	38.8	Others	6.7	5.6

(1) Fuel gas and fuel oil produced from gas oil column bottom are treated as utility in the case with (w/) utility, but not in the case without (w/o) utility

Table 14

CO₂ emission and sources in the SMR_CCS and SMR_VT processes.

Source	Carbon (%)	CO ₂ (mol%)	P_{CO_2} (bar)	CO ₂ removal	SO ₂ removal	Technology	CO ₂ removal (%)
POX (syngas)	11	36	18.5	Yes	Yes	Selexol, Amine	83.6 98.3
SMR (syngas)	12	19	3.9	Yes	No	Amine	98.3
SMR furnace (flue gas)	7	7	0.07	Yes	No	Amine	86.3
Gas turbine (flue gas)	9	3	0.03	Yes ⁽¹⁾	No	Amine	66.5
Others (flue gas)	8			No	No	N/A	

(1) Not considered in the SMR_VT processes

Table 15

CO₂ emission and sources in the CG_CCS and CG_VT processes.

Source	Carbon (%)	CO ₂ (mol%)	P_{CO_2} (bar)	CO ₂ removal	SO ₂ removal	Technology	CO ₂ removal (%)
CG (syngas)	39	40	21.6	Yes	Yes	Selexol	95.0
Gas turbine (flue gas)	12	3	0.03	Yes ⁽¹⁾	No	Amine	69.8
Others (flue gas)	6			No	No	N/A	

(1) Not considered in the CG_VT processes

Table 16

Configurations and operating conditions of the AGR units.

Column	Pressure (bar)	Sour gas from	Clean gas to
HP CO ₂ absorber	50.5	POX/CG (syngas)	H ₂ recovery
IP absorber ⁽¹⁾	20.7	SMR (syngas) and/or Selexol CO ₂ absorber (syngas)	H ₂ recovery
LP absorber ⁽²⁾	1.0	Gas turbine (flue gas) and/or SMR furnace (flue gas)	Stack

(1) Not considered in the CG_CCS and CG_VT processes

(2) Not considered in the SMR_VT and CG_VT processes

Based on the process model developed in Aspen Plus, the utility consumption and cost of the CO₂ removal and compression units are calculated and shown in Table 17 for all four configurations with a plant capacity of 10000 bbl/day. For the SMR_CCS (base case) process, two different amine solvent are considered- MEA and MDEA/PZ. Utility consumptions in the Selexol unit, the amine unit and the CO₂ compression unit are similar to the data available in the open literature [2, 46-48]. The reboiler duty of the solvent stripper is 3590 kJ/kg if MEA is used as a solvent in the SMR_CCS process. This duty can be reduced by 14% if using MDEA/PZ as the solvent [2]. Hence, MDEA/PZ is selected for removing CO₂ from IP and LP CO₂-containing streams in all case studies and sensitivity studies. Table 17 also indicates that utility costs for the CG_CCS and SMR_CCS processes are similar. The CCS utility cost for the CG_VT process is lower than the SMR_VT process, even though more CO₂ needs to be captured in the CG_VT process due to the lower carbon efficiency. The reason is that P_{CO_2} of most CO₂-containing streams to be sent to the AGR unit is higher in the CG_CCS and CG_VT processes than that in the SMR_CCS and SMR_VT processes, as shown in Table 14 and 15. As a result, in the CG_CCS and CG_VT processes, most of the CO₂ is captured by the Selexol unit instead of the amine unit resulting in lesser utility penalty for CO₂ capture. The study shows that the CCS technology plays a key role in the overall utility consumption in these plants. While this paper considers only solvent-based technologies due to their maturity, novel technologies for CO₂ capture such as those based on solid sorbents or membranes can be potentially evaluated as alternatives for reducing the penalty for CO₂ capture.

Table 17

Utility consumptions in and costs for the CCS units.

Process	SMR_CCS	SMR_CCS	SMR_VT	CG_CCS	CG_VT
CO ₂ captured (kmol/hr)	2660	2660	1733	4245	3367
Amine solvent	MEA	MDEA/PZ	MDEA/PZ	MDEA/PZ	N/A

Utility consumptions (electricity (MW)/IP steam (GJ/hr)/LP steam (GJ/hr)/cooling water (GJ/hr))					
Selexol unit	1.98/3/0/57	1.98/3/0/57	1.98/3/0/57	8.32/29/0/255	8.32/29/0/255
Amine unit ⁽¹⁾	0.94/0/309/389	0.92/0/297/377	0.34/0/78/77	0.46/0/229/343	0/0/0/0
Compression	9.59/0/0/48	9.59/0/0/48	0/0/0/0	11.58/0/0/61	0/0/0/0
Total	12.5/3/309/494	12.5/3/297/482	2.3/3/78/134	20.4/29/229/659	8.3/29/0/255
Cost ⁽²⁾ (\$/h)	5077	4913	1265	4919	993

(1) If high extent of CCS is considered, flue gas needs to be cooled before sending it to the amine system. The extra cooler is included in the amine unit.

(2) Costs of electricity, IP steam, LP steam and cooling water are assumed to be \$16.8, \$14.19, \$13.28 and \$0.354 per GJ [84].

3.3. Material and energy balance and model validation

Using the steady-state process model developed in Aspen Plus[®] and the design of the AGR unit shown in Section 3.2, material and energy balances are computed for all four configurations. For the base case, SMR_CCS, the flow rate of the key species in the main streams numbered in Fig. 1 can be found in Appendix B. Due to the limited information on applications of CCS technologies for DCL processes, simulation results are only validated for the SMR_VT and CG_VT processes. The utility consumption in CCS related facilities is validated separately in Section 3.2. It is generally accepted that the DCL processes without CCS usually have a thermal efficiency between 60% and 70% [75]. As shown in Table 18, results from our study are in-between the values reported by HTI (73.4%) and Shenhua (59.8%) and seem reasonable [1, 21 54, 85]. The differences are mainly due to different types of coal, sources of hydrogen and process utilities. The carbon and hydrogen content varies with the types of coal, which leads to different hydrogen requirement for liquefaction. Because of the different H/C ratio in coal and shale gas, the hydrogen production efficiency is very different between the coal gasification process and shale gas steam reforming process. Due to the difference in heating value and conversion efficiency of different type of energy sources, types of power and fuel source also affect the overall thermal efficiency of the direct CBTL processes. Detailed material and energy balances for all four configurations can be found in Table 19, which indicates that the thermal efficiency of the direct CBTL plant can be significantly increased by producing hydrogen from shale gas. Application of CCS will reduce the thermal efficiency by 2.2% if H₂ is produced from steam reforming or 2.1% if H₂ is produced by gasification, which is similar because the penalty of CCS is similar as discussed in Section 3.2. It can be concluded from Table 19 that utilization of shale gas or natural gas in the DCL process can increase the competitiveness of this technology, if shale gas or natural gas is available at lower price within reasonable transportation distance.

Table 18

Comparison between the simulation results and data in the open literature.

Process	SMR_VT	CG_VT	HTI design ⁽¹⁾	Modified HTI design ⁽²⁾	Bechtel/Amoco design ⁽³⁾	Modified Bechtel/Amoco design	Shenhua design
Reference			[29]	[29]	[1]	[1]	[85]
Biomass (wt %)	8	8	0	0	0	0	0
Hydrogen source	Shale gas	Coal/biomass	Natural gas	Coal	Coal	Coal	Coal
Power and fuel source	Fuel gas ⁽⁴⁾	Fuel gas ⁽⁴⁾	N/A	N/A	Natural gas	Coal	Coal
Efficiency (HHV, %)	66.5	62.1	73.4	70.9	61.6	59.0	59.8

(1) In the original HTI design, utility consumptions are not considered during the efficiency calculation.

(2) It is assumed that the effective thermal efficiency is 57.5% on HHV basis for producing H₂ from coal gasification. [1]

(3) Estimations are based on the HTI technology for liquefaction, while utility consumptions are considered.

(4) Fuel gas is generated insider plant mainly from the liquefaction unit and product upgrading units.

Table 19

Material and energy balances of the direct CBTL plant (HHV basis⁽¹⁾).

Process	SMR_CCS	SMR_VT	CG_CCS	CG_VT
Energy inputs				
Coal, tonne/hr (GJ/hr)	100.1 (2962)	100.1 (2962)	151.4 (4479)	151.4 (4479)
Biomass, tonne/hr (GJ/hr)	9.3 (163)	9.3 (163)	14.1 (247)	14.1 (247)
Shale gas, tonne/hr (GJ/hr)	21.6 (1105)	21.6 (1105)	N/A	N/A
Energy outputs				
Gasoline, bbl/day (GJ/hr)	2443 (595)	2443 (595)	2443 (595)	2443 (595)
Diesel, bbl/day (GJ/hr)	7557 (1936)	7557 (1936)	7557 (1936)	7557 (1936)
Net power (MW)	52.4	77.8	84.5	111.9
Thermal efficiency (%)	64.3	66.5	60.0	62.1

(1) HHVs of gasoline and diesel are set to be 5.84 and 6.15 GJ/bbl [1].

3.4. Effects of the biomass to coal mix ratio

In this study, three biomass/coal weight ratios are investigated. The upper bound of biomass/coal weight ratio is set to be 20/80, because the capacity of BTL or CBTL plants is constrained due to the high transportation cost, low energy density and limited long-term availability of biomass.[16,17] Table 20 and

Table 21 show that the thermal efficiency and carbon efficiency of the direct CBTL plant keep increasing for both SMR_CCS and CG_CCS processes, as more biomass is added to the liquefaction reactor. Even though H₂ consumption in the hydrotreating processes increases with the biomass/coal ratio due to the higher oxygenates contents, overall H₂ consumption in the direct CBTL plant decreases with the biomass/coal ratio, because the higher H/C ratio in the biomass reduces the H₂ consumption in the main liquefaction reactor more significantly. As a consequence, an increase in the biomass/coal ratio decreases the amount of shale gas or additional coal and biomass required for H₂ production, leading to an increase in the overall carbon efficiency and a decrease in the amount of CO₂ needed to be captured to achieve overall 90% carbon capture. With less CO₂ captured, less steam and electricity are consumed by the CCS facilities. Hence, the overall thermal efficiency of the CBTL plants is increasing with the biomass/coal ratio for both SMR_CCS and CG_CCS processes. Even though the simulation results shows that adding biomass to the traditional DCL process can increasing the process efficiency and reduce CO₂ emission, it should be noted that the overall cost of biomass and the capital cost of the pre-processing unit is usually higher than coal due to the lower energy density. [4] To decide whether to introduce biomass and what biomass/coal ratio to use, other than efficiency calculation shown here, additional studies such as techno-economic analysis, life-cycle analysis and biomass logistic analysis are required. [17]

Table 20

Effects of the coal biomass mix ratio (SMR_CCS, 10k bbl/day).

Biomass/coal (wt/wt)	8/92	15/85	20/80
Coal (tonne/hr)	100.1	90.1	84.2
Biomass (tonne/hr)	9.3	17.6	22.7
Shale gas (tonne/hr)	21.6	20.7	20.3
Thermal efficiency (% , HHV)	64.3	66.5	67.6
Total H ₂ consumption (% daf feed)	8.61	8.24	8.05
Liquefaction H ₂ consumption (% daf feed)	6.70	6.20	6.00
Carbon efficiency (%)	53.9	56.4	57.6
CO ₂ captured (kmol/hr)	2660	2366	2240

Table 21

Effects of the coal biomass mix ratio (CG_CCS, 10k bbl/day).

Biomass/coal (wt/wt)	8/92	15/85	20/80
Coal (tonne/hr)	151.4	138.8	132.0
Biomass (tonne/hr)	14.1	26.8	35.4
Thermal efficiency (% , HHV)	60.0	61.5	62.1
Total H ₂ consumption (% daf feed)	8.61	8.24	8.05

Liquefaction H ₂ consumption (% daf feed)	6.70	6.20	6.00
Carbon efficiency (%)	43.5	45.1	45.6
CO ₂ captured (kmol/hr)	4245	3959	3852

3.5. Effects of the extent of CCS

As mentioned earlier, CCS is not considered in the SMR_VT and CG_VT processes, where CO₂ is removed from the syngas for hydrogen purification and directly vented to the atmosphere. If the concept of carbon tax or other potential GHG emission related regulation is implemented, the CCS facility will be a necessary part of those alternative fuel production processes. The extent of CCS will be determined by local regulations if applicable. As the penalty of CCS does not increase linearly with the extent of CCS, it is necessary to redesign the process appropriately while evaluating effects of different level of CCS. For the SMR_CCS and CG_CCS processes, effects of low and high extent of CCS are studied. If low extent of CCS is considered, the removed CO₂ from the syngas is sent to the CO₂ compressor for sequestration, and no additional CO₂ needs to be removed from the flue gas. On the other hand, when high extent of CCS is considered in the SMR_CCS and CG_CCS processes, additional CO₂ is captured from the flue gas and sent to the CO₂ compressor along with the CO₂ captured from the syngas for being sent to the CO₂ pipeline. Table 22 and 23 show the effect of the extent of CCS on the thermal efficiency and CO₂ emission with different biomass/coal ratios and hydrogen sources. It is observed that the CO₂ emission of the direct CBTL plant with the hydrogen produced from the shale gas can be reduced by more than half with the thermal efficiency reduced by only 0.5%, if low extent of CCS is considered. On the other hand, high extent of CCS will reduce the thermal efficiency by another 1-1.5% because of the higher penalty of post-combustion CO₂ capture facilities. The difference between low and high extent of CCS is higher in direct CBTL plants with hydrogen produced from gasification, because most of the CO₂ is generated in the gasification unit with higher partial pressure, and therefore the Selexol technology that has lower penalty than the amine-based technologies can be applied for CO₂ capture. It is also noticed that with the increasing biomass/coal ratio for both cases, the CCS penalty is reduced, because less CO₂ needs to be captured.

Table 22

Effects of the extent of CCS (SMR_CCS and SMR_VT).

Biomass/coal (wt/wt)	8/92			20/80		
Extent of CCS	High	Low	No	High	Low	No
CO ₂ emission (kg CO ₂ /GJ product)	12.0	26.3	53.2	11.5	21.9	47.2
Thermal efficiency	64.3	66.0	66.5	67.6	68.7	69.2

(HHV, %)

Table 23

Effects of the extent of CCS (CG_CCS and CG_VT).

Biomass/coal (wt/wt)	8/92			20/80		
Extent of CCS	High	Low	No	High	Low	No
CO ₂ emission (kg CO ₂ /GJ product)	14.3	27.3	77.4	13.8	23.5	72.7 ⁽¹⁾
Thermal efficiency (HHV, %)	60.0	61.2	62.1	62.1	63.1	63.6

(1)The CO₂ emission from the CG_VT process with low biomass/coal ratio is 72.7 kg CO₂ per GJ product, about 0.5 tonne/bbl oil, which is similar to the data reported by Shenhua [7].

3.6. Direct CBTL plants vs indirect CBTL plants

ICL and DCL are two commercially proven but very different approaches to produce transportation fuels from coal. The performance of the direct and indirect CBTL plants with a biomass/coal weight ratio of 8/92 is compared in this section, based on the detailed plant-wide models developed in this study and our previous studies [2, 3]. Table 24 shows that the CO₂ emission from the indirect CBTL plant is much higher than the direct CBTL plant, while the thermal efficiency is much lower. That is because more carbon in the feedstock is converted to fuels instead of CO₂ in the direct liquefaction processes. Table 24 also indicates that the comparative CCS penalty is less in the indirect CBTL plant with high extent of CCS, because most of the CO₂ is produced in either gasification or Fisher-Tropsch unit and is available at higher partial pressure. In addition, no CO₂ needs to be removed from low pressure flue gas in the indirect approach. Even though the direct CBTL plant, especially with shale gas utilization, is superior to the indirect CBTL plant in terms of carbon and thermal efficiency, it should be noted that a detailed techno-economic analysis including assessment of availability of shale gas, in particular, is needed for fair comparison and final decision on commercial application.

Table 24

Performance of the direct and indirect CBTL plants.

Process	Indirect		Direct			
Hydrogen source	N/A		Shale gas		Coal/biomass	
Carbon efficiency (%)	36.4		53.9		43.5	
Extent of CCS	High	No	High	No	High	No
Thermal efficiency (HHV, %)	46.6	48.0	64.3	66.0	60.0	62.1

CO ₂ emission (kg CO ₂ /GJ product)	18.9	118.6	12.0	53.3	14.3	77.4
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4. Conclusions

Plant-wide models of direct CBTL plants with four different configurations are developed to analyze the effect of shale gas utilization and CCS on the plant performance. Utility consumption in the liquefaction and product recovery section can be reduced by 52% through heat integration. The AGR unit is designed based on the carbon balance and the CO₂ partial pressure. Simulation results are validated by comparing with the data available in the open literature. The process model shows that the carbon efficiency of the direct CBTL plant without shale gas utilization is 43.5%, which is 7.1% higher than the indirect CBTL plant with a biomass/coal weight ratio of 8/92. The carbon efficiency can be increased to 53.9% if shale gas is utilized for hydrogen production. It is also observed that the direct CBTL plant with hydrogen produced from the shale gas has the highest thermal efficiency, 66.5% without CCS and 64.3% with high extent of CCS, while the indirect CBTL plant has lower thermal efficiency because of its poor carbon efficiency. Carbon and thermal efficiencies of the direct CBTL plant are found to increase with the biomass/coal ratio regardless of the hydrogen source, because the higher H/C ratio in biomass than in coal reduces hydrogen consumption in the liquefaction unit. Sensitivity studies on the extent of CCS show that the penalty per unit of CO₂ capture increases with the extent of CCS, because it costs more utility to capture CO₂ from low pressure sources. Similarly, utility consumption in the CCS facilities in the direct liquefaction plant is higher than in the indirect liquefaction plant with high extent of CCS, due to CO₂ capture from the low pressure flue gas. In general, the direct CBTL plant with shale gas utilization has the best performance in terms of carbon and thermal efficiency. In closing, we would like to note this study has mainly focused on process systems analysis, but for selecting the optimal process technology and process configuration, other studies such as optimization, techno-economic analysis, and life-cycle analysis need to be conducted where the process model developed in this work can be leveraged.

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Appendix A. Design of the distillation columns

Specifications of the atmospheric and vacuum distillation columns in the product recovery section are listed in Table A.1 to Table A.4 [86,87].

Table A.1

Specifications of the atmospheric distillation column.

Specifications	Value
Number of trays	
Main column	29
Heavy naphtha side-stripper	5
Distillate side-stripper	5
Locations	
Feed to main column (Furnace)	26
Stripping steam to main column (Above stage)	30
Heavy naphtha side-stripper draw and return	15, 14
Distillate side-stripper draw and return	24, 23

Table A.2

Operating conditions in the atmospheric distillation column.

Operating Condition	Value
Main Column	
Condenser temperature	37.8 °C
Overhead pressure	240 kPa
Pressure drop per tray	1.38 kPa
Feed furnace fractional overflash	3.2 %LV
Bottom product/feed	0.62 kg/kg
Stripping steam/bottom product	4.54 kg/bbl
Side-strippers	
Stripping steam/heavy naphtha	2.27 kg/bbl
Stripping steam/diesel	2.27 kg/bbl

Table A.3

Specifications of the vacuum distillation column.

Specification	Value
Total number of trays	6
Feed to main column (Furnace)	6
Stripping steam to main column (Above stage)	7
LVGO sidestream product	2
Top pump-around draw and return	2, 1
HVGO sidestream product	4
HVGO pump-around draw and return	4, 3

Table A.4

Operating conditions in the vacuum distillation column.

Operating Condition	Value
Overhead pressure	60 mmHg
Bottom pressure	70 mmHg
Feed furnace fractional overflash	0.6 %LV
Stripping steam/bottom product	2.27 kg/bbl

Appendix B. Material balance of the direct CBTL plant base case

Table B.1 provides the temperature, pressure and key component flowrates for main streams in the SMR_CCS process with a capacity of 10000 bbl/day and a biomass/coal weight ratio of 8/92. The streams are numbered in Fig. 1.

Table B.1

Stream summary of the SMR_CCS process.

Stream	1	2	3	4	5	6	7	8	9	10	11
Temperature (°C)	27	21	35	432	267	414	93	302	35	36	36
Pressure (bar)	1	20	22	208	1	208	3	55	55	3	3
Flow rate (kg/s)											
Coal	27.81			1.03				1.03			
Biomass	2.59										
H ₂ O			0.06	3.18		2.72			0.01		
CO ₂		0.14	11.55	1.88		1.77			9.89		
CO			0.12	0.63		0.61			0.30		
H ₂			2.04	2.52		2.43			0.74	2.41	0.14
H ₂ S				2.01		1.85			0.22		
NH ₃				0.88		0.81					
CH ₄		4.73	1.67	1.89		1.81			0.02		
C ₂ -C ₄		1.09		3.50		3.23					
C ₅ -177 °C				5.15		4.13	3.56				
177-288 °C				8.24		4.89	6.65				
288-344 °C				8.05	2.59	3.43	6.29				
344-454 °C				41.37	40.62	10.81	1.11				
454 °C +				15.63	13.57	1.09		2.53			
Ash				3.04	0.03			2.88			

Nomenclature

A = ash

AGR = acid gas removal

ASU = air separation unit

BFD = block flow diagram

CBTL = coal biomass to liquids

CCS = CO₂ capture and storage

CSD = critical solvent deashing

CTSL = catalytic two stage liquefaction

DCL = direct coal liquefaction

EDS = Exxon Donor Solvent

EOS = equation of state

FBP = final boiling point

FC = fixed carbon

FG = fuel gas

CG = co-gasification

GHG = greenhouse gases

GT = gas turbine flue gas

HCR = hydrocarbon recovery

HCU = hydrocarbon upgrading

HDT = hydrotreating

HP = high pressure

HRSG = heat recovery and steam generation

HTI = Hydrocarbon Technologies Inc.

HTS = high temperature shift

HVGO = heavy vacuum gas oil

IBP = initial boiling point

ICL = indirect coal liquefaction

IGCC = integrated gasification combined cycle

LG = light gas

IP = intermediate pressure

LP = low pressure

LTS = low temperature shift

LVGO = light vacuum gas oil

M = moisture

MAF = moisture and ash free

MDEA = methyl diethanolamine

MEA = monoethanolamine

MON = motor octane number

NBP = normal boiling point

PERC = Pittsburgh Energy Research Center

POC = proof of concept

POX = partial oxidation

PSA = pressure swing absorption

PZ = piperazine

RFM = reformate

RON = research octane number

ROSE-SR = Residual Oil Supercritical Extraction-Solids Rejection

SMR = steam methane reforming

SRC = solvent refined coal

VM = volatile materia

ST = steam turbine

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