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Liquid Fuels from Alternative Carbon Sources Minimizing Carbon Dioxide Emissions

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The energy needs of the world continue to grow, as does the resulting environmental impact. Policy makers continue to call for alternative energies to replace today's petroleum-based liquid fuels. However, liquid fuels have significant advantages, and it is probably unwise to abandon the existing infrastructure without appropriately exploring alternatives to lessen the environmental burden of producing liquid fuels. Biomass and coal are often proposed as alternatives to petroleum-based carbon sources, but those processes lose a significant amount of their potential product to unwanted carbon dioxide emissions. However, combining biomass and coal with cleaner natural gas yields processes with less environmental impact to produce liquid fuels with small, zero, or even negative carbon dioxide emissions. Our process synthesis approach is applied to commonly encountered liquid fuel production methods to identify promising routes and to establish feasibility limits on those less promising alternatives. *AIChE J*, 59: 2062–2078, 2013
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Introduction

To reduce the emission of greenhouse gases to the environment, today's fossil fuels need to be replaced with more renewable resources. However, this transition will not occur overnight, and the use of fossil fuels is expected to continue for at least another 100 years as the transition occurs.[1] Therefore, for the sake of future generations, it is necessary to explore solutions to reduce the environmental burden of current processes to generate electricity and liquid fuels.

As a society, we face many problems and challenges replacing our current gasoline/liquid fuel dominated infrastructure for transportation with a presumably better system. The advantages of using liquid fuels are enormous in terms of their ease of handling, current delivery infrastructure and energy density, and we should not be in a hurry to change to new systems without examining new ways of making liquid fuels.[2,3] Thus, an ideal short-/medium-term solution is a liquid fuel produced at a fraction of the greenhouse gas emissions of today's technology.

We will not be able to stop the CO_2 emissions of transportation vehicles immediately, but we can address the inefficiencies of power plants and refineries and their emissions, which are estimated to contribute up to 57% of total CO_2 emissions in the USA.[4] Such a solution will be able to lessen the burden on today's environment, as new, more sustainable technologies are developed.

Conventional oil production is expected to peak between 10 and 50 years from now,[2] so dwindling resources necessitate an investigation of alternative fuel sources to produce electricity and liquid fuel. Hydrogen is commonly suggested as the fuel of the future. However, hydrogen is simply an energy carrier, as it is rarely found in nature in a combustible form, and other fuel sources are required to produce it.[4,5] Therefore, its use offers few benefits over the fuel used to generate it. Natural gas (mainly methane), on the other hand, is commonly found in nature—that is, deep coal beds[6] and off gas from landfills and livestock[7]—and is a generally cleaner burning fuel, releasing 20% less CO_2 per British Thermal Unit of fuel compared with gasoline.[4] However, natural gas is lower in energy density and difficult and inefficient to store, in addition to not meshing with the current liquid fuels infrastructure. Liquid fuels from biomass, that is, ethanol, are gaining attention, as biomass is plentiful, in addition to capturing exhaust CO_2 during growth.[2] However, there are many drawbacks with producing liquid fuels solely from biomass. First, biomass requires massive amounts of land for growth to meet the energy needs to today's society, with estimates that devoting all US corn and soybean production would only offset 12 and 6% of today's gasoline and diesel needs, respectively.[8] Also, current enzymes to break down biomass not threatening the food supply, for example, switchgrass, corn stover and trees, are expensive and too slow for commercial production.[9] Obviously, each potential

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technology has its benefits and drawbacks, and the final decision will depend on many factors, with each holding promise.

One emerging route of biomass conversion to liquid fuels is to use an adapted form of technology developed for the coal-to-liquids (CTL) process known as Fischer–Tropsch (F–T) technology.[2] The F–T process converts synthesis gas—a stoichiometric mixture of hydrogen and carbon monoxide—to synthetic hydrocarbons. Traditionally, synthesis gas (syngas) is generated through the gasification of coal in the presence of steam and oxygen, with a carbon conversion for the overall process (carbon from coal ending up in liquid fuel) in the neighborhood of 25%.[10] The remaining carbon is released to the atmosphere as CO_2, which, when combined with the liquid fuel combustion exhaust, generates almost double the CO_2 emissions over conventional liquid fuels derived from crude oil.[11] Replacing the coal with renewable biomass introduces an atmospheric CO_2 sink during the cycle of new growth,[12] but combustion of the biomass to produce the syngas still generates large amounts of CO_2.[13] However, if one were able to drastically reduce the CO_2 emissions from such a process, it would be possible to produce liquid fuels from a renewable source with a smaller carbon footprint. We present such a method to produce liquid fuels with a net use of CO_2, thus, minimizing the environmental impact, yet maximizing the conversion of carbon to fuel.

One approach to reducing CO_2 emissions resulting from synthetic fuel production processes that is gaining traction is the use of hybrid feed stocks, reviewed recently by Floudas et al.[14] Hybrid processes use two or more of coal, biomass and natural gas to produce some combination of liquid fuels, electricity and other chemicals, such as methanol. Coal and biomass to liquids processes have garnered much interest in the USA, because they take advantage of the scale of the coal industry as well as the environmental benefits of biomass to produce a fuel that meshes with the current energy infrastructure while utilizing domestic resources projected to last for the next century.[10,15–18] Coal and gas to liquids (CGTL)[19–22] and biomass and gas to liquids (BGTL)[23,24] processes aim to utilize natural gas deposits nearby other energy sources, to produce a more economically viable fuel to transport and utilize elsewhere.[25] Recently, some extensive investigations have been undertaken to evaluate the potential of a hybrid F–T process utilizing coal, biomass and natural gas, as well as hydrogen produced from noncarbon sources, to meet the transportation energy requirements of the USA with minimal CO_2 emissions and maximum carbon conversion.[26–30] Such research highlights the potential of this approach to meet the growing energy demands of today's society, whereas at the same time reducing environmental impacts. However, as Kreutz et al.[10] mention, "there is not yet available a comprehensive analytical framework for deciding the most promising ways forward," which is the main objective of the work presented here.

New Process Design Approach

Some of the sunlight reaching earth is stored chemically (as carbonaceous material) by plants.[12] Over the past millions of years some of this plant material has been converted by geological processes to coal and oil. These fossil fuels and the current carbonaceous biological materials on our planet are our main (excluding nuclear) energy reserves, and this energy is in the form of chemical potential.

Unlocking this chemical potential as best we can means using and transforming energy and materials efficiently. Hence, if we do not develop processes to effectively unlock this chemical potential, we produce more carbon dioxide for a given amount of product, whether this product be fuel, electricity or chemicals.[31] If we do not use this chemical potential, when the transformations are taking place, they are lost forever. This is like taking a mass down a hill. We can use it to do work, as we take it down or let it roll down. Once it is at the bottom of the hill it is too late to do anything!

Liquid fuel processing plants are very complex arrangements of reactors, separators, mixers and heat exchangers, which are collectively known as unit operations. Chemical engineers have traditionally developed tools for improving the different unit operations. Computer programs have been used to synthesize processes by putting together superstructures of many units with complex interconnections and then finding the best way of putting them together.[32,33] Recent work has focused on superstructure optimization of coal, biomass and gas to liquids (CBGTL) processes determining optimal configurations of existing commercial equipment.[27,28] While useful and correct for the given units, there is no way of knowing if there is not a better alternative process arrangement not considered in the optimization. With this in mind, new tools have been developed to analyze processes from a thermodynamic perspective.[5,34,35] The viewpoint is a macroscopic one focused on how the plant transforms the feed materials into products, rather than what occurs in each individual unit operation. An attempt is made to assess what would happen if we were able to operate the plant as efficiently as theoretically possible (reversibly). The answer one gets is different for different process flow sheets. These efficiencies then become targets, and we can compare between flow sheets. One is now in a position to see what has been done that leads to high carbon dioxide emissions. This opens up opportunities to put the process together in such a way to most efficiently convert the chemical potential of carbonaceous materials to chemical potential in the product chemicals to reduce emissions.

Implementation

One cannot choose the inputs and outputs from a process randomly. To have an attainable set of outputs, they have to satisfy certain constraints. In a plant operating at steady state, there are three types:

1. There are a set of mass balance constraints, namely all atoms of material entering as feed must leave in a product stream.
2. There is an energy balance, namely that all energy entering the system that is not used in chemical transformation must be rejected, that is, the change in enthalpy between the products and the reactants must be less than zero ($\Delta H_{\text{process}} \leq 0$). A process with $\Delta H_{\text{process}} > 0$ is not feasible, because energy is required to convert the feed to the products and to get this energy some fuel has to be burnt. The products of this burning then need to be accounted for as part of the products in Eq. 1.
3. Finally, the chemical plant with all its inputs and outputs can be thought of as a universe, and we know from the

second law of thermodynamics this means that the entropy must be zero or increase. Furthermore, the closer to zero we get the more efficient the plant, and this effectively means less carbon dioxide emissions. It turns out for many reasons it is more useful to use this result in relation to Gibbs free energy. In this form, we say that for a plant to operate the change in the Gibbs free energy, including work terms, must be either zero or negative ($\Delta G_{\text{process}} \leq 0$) and the closer to zero the better. This is effectively a work balance on the plant that gives rise to an inequality with a desired target.

The important thing when using these ideas is not to use them sequentially, but simultaneously as decisions on one affect the others.

All these facts are known to practitioners in the field. However, they have not been effectively used in synthesizing a plant. Thus, the major technological advance is the way where these are used. Thus, one of the most exciting ideas to come out of this is that we can now view a chemical plant as a heat engine that provides work to the process to cause a desired transformation. In the end, we now have targets for our processes, and then it becomes an exercise in the ingenuity of the experienced designers to design flow sheets that can as near as possible meet these targets. Thus, we synthesize the process to meet the targets that we have shown are the most desirable. As will be discussed in this article, these methods enable us to come up with transformational technologies. The goal of this work is to utilize these transformational technologies to design a process to produce 1 mol of liquid fuel, represented here as CH_2, from a carbon source other than petroleum—biomass, coal and/or natural gas, while minimizing the CO_2 footprint. The intention is to demonstrate that the perception that synthetic fuel plants must always be large producers of greenhouse gases is false, and it is theoretically possible to develop processes from the basic laws of thermodynamics that have minimal environmental impact. In addition, it is demonstrated here how one can retrofit existing CTL plants, which are responsible for large levels of greenhouse gas emissions, with additional processes to consume this CO_2 and yield an overall reduced carbon footprint, while still producing the desired liquid fuel.

As done by Patel et al.,[34] feed and product materials are only assumed to be those readily available in nature—CO_2, O_2, H_2O, CH_4, biomass and coal—and that all feed and product streams enter and leave the process at standard temperature and pressure—termed a "simple process." Pure streams of CO_2 and O_2 will require some separation, but at this stage of evaluation, they are assumed to be available. Heats of formation and Gibbs free energies for the above species are provided in Table 1.

A note should be made here about how the values for the heats and Gibbs free energies of formation for fuel and biomass were calculated. Values for the formation energies for the gas phase of a fuel monomer (CH_2) were taken as the average value for a monomer of the series of gas fuel values from octane through dodecane. In other words, the value for the heat of formation for octane (-208.8 kJ mol^{-1}) was divided into eight units (one for each carbon atom), and this value (-26.1 kJ mol^{-1}) was averaged with the same values for nonane, decane, undecane and dodecane to yield the utilized value of -25.1 kJ mol^{-1}. This procedure was repeated for the Gibbs free energy as well. The values for octane–dodecane were taken from Perry's Handbook.[36] These values were then used in conjunction with the heats of vaporization and liquid and gas heat capacities of each of the species from octane–dodecane to determine the liquid fuel monomer enthalpy following a reversible path from the gas-phase values at T_0 to the gas-phase values at T_{boil} to the liquid-phase values at T_{boil} to the liquid-phase values at T_0. The fuel monomer (CH_2) is used as a generic representation of liquid fuels in this work (and others[24,31,37]) to simplify the mass, energy and work balances. In reality, liquid fuel is a mixture of many hydrocarbons, and more detailed analyses require more detailed representations of the liquid fuel product.[10,19,20] However, utilizing the monomer enables straightforward determination of targets for ideal operation, allowing simple comparison between alternatives.

Table 1. Heats of Formation and Gibbs Free Energies at Standard Temperature and Pressure for Each of the Species Considered

Compound	Chemical Formula	ΔH_f° (kJ mol^{-1})	ΔG_f° (kJ mol^{-1})
Water	$H_2O_{(l)}$	-285.8	-237.2
Water	$H_2O_{(g)}$	-241.8	-228.6
Methane	CH_4	-74.8	-50.7
Carbon monoxide	CO	-110.5	-137.2
Carbon dioxide	CO_2	-393.5	-394.4
Hydrogen	H_2	0	0
Oxygen	O_2	0	0
Coal	C	0	0
Fuel	$CH_{2(l)}$	-31.0	1.4
Fuel	$CH_{2(g)}$	-25.1	3.2
Biomass	$CH_{1.5}O_{0.7}$	-113.0	-103.0

For the values for biomass, though quite variable, a typical ultimate chemical of biomass yields around 48% carbon, 45% oxygen and 6% hydrogen by mass with the balance consisting of nitrogen, sulfur and other minerals,[12,38] giving a representative chemical formula for biomass of $CH_{1.5}O_{0.7}$.[38] The heat of formation for biomass was taken from the same source as the chemical formula.[38] The value for the Gibbs free energy was calculated using the method of Griffiths,[39] which assumes that the enthalpies and Gibbs free energies of reaction of organic compounds have a relationship to each other.

Coal to Liquid Fuels (CTL)

Coal is plentiful, especially in the industrialized nations that are consuming the majority of fossil fuels throughout the world—USA, India and China. Making use of the coal with zero carbon dioxide emissions is extremely attractive both from an environmental standpoint and for national security, as using domestic resources removes the reliance on foreign fuel reserves. This approach to utilizing coal to create liquid fuels is through coal gasification to syngas, followed by F–T synthesis to convert the syngas into liquid fuel and water. An overall balance for the current CTL process is shown as follows

$$1.5\boldsymbol{C}_{(s)} + 1\boldsymbol{H}_2\boldsymbol{O}_{(l)} \Rightarrow 0.5\boldsymbol{CO}_{2(g)} + 1\boldsymbol{CH}_{2(l)} \tag{1}$$

Note that Eq. 1 is a mass balance across the entire process and is not a reaction. Therefore, this equation represents the input and output streams entering a CTL process. Here, we have assumed that coal is pure carbon. In reality, coal contains small amounts of other species (hydrogen, nitrogen, chlorine, sulfur and ash),[40] which will necessitate additional treatment and separation equipment in the process, which we neglect in this first approach to process analysis, to establish a standardized point of comparison between multiple processes. We immediately notice that using water we are automatically ensuring that at least 33% of our carbon must be emitted as carbon dioxide. The real situation is actually worse, as the process requires 58 kJ mol^{-1} CH_2 of heat to be added and about 41 kJ mol^{-1} of work to be added. Therefore, additional coal will need to be burned in the presence of oxygen to provide the heat and work required to run the process (to achieve $\Delta H_{\text{process}} \leq 0$ and $\Delta G_{\text{process}} \leq 0$). The new process mass balance is shown in Eq. 2 as follows

$$1.647\boldsymbol{C}_{(s)} + 1\boldsymbol{H_2O}_{(l)} + 0.147\boldsymbol{O}_{2(g)} \Rightarrow 0.647\boldsymbol{CO}_{2(g)} + 1\boldsymbol{CH}_{2(l)} \tag{2}$$

with $\Delta H_{\text{process}} = 0\ \text{kJ}\quad \text{mol}^{-1}$ and $\Delta G_{\text{process}} = -16.8\ \text{kJ}\ \text{mol}^{-1}$. In practice, making liquid fuel from coal via the F–T process is even more inefficient, in that >70% of the carbon fed into the process ends up as carbon dioxide.[41] In fact, the largest point source of carbon dioxide emissions in the world is the Sasol CTL plant in Secunda, South Africa.[42] As a result, when using coal as the carbon source and water as the hydrogen source to produce liquid fuels, one must be aware that the maximum carbon efficiency (mole of product per mole of fossil fuel) is 60%. Because the optimal CTL process must produce at least some CO_2, it is an ideal candidate for carbon capture and sequestration (CCS). Recent research has suggested ways in which hydrogen from noncarbon sources, and CCS can be utilized to increase the carbon efficiency close to 100%[2,26]; however, the costs of such a process are currently prohibitive. We ask ourselves if there is a better way to produce liquid fuels from carbon sources, but with reduced environmental impact.

Natural Gas to Liquid Fuels (GTL)

An attractive alternative to coal as a carbon source for liquid fuels is natural gas. Natural gas (assumed to be pure methane) is hydrogen rich and, therefore, is an ideal feedstock to produce liquid fuels. As with coal, natural gas will contain some impurities (<10%), such as higher hydrocarbons, nitrogen and carbon dioxide,[40] which are neglected at this level of investigation. It can be shown following the analysis of Patel et al.[34] that the theoretical limit of the gas-to-liquids (GTL) process can operate reversibly ($\Delta G = 0$) and consume carbon dioxide in the production of liquid fuels, as provided in Eq. 3 as follows

$$0.774\boldsymbol{CH}_{4(g)} + 0.226\boldsymbol{CO}_{2(g)} + 0.048\boldsymbol{O}_{2(g)} \Rightarrow 0.548\boldsymbol{H_2O}_{(l)} + 1\boldsymbol{CH}_{2(l)} \tag{3}$$

In addition this process has a $\Delta H_{\text{process}} = -40.6\ \text{kJ}\quad \text{mol}^{-1}$, meaning that the process is overall exothermic and about 40.6 kJ of heat can be recovered for other purposes. In addition, the carbon efficiency of the process is 129%. An efficiency of greater than 100% is possible, as you produce usable fuel from a nonfossil source (CO_2), which increases the potential of the process. Hence, if the choice exists for liquid fuels production from coal or methane, the methane route is easily the more environmentally friendly of the two. Such results highlight the current trend of the major players in the synthetic liquid fuels industry to increase focus on the more efficient and, thus, less environmentally impactful, GTL process.[43] However, their processes still produce up to 1.5 kg of CO_2 per kg of gas, so they are far from this theoretical limit.[44] In addition, as the optimal GTL process does not emit any CO_2 (Eq. 3), removing CO_2 through CCS[23] negatively affects the overall process efficiency and results in lost heat and reduced yield of the desired product.[21]

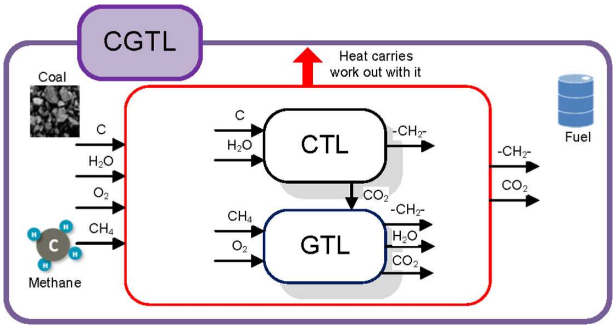

Figure 1. Schematic representation of the CGTL combined process. Some images courtesy of Department of Energy/Energy Information Administration.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Reduced CO_2 Emissions from a CTL Process

Suppose that a CTL process exists, and it is desired to determine the possibilities to reduce the plant's overall production of carbon dioxide. This scenario is increasingly relevant, as the discussion about introducing a carbon tax continues to progress, and the ability and cost of carbon sequestration continues to be prohibitive. As shown in the previous sections, the GTL process is a carbon dioxide sink, whereas the CTL process is a carbon dioxide producer. Therefore, integrating the processes may be a means to produce liquids fuels with reduced carbon dioxide emissions. One can write the overall process mass balance (combining Eqs. 2 and 3 to produce only a single mole of CH_2) to yield the overall CGTL process mass balance as given in Eq. 4.

$$0.824\boldsymbol{C}_{(s)} + 0.387\boldsymbol{CH}_{4(g)} + 0.226\boldsymbol{H_2O}_{(l)} + 0.098\boldsymbol{O}_{2(g)} \Rightarrow 0.211\boldsymbol{CO}_{2(g)} + 1\boldsymbol{CH}_{2(l)} \tag{4}$$

This joint process is represented in the schematic in Figure 1.

This joint process is exothermic ($\Delta H_{\text{process}} = -20.5\ \text{kJ}\quad \text{mol}^{-1}$) and work producing ($\Delta G_{\text{process}} = -8.6\ \text{kJ}\quad \text{mol}^{-1}$) with a carbon efficiency of 82%, meaning that it is thermodynamically feasible with a carbon efficiency greater than that of the CTL process and less than that of the GTL process. This is an extremely powerful result, suggesting that rather than abandoning existing CTL technology due to pressure from environmental considerations, instead invest in additional technology to interface with the existing plant and convert an unwanted byproduct into useful product. Overall, for the production of 1 mol of CH_2, the production of CO_2 is reduced by over three times, drastically improving the attractiveness of producing liquid fuels through F–T processes. However, notice that the process energy and work

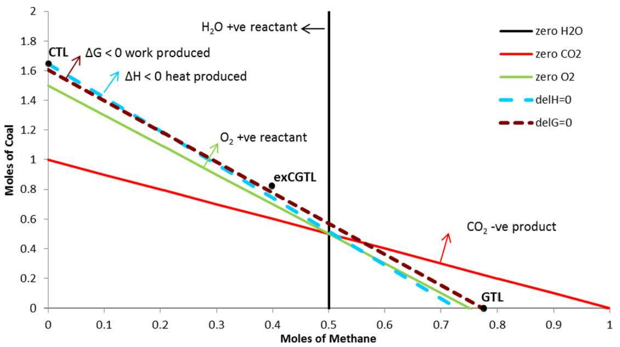

Figure 2. Operating regime for the CGTL process. Point CTL represents the CTL process, point GTL represents the GTL process and point exCGTL represents the joint process, combining a GTL process with an existing CTL process.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

values are both negative, meaning that the process is not operating adiabatically ($\Delta H = 0$) or reversibly ($\Delta G = 0$), which are desired operating targets for this process synthesis approach. This suggests that there is a possibility to improve the joint process even further.

Joint Coal and Methane to Liquids Process (CGTL)

To investigate this, the procedure of Patel et al.[34] is utilized to analyze the CGTL process with methane, coal, carbon dioxide, water, oxygen and liquid fuel as the possible species present. The objective is to produce 1 mol of CH_2 from a mixture of coal and methane, with limited or no production (or even consumption) of CO_2, either adiabatically and work producing ($\Delta H = 0$; $\Delta G < 0$) or reversibly and exothermic ($\Delta H < 0$; $\Delta G = 0$). The space representing all processes consuming up to 2 mol of coal and up to 1 mol of methane is shown in Figure 2.

Each point in Figure 2 represents a separate process, consuming methane, and coal given by the coordinates of that point, and the moles of the remaining species (oxygen, carbon dioxide and water) are either positive (as a feed to the process) or negative (as a product from the process). The zero H_2O, zero CO_2 and zero O_2 lines in Figure 2 represent the points at which each species is not present in the overall process mass balance. The ΔH and ΔG lines represent the combinations at which the overall process is either adiabatic or reversible, respectively. From this figure, we can see all processes that operate with a joint feed of methane and coal, to choose a process that best satisfies the process objectives. For instance, the CTL process is represented by point CTL and resides at the point of intersection between the vertical axis (zero moles of methane fed) and the $\Delta H = 0$ line (adiabatic process target). Similarly, the GTL process resides at the point of intersection between the horizontal axis (no coal fed) and the $\Delta G = 0$ line (reversible process target). Finally, the joint process described in the previous section (Figure 1) resides at the exCGTL point (exothermic and work producing). From this figure, we can begin to apply our constraints described by the process objective to determine the optimal point (or points) of operation. A process is only feasible if it is exothermic (or in the limit adiabatic) and work producing (or in the limit reversible). Thus, all processes must reside in the union of the region on the negative side of the $\Delta H = 0$ and $\Delta G = 0$ lines. In addition, it is desired for carbon dioxide to either be consumed or not present in the overall process mass balance, which then restricts all processes to the shaded purple region in Figure 3. The further one operates from the zero CO_2 line into the shaded region, the more CO_2 the process consumes.

Notice that the previous process (point exCGTL) does not fall within this region. This is because carbon dioxide is produced in this process, so it does not satisfy our original process objectives. Not just a single point satisfies the overall process requirements, but there exists an entire region, with the final point selected based on further criteria. For example, if the desire is to maximize the consumption of carbon dioxide from an exothermic, reversible process, one would operate at the GTL point as shown in Figure 3. This point also corresponds to the point of maximum carbon efficiency (129%), with any point in the region having a carbon efficiency ranging from 100% (along the zero CO_2 line) to 129% at point GTL. Any point along the $\Delta G = 0$ line is exothermic and reversible, whereas at no point is the process adiabatic and work producing. Finally, the point of maximum coal consumption (thus, minimum methane consumption), without any CO_2 production, is represented by point maxCGTL. This is the point that is chosen for optimal operation, as coal is usually available in larger quantities. The overall process mass balance at this point is then

$$0.437\boldsymbol{C}_{(s)} + 0.563\boldsymbol{CH}_{4(g)} + 0.063\boldsymbol{O}_{2(g)} \Rightarrow 0.126\boldsymbol{H}_2\boldsymbol{O}_{(l)} + 1\boldsymbol{CH}_{2(l)} \quad (5)$$

This process is reversible ($\Delta G_{\text{process}} = 0$), exothermic ($\Delta H_{\text{process}} = -25.0\text{kJ} \quad \text{mol}^{-1}$) and has a carbon efficiency of 100%. Thus, the chemical potential of the feed materials is clearly conserved in the product, and the process is feasible from a thermodynamic viewpoint. Such a joint process suggests, for instance, that extracted coal bed methane can be used to produce liquid fuels with existing coal reserves. This could have considerable advantages for using stranded coal reserves, as natural gas may not need to be brought in from another source. Even more interesting is the possibility of doing underground coal gasification where the coal bed methane is actually present *in situ*. Diminishing oil supplies will necessitate the use of coal in the near future in nations

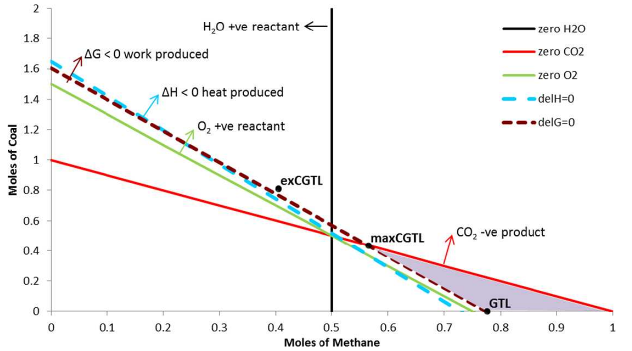

Figure 3. Feasible operation region satisfying the process constraints for CGTL processes.

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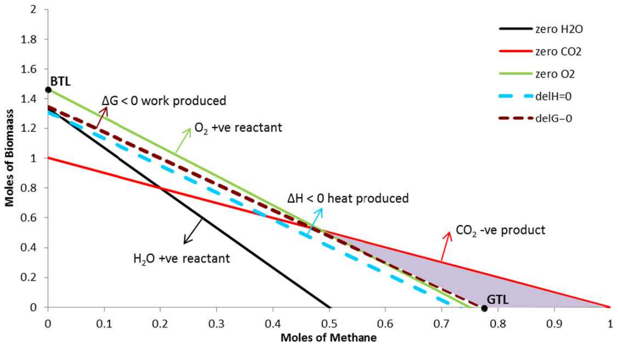

Figure 4. Feasible operation region satisfying the process constraints for BGTL processes.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with large coal reserves and energy needs (e.g., USA, China and India). This analysis shows that it is possible to utilize such resources with less of an environmental impact. Furthermore, the ability to use domestic coal resources in the US to produce liquid fuels can facilitate energy independence. Here, using only thermodynamic considerations, we have demonstrated the ability to combine a "dirty" process by most metrics (CTL) with a clean process (GTL), to produce a more attractive process (CGTL), satisfying a given objective.

Biomass to Liquid Fuels (BTL)

However, both natural gas and coal are limited fossil fuels, and it is desired to develop a process to produce liquid fuels from a more sustainable resource. Biomass is often suggested as an alternative carbon source to coal for producing liquid fuels, and such a process is termed the biomass-to-liquids (BTL) process. Biomass can be anything from corn to wood to algae. It is attractive, because growing biomass captures atmospheric CO_2, and, thus, the process is more sustainable. Using this chemical formula and the procedure outlined in Patel et al.[34] to identify the scenario to produce 1 mol of liquid fuel, with $\Delta H_{\text{process}} \leq 0$ and $\Delta G_{\text{process}} \leq 0$ from biomass, yields the following process mass balance

$$1.463\boldsymbol{CH}_{1.5}\boldsymbol{O}_{0.7(s)} \Rightarrow 0.463\boldsymbol{CO}_{2(g)} + 0.098\boldsymbol{H}_2\boldsymbol{O}_{(l)} + 1\boldsymbol{CH}_{2(l)} \tag{6}$$

This means that, similar to the CTL process, the best case scenario is that 32% of the carbon entering the process leaves as carbon dioxide. However, this situation is slightly better than the CTL process, because both the process enthalpy ($\Delta H_{\text{process}} = -75.9\text{kJ mol}^{-1}$) and free energy ($\Delta G_{\text{process}} = -53.8\text{kJ mol}^{-1}$) are negative, suggesting that the process is feasible from a thermodynamic perspective. Thus, the environmental benefit of the emerging BTL process over commercialized CTL technology lies in the capture of atmospheric CO_2 during growth, not in subsequent processing to liquid fuels.

Biomass + Natural Gas to Liquid Fuels (BGTL): A Combination Process

As we had shown previously, CTL alone was not attractive, but when combined with GTL, the story was different. Does the same hold true for combining BTL and GTL? This is a potentially attractive alternative to both extend the life of current natural gas supplies and utilize renewable biomass. Again, following the procedure in Patel et al.,[34] we can develop a region satisfying the following constraints: consumption of biomass and methane to produce 1 mol of liquid fuel, with limited or no carbon dioxide production (or even consumption). This region is shown in Figure 4.

Once again, the GTL process lies on the horizontal axis (no biomass feed) at the point of intersection with the $\Delta G = 0$ line, and the BTL process resides on the vertical axis (no methane feed) at the point of intersection with the zero oxygen line. The formation of oxygen as a product is highly unlikely, especially in the presence of a carbon source, as combustion will proceed to consume both the carbon source and the oxygen. That is why zero oxygen is used as the target for the biomass process, instead of an adiabatic or reversible process. We can see that the region satisfying the process constraints (shaded purple region) lies in the bottom right of this figure. To see which lines bound the region, the region is expanded in Figure 5.

We can see that the region is bounded by the $\Delta G = 0$ line, the zero O_2 line, as well as the zero CO_2 line. The zero O_2 line crosses the $\Delta G = 0$ line at about 0.554 mol of methane, and as discussed, a product of oxygen is unlikely, so the small region between the $\Delta G = 0$ line and the zero O_2 line is excluded from the region satisfying the constraints. Therefore, the scenario is slightly different from the CGTL case, in that the process that requires the least amount of methane to be 100% carbon efficient is not reversible as well. Biomass is a renewable resource, whereas methane is not, and as a result it is desired to utilize the least methane and the most biomass, while producing no carbon dioxide emissions (carbon efficiency ≥ 100%). Point maxB in Figure 5 corresponds to the overall process mass balance shown in Eq. 7 and represents the process with the highest consumption of biomass for a process with ≥100% carbon efficiency.

$$0.487\boldsymbol{CH}_{4(\boldsymbol{g})} + 0.513\boldsymbol{CH}_{1.5}\boldsymbol{O}_{0.7(s)} \Rightarrow 0.359\boldsymbol{H}_2\boldsymbol{O}_{(l)} + 1\boldsymbol{CH}_{2(l)} \tag{7}$$

This process does not consume (or produce) oxygen or carbon dioxide (100% carbon efficient) and is work producing ($\Delta G_{\text{process}} = -6.2\text{kJ mol}^{-1}$) and exothermic ($\Delta H_{\text{process}} = -39.3\text{kJ mol}^{-1}$). The process is mass balance limited, as the process target is neither reversible

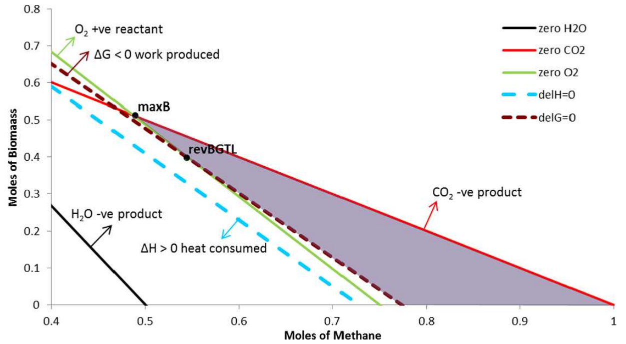

Figure 5. Zoom in on the feasible operation region satisfying the process constraints for BGTL processes.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table 2. Process Mass Balances for All Processes Reviewed in This Article

Process	Description	Equation Number	Process Mass Balance	Process AH (kJ/mol^{-1})	Process AG (kJ/mol^{-1})	Carbon Efficiency (%)
CTL	No oxygen demand — not feasible	1	$1.5C + 1H_2O \Rightarrow 0.5CO_2 + 1CH_2$	58.0	41.3	67
CTL	Thermodynamic target process	2	$1.647C + 1H_2O + 0.147O_2 \Rightarrow 0.647CO_2 + 1CH_2$	0.0	−16.8	61
GTL	Thermodynamic target process	3	$0.774CH_4 + 0.226CO_2 + 0.048O_2 \Rightarrow 0.548H_2O + 1CH_2$	−40.6	0.0	129
CGTL	Thermodynamically feasible, operation at 1:1 ratio	4	$0.824C + 0.387CH_4 + 0.098O_2 + 0.226H_2O \Rightarrow 0.211CO_2 + 1CH_2$	−20.5	−8.6	82
CGTL	Maximum coal consumption, no CO_2 emissions and reversible	5	$0.437C + 0.563CH_4 + 0.063O_2 \Rightarrow 0.126H_2O + 1CH_2$	−25.0	0.0	100
BTL	No oxygen demand — feasible	6	$1.463CH_{1.5}O_{0.7} \Rightarrow 0.463CO_2 + 0.098H_2O + 1CH_2$	−75.9	−53.8	68
BGTL	Maximum biomass consumption, no CO_2 emissions	7	$0.487CH_4 + 0.513CH_{1.5}O_{0.7} \Rightarrow 0.359H_2O + 1CH_2$	−39.3	−6.2	100
BGTL	Maximum biomass consumption, reversible, CE $\geq$ 100%	8	$0.551CH_4 + 0.388CH_{1.5}O_{0.7} + 0.061CO_2 \Rightarrow 0.393H_2O + 1CH_2$	−34.4	0.0	106

($\Delta G_{\text{process}} = 0$) nor adiabatic ($\Delta H_{\text{process}} = 0$). This work and heat could possibly be used for other purposes, or simply lost to the environment. The process represented by point revBGTL corresponds to the overall process mass balance shown in Eq. 8 and represents the reversible process with the highest consumption of biomass, with a carbon efficiency $\geq$100%.

$$0.551\boldsymbol{CH}_4 + 0.388\boldsymbol{CH}_{1.5}\boldsymbol{O}_{0.7} + 0.061\boldsymbol{CO}_2 \Rightarrow 0.393\boldsymbol{H}_2\boldsymbol{O} + 1\boldsymbol{CH}_2 \quad (8)$$

This process consumes carbon dioxide (carbon efficiency = 107%) and is reversible ($\Delta G_{\text{process}} = 0$ kJ mol^{-1}) and exothermic ($\Delta H_{\text{process}} = -34.4$ kJ mol^{-1}). Obviously, both processes are extremely attractive, capitalizing on the chemical potential of the feed materials, utilizing renewable biomass and contributing no carbon dioxide to the atmosphere. Depending on the exact situation, one of the above-mentioned processes may be more attractive than the other, and this analysis demonstrates the potential of the BGTL process. This result supports recent interest in the BGTL process,[23,24] to combine the currently feasible GTL technology[45] and the development of the BTL technology at commercial scale.[10] As an example, for stranded natural gas reserves near a source of biomass, this process can produce easily transportable liquid fuels from otherwise unusable sources. In addition, municipal waste dumps naturally produce methane gas, as the materials they contain decompose. Therefore, if the methane gas is captured, this approach can be used to produce desirable liquid fuels from one undesirable source (municipal waste) and one currently underutilized source (landfill methane). The benefits of such an approach are many-fold, related to the conversion of problematic waste (methane vented to the atmosphere and landfill solids) to a useful and valuable commodity. By combining an attractive process (GTL) with an unattractive process (BTL), an even more attractive joint process (BGTL) has been devised and shown to be thermodynamically feasible ($\Delta H_{\text{process}}$ *and* $\Delta G_{\text{process}} \leq 0$).

The processes reviewed so far are presented in Table 2.

Turning Process Mass Balances into Process Flow Maps

Thus far, we have demonstrated the potential of combining coal- and biomass-to-liquids process with the gas-to-liquids processes to create less environmentally taxing joint processes than single carbon feed source operations. But how are these potential process mass balances converted into useful information for flow sheet development? This is where the experience and knowledge of a process designer is of utmost importance, and the final flow sheet may vary greatly from one to the next. The general methodology of how a process flow map can be constructed given the overall process mass balance is presented later. We refer to the product of this methodology as a process flow map, because it is not the same as a process flow sheet in which true unit operations are incorporated and detailed information about each stream is determined. However, this analysis produces a preliminary flow map that identifies considerations for the more detailed design, that is, mass, energy and work integration, high and low process temperatures, recycle streams and so forth. This process flow map can be thought of as a philosophy document to justify decisions that were made to maximize product and minimize emissions. Following this procedure, a detailed design, such as that performed by Floudas and coworkers[26–30] for CBGTL processes should be undertaken to include additional complexities in the overall design. Nevertheless, without this high-level analysis presented here, there is no way of knowing whether the more complex flow sheet designed and simulated is near to the theoretical limit. As a result, the two approaches work well together, with this approach developing the basic structure and the detailed design and simulation incorporating additional complexities as required, all working toward a process with maximum product production and minimal emissions.

Determine the species involved in your process

The overall process mass balance target provides a start to the list of species that will be present in the process. This means that methane, biomass and carbon dioxide will be used to produce liquid water and liquid fuel. However, a chemical path to convert these feeds into these species is not realistic. Therefore, we need to consider producing intermediates using known and existing technology. This is where prior knowledge and experience of the design team is required—particularly the chemistry team. It is necessary to evaluate and suggest chemical pathways to produce the desired products from the suggested reactants that are feasible. As discussed earlier, F–T synthesis is one known chemical pathway to produce liquid fuels, but this requires a mixture of hydrogen and carbon monoxide, as shown in Eq. 9.

$$2\boldsymbol{H}_{2(g)} + 1\boldsymbol{CO}_{(g)} \rightarrow 1\boldsymbol{H}_2\boldsymbol{O}_{(g)} + 1\boldsymbol{CH}_{2(g)} \tag{9}$$

Therefore, these two species are added to those present in Eq. 8. To ensure the system mass is balanced, the equation must also be balanced. Also note that water and liquid fuel are present as a gas in Eq. 9, and, therefore, these must also be added to the list of species considered. Note that these do not affect our analysis, because these species will be intermediates, which means that they will not appear as either products or reactants for our overall process, so our overall process mass balance remains unchanged. Also note that Eq. 9 is now written as a reaction (→), because it is a known chemical pathway. Our list of species considered is now at nine—methane, biomass, carbon dioxide, liquid, vapor water, liquid, gas fuel, carbon monoxide and hydrogen.

Determine the number of independent reactions

The number of independent mass balances representing reactions is determined by subtracting the number of atom balances from the number of species.[46] Here, we have three atoms (carbon, hydrogen and oxygen) and nine species, so we must select six independent mass balances to represent our reactions. We make a distinction here, because the independent mass balances may be reactions that occur (such as all reactions presented here), but they need not be. From here on we will call these independent mass balances representing reactions, simply reactions.

Develop the set of independent reactions

Each of the species involved in the process must appear in at least one of the reactions. Those species that are in the list, but do not appear in the overall process target mass balance must appear at least once as a reactant and product, to ensure that it can be produced and consumed by the set of independent reactions. We know that the F–T reaction (Eq. 9) will be one of the reactions, so let us begin there. Carbon monoxide and hydrogen do not appear in Eq. 8, so they must be formed from methane, biomass and/or carbon dioxide. Steam reforming and steam gasification are two known pathways to convert methane and biomass, respectively, into carbon monoxide and hydrogen. These two reactions are shown in Eqs. 10 and 11 as follows.

$$\boldsymbol{CH}_{4(g)} + \boldsymbol{H}_2\boldsymbol{O}_{(g)} \rightarrow 3\boldsymbol{H}_{2(g)} + \boldsymbol{CO}_{(g)} \tag{10}$$

$$\boldsymbol{CH}_{1.5}\boldsymbol{O}_{0.7} + 0.3\boldsymbol{H}_2\boldsymbol{O}_{(g)} \rightarrow 1.05\boldsymbol{H}_2 + \boldsymbol{CO}_{(g)} \tag{11}$$

One can see that biomass and methane are used as feeds, matching the overall process mass balance, whereas carbon monoxide and hydrogen are produced for use as an intermediate to form fuel. Water vapor is used as a feed in Eqs. 10 and 11 and a product in reaction 9, as desired. The species still not appearing in any reaction are liquid water, liquid fuel and carbon dioxide. Including liquid fuel and liquid water is easy by including the phase change (condensation) reactions for each species. These are shown in Eqs. 12 and 13.

$$\boldsymbol{H}_2\boldsymbol{O}_{(g)} \rightarrow \boldsymbol{H}_2\boldsymbol{O}_{(l)} \tag{12}$$

$$\boldsymbol{CH}_{2(g)} \rightarrow \boldsymbol{CH}_{2(l)} \tag{13}$$

Finally, carbon dioxide as a feed must be considered, but only including the species considered so far. A reaction common to reforming is the water–gas shift (WGS) reaction, shown in Eq. 14.

$$\boldsymbol{CO}_{2(g)} + \boldsymbol{H}_{2(g)} \rightarrow \boldsymbol{H}_2\boldsymbol{O}_{(g)} + \boldsymbol{CO}_{(g)} \tag{14}$$

Therefore, our six independent reactions are shown in Eqs. 9–14. Each of these equations represents a chemical transformation that will occur somewhere in our process, whether as a reaction in the traditional sense of the word, or as a mass balance over a subprocess.

Calculate reaction energy and work requirements and the Carnot temperature

Knowing each of the independent reactions, one can determine the ΔH and ΔG for each reaction and use that information to calculate the Carnot temperature of each process. The Carnot temperature is important, because it represents the temperature at which heat added to (removed from) a process will carry in (out) the required amount of work as well.[35,47,48] Sempuga et al.[48] have shown how to determine whether processes are feasible or not using their Carnot temperature. The six independent reactions, along with their enthalpies, Gibbs free energies and Carnot temperatures are shown in Table 3.

One can see that each of the Carnot temperatures is not only positive but also reasonable (<1400 K), suggesting that each of these mass balances are likely feasible as actual reactions. If the Carnot temperature was negative or unrealistically high, it would be more likely that there would be an additional set of intermediates that would need to be considered in the analysis. However, this is not the case, so the next step is to determine the extent of each of the independent reactions to achieve the overall process mass balance target.

Determine the extent of each of the independent reactions

Summing all of the reactions in Table 3 as written (an extent of 1 for each), does not produce an overall process mass balance matching the overall process mass balance target (Eq. 8). Therefore, each of the reactions must proceed only a certain amount. This amount may be different for each independent reaction and can be determined systematically with the following procedure. There are 26 unknowns at this point—initial and final number of moles for each of the nine species, extent of each of the six independent reactions and the enthalpy and Gibbs energy of the overall process. Some of this information is available from the overall process mass balance target, but the procedure will be left as general as possible to allow the greatest flexibility of the method.

Represent the extent of each of the independent reactions with a variable called the reaction extent, e_j where j is the

Table 3. Independent Reactions for the revBGTL Process

Reaction	Decription	Equation Number	Reaction ΔH (kJ mol^{-1})	Reaction ΔG (kJ mol^{-1})	T_{carnat} (K)
$CO_{(g)} + 2H_{2(g)} \rightarrow CH_{2(g)} + H_2O_{(g)}$	Synthesis	9	−156.4	−88.2	683
$CH_{4(g)} + H_2O_{(g)} \rightarrow CO_{(g)} + 3H_{2(g)}$	Reforming	10	206.1	142.1	959
$CH_{1.5}O_{0.7(s)} + 0.3H_2O_{(g)} \rightarrow CO_{(g)} + 1.05H_{2(g)}$	Gasification	11	75.0	34.4	550
$H_2O_{(g)} \rightarrow H_2O_{(l)}$	Water phase	12	−44.0	−8.6	370
$CH_{2(g)} \rightarrow CH_{2(l)}$	Fuel phase	13	−6.0	−1.8	429
$H_{2(g)} + CO_{2(g)} \rightarrow CO_{(g)} + H_2O_{(g)}$	Water–Gas Shift	14	41.2	28.6	974

reaction number, 9–14 in this case. For example, the extent of the synthesis reaction is represented by e_9.

1. Write the amount of moles (N_i) of each species as a function of the initial number of moles of that species (N_i^0) and the amount consumed in each of the reactions. For example, the number of moles of carbon monoxide can be represented by the following equation: $N_{CO} = N_{CO}^0 + e_{10} + e_{11} + e_{14} - e_9$, because carbon monoxide is produced in the reforming, gasification and WGS reactions, whereas it is consumed in the synthesis reaction. Note that the extent in the above equation is multiplied by the stoichiometric coefficient of that particular species in the independent reaction (unity for CO in all cases). Repeat this for each of the nine species to develop a set of nine equations.

2. Write the overall process enthalpy ($\Delta H_{\text{process}}$) and Gibbs free energy ($\Delta G_{\text{process}}$) as a function of each of the reaction extents. Each independent reaction has its own ΔH_{rxn} and ΔG_{rxn} as shown in Table 3, and the summation of these multiplied by each reaction extent is equal to the overall process value. Including these two equations brings the total number of equations to 11.

3. Apply process assumptions to reduce the unknowns. Knowing the overall process mass balance target, one can make some simplifying assumptions about the system. For example, we know that liquid water and liquid fuel will be products, and hence, $N_{H_2O_{(l)}}^0 = N_{CH_{2(l)}}^0 = 0$, whereas methane, biomass and carbon dioxide will be feeds, or $N_{CH_4} = N_{CH_{1.5}O_{0.7}} = N_{CO_2} = 0$. In addition, the number of moles entering and leaving of the species that were considered that do not appear in the overall process mass balance target (carbon monoxide, hydrogen, steam and fuel in gas form) are zero, or $N_{CO} = N_{CO}^0 = N_{H_2} = N_{H_2}^0 = N_{H_2O_{(g)}} = N_{H_2O_{(g)}}^0 = N_{CH_{2(g)}} = N_{CH_{2(g)}}^0 = 0$. Applying these assumptions, the number of unknowns is reduced to 13, with 11 equations.

4. Apply process constraints to determine the overall process mass balance target. At this point, we must apply two constraints to solve the system. In our case, we desire to produce 1 mol of liquid fuel ($N_{CH_{2(l)}} = 1$), which will be used as the basis. In addition, we have shown in the previous section (Figure 5) that the BGTL process is work limited ($\Delta G_{\text{process}} > 0$ when $\Delta H_{\text{process}} = 0$). Hence, our feasible target is a reversible process ($\Delta G_{\text{process}} = 0$). Therefore, we have reduced the number of unknowns to 11 with 11 equations, and, thus, the system of equations can be solved using linear programming.

The results of the solution are shown in Table 4.

We can then look at each of the independent reactions and confirm that the overall process mass balance (sum of all reactions) is identical to the overall process mass balance target.

$$2\boldsymbol{H}_{2(g)} + 1\boldsymbol{CO}_{(g)} \rightarrow 1\boldsymbol{H}_2\boldsymbol{O}_{(g)} + 1\boldsymbol{CH}_{2(g)} \qquad e_9 = 1 \tag{15}$$

$$0.551\boldsymbol{CH}_{4(g)} + 0.551\boldsymbol{H}_2\boldsymbol{O}_{(g)} \rightarrow 1.653\boldsymbol{H}_{2(g)} + 0.551\boldsymbol{CO}_{(g)} \qquad e_{10} = 0.551 \tag{16}$$

$$0.388\boldsymbol{CH}_{1.5}\boldsymbol{O}_{0.7} + 0.116\boldsymbol{H}_2\boldsymbol{O}_{(g)} \rightarrow 0.407\boldsymbol{H}_2 + 0.388\boldsymbol{CO}_{(g)} \qquad e_{11} = 0.388 \tag{17}$$

$$0.393\boldsymbol{H}_2\boldsymbol{O}_{(g)} \rightarrow 0.393\boldsymbol{H}_2\boldsymbol{O}_{(l)} \qquad e_{12} = 0.393 \tag{18}$$

$$\boldsymbol{CH}_{2(g)} \rightarrow \boldsymbol{CH}_{2(l)} \qquad e13 = 1 \tag{19}$$

$$0.061\boldsymbol{CO}_{2(g)} + 0.061\boldsymbol{H}_{2(g)} \rightarrow 0.061\boldsymbol{H}_2\boldsymbol{O}_{(g)} + 0.061\boldsymbol{CO}_{(g)} \qquad e_{14} = 0.061 \tag{20}$$

Draw a preliminary, mass integrated process flow map

With these extents known, it is also possible to draw a preliminary mass integrated flow map. This is shown in Figure 6.

Table 4. Values of the 26 Unknowns for the revBGTL Process Target

Unknown	Description	Value
$N_{CH_4}^0$	Entering moles of methane	0.551
$N_{CH_{1.5}O_{0.7}}^0$	Entering moles of biomass	0.388
$N_{CO_2}^0$	Entering moles of carbon dioxide	0.051
$N_{H_2O_{(g)}}^0$	Entering moles of water vapor	*0*
$N_{H_2O_{(l)}}^0$	Entering moles of liquid water	*0*
$N_{H_2O_{(g)}}^0$	Entering moles of gas phase fuel	*0*
$N_{H_2O_{(l)}}^0$	Entering moles of liquid phase fuel	*0*
N_{CO}^0	Entering moles of carbon monoxide	*0*
$N_{H_2}^0$	Entering moles of hydrogen	*0*
N_{CH_4}	Exiting moles of methane	*0*
$N_{CH_{1.5}O_{0.7}}$	Exiting moles of biomass	*0*
N_{CO_2}	Exiting moles of carbon dioxide	*0*
$N_{H_2O_{(g)}}$	Exiting moles of water vapor	*0*
$N_{H_2O_{(l)}}$	Exiting moles of liquid water	0.393
$N_{CH_{2(g)}}$	Exiting moles of gas phase fuel	*0*
$N_{CH_{2(l)}}$	Exiting moles of liquid phase fuel	1
N_{CO}	Exiting moles of carbon monoxide	*0*
N_{H_2}	Exiting moles of hydrogen	*0*
e_9	Extent of the synthesis reaction	1.000
e_{10}	Extent of the reforming reaction	0.551
e_{11}	Extent of the gasification reaction	0.388
e_{12}	Extent of the water phase change	0.393
e_{13}	Extent of the fuel phase change	1.000
e_{14}	Extent of the water–gas shift reaction	0.061
$\Delta H_{\text{process}}$	Enthalpy change of the process	−34.5
$\Delta G_{\text{process}}$	Gibbs energy change of the process	0.0

Assumptions are italicized, whereas constraints are shaded. All other values come from the linear program solution.

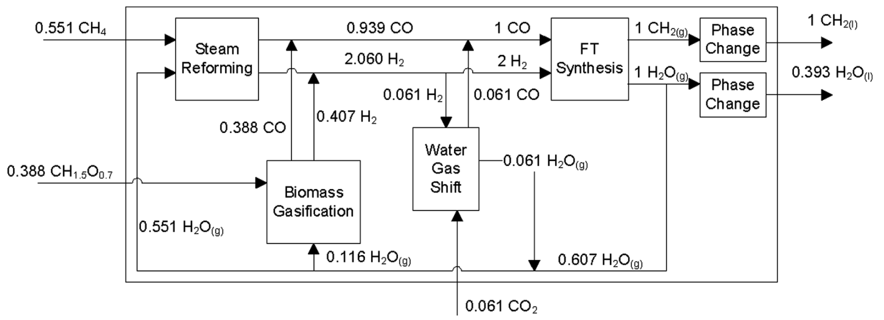

Figure 6. Feasible operation region satisfying the process constraints for BGTL processes.

Each independent reaction has its own "process box" where the inputs and outputs to that box correlate to its reaction extent as shown in Eqs. 15. In addition, one can look at the flows into and out of the overall box and see that the overall process mass balance is obtained. This preliminary flow map provides a starting point to determine the feasibility and the appropriate operating conditions for each of the process boxes. It must be noted here that each process box does not necessarily correspond to a single unit operation within the final flow sheet. Instead, each process box represents the amount of that particular reaction that occurs within the overall process. For example, the WGS reaction may occur in different proportions within a shift reactor in the process flow sheet, as well as the gasifier and in the F–T synthesis reactor (depending on the catalyst), with the total amount of WGS equal to 0.061. This also means that you can have reverse WGS occurring in one unit and then an additional amount of the forward WGS reaction occurring elsewhere to match the total amount specified. The total amount that occurs in each unit in the real process flow sheet is determined by many factors including the designer preferences, the choice of catalyst and operating conditions.

Determine feasibility of each process box

To this point, our analysis assumes that the conversion of the input species to the output species occurs at ambient conditions, which is obviously an unreasonable assumption, as the chemistry does not exist for such a transformation. Therefore, the next step is to determine at what temperature these conversions are possible (if at all) and inspect the effect these operating temperatures have on the overall process. Important to the successful conversion of the feed materials to the desired products is an analysis of the reaction equilibrium. We start with the definition of the reaction equilibrium that relates the concentration of the products to the concentration of the reactants. Prior knowledge tells us that the operating temperatures of the six independent reactions are at or above the boiling point of each of the liquid species (water and fuel), and, therefore, each species will exist in its gas state. Therefore, we can express the concentration of each species in terms of the partial pressure of the products and reactants assuming ideality.

$$K = \frac{\pi P^{\upsilon}_{\text{products}}}{\pi P^{\upsilon}_{\text{reactants}}} \tag{21}$$

where π is the successive product, and the partial pressures are raised to the power of the associated stoichiometric coefficients υ.

The total pressure can be written in terms of the partial pressure of each species

$$P_i = y_i P \tag{22}$$

where y_i is the mole fraction of each species i, and P is the total pressure. The mole fraction of each species is represented by

$$y_i = \frac{N_i}{N_T} \tag{23}$$

where N_i is the number of moles of species i and N_T is the total number of moles in the unit. The number of moles of each species can be written in terms of the reaction extent for that unit, similar to how the total number of moles of each species was written in terms of the extents of each of the independent reactions in section "Determine the Extent of Each of the Independent Reactions," Step 5. For example, the number of moles of water vapor entering the steam reforming unit can be represented by $N_{H_2O_{(g)},ref} = N^0_{H_2O_{(g)},ref} - e_{ref}$, where $N_{H_2O_{(g)},ref}$ is the number of moles of water vapor exiting the reformer, $N^0_{H_2O_{(g)},ref}$ is the number of moles of water vapor entering the reformer and e_{ref} is the reaction extent of the steam reformer. Combining these steps together, one can determine the reaction equilibrium constant as a function of the number of moles of each species entering the unit, the pressure of the unit and the desired reaction extent of the unit. In addition, assuming constant heat capacities, we can also write the same reaction equilibrium constant in terms of its temperature and enthalpy of reaction as shown in Eq. 24 as follows

$$K(T) = K^0 exp\left[\frac{-\Delta H_{rxn}}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \tag{24}$$

where K^0 can be calculated from

$$K^0 = exp\left(\frac{-\Delta G_{rxn}}{RT_0}\right) \tag{25}$$

T_0 is the ambient temperature in kelvin (K) and R is the universal gas constant 0.008314 J mol^{-1} K^{-1}. Therefore, we now have a way to calculate the necessary temperature, pressure and feeds entering a unit to achieve a desired extent, considering the specifics of the reaction occurring within that unit. Hence, the operating conditions are not chosen independently of the desired reaction extents, but must be chosen to achieve a certain extent to satisfy the overall process mass balance target.)

We will implement these steps moving from left to right in the flow map shown in Figure 6, starting with the reforming step.

Steam Reforming of Methane. The desired molar flows around the steam reformer unit are shown in Figure 7. What is still unknown is if the desired amount of hydrogen and

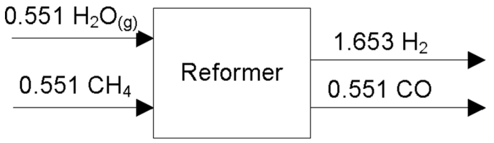

Figure 7. Desired flows around the steam reforming unit.

carbon monoxide can be produced at a reasonable temperature from an equimolar feed of methane and steam.

The equilibrium constant written in terms of the partial pressures of each of the species is shown in Eq. 26 as follows

$$K = \frac{P_{CO}P_{H_2}^3}{P_{CH_4}P_{H_2O}} = P^2\frac{y_{CO}y_{H_2}^3}{y_{CH_4}y_{H_2O}} \tag{26}$$

Notice the exponent of three on the partial pressure of hydrogen, because three times as much hydrogen is produced as any of the other species, as shown in Eq. 10. Each partial pressure can be written in terms of the number of moles of each species, giving the result in Eq. 27.

$$K = P^2\frac{N_{CO}N_{H_2}^3}{N_T^2 N_{CH_4}N_{H_2O}} \tag{27}$$

The number of moles of each species as a function of the extent of the reforming reaction is shown in the set of equations as follows

$$N_{CO,ref} = N^0_{CO,ref} + e_{ref} \tag{28}$$

$$N_{H_2,ref} = N^0_{H_2,ref} + 3e_{ref} \tag{29}$$

$$N_{CH_4,ref} = N^0_{CH_4,ref} - e_{ref} \tag{30}$$

$$N_{H_2O_{(g)},ref} = N^0_{H_2O_{(g)},ref} - e_{ref} \tag{31}$$

and the total number of moles of the system is

$$N_T = N_{H_2O_{(g)},ref} + N_{CH_4,ref} + N_{CO,ref} + N_{H_2,ref} \tag{32}$$

No moles of hydrogen and carbon monoxide are fed to the unit ($N^0_{CO,ref} = N^0_{H_2,ref} = 0$), so the resulting equilibrium constant written in terms of pressure, reaction extent and the number of moles of the reactants fed to the unit is

$$K = P^2\frac{27e_{ref}^4}{\left(2e_{ref} + N^0_{CH_4,ref} + N^0_{H_2O_{(g)},ref}\right)^2\left(N^0_{H_2O_{(g)},ref} - e_{ref}\right)\left(N^0_{CH_4,ref} - e_{ref}\right)} \tag{33}$$

One can now input the desired feed moles as shown in Figure 7 to determine K. However, notice that if $N^0_{CH_4,ref} = 0.551$ and $e_{ref} = 0.551$, Eq. 33 is undefined. Therefore, we choose an extent that is slightly less than that desired, that is, $e_{ref} = 0.999*0.551 = 0.5504$, in order for the mathematics to work out. The result is $K = 1.68 \times 10^6$, for $P = 1$ atm. Using this value, Eqs. 24 and 25, as well as $T_0 = 298$ K, $\Delta H_{ref} = 206.1\text{kJ mol}^{-1}$ and $\Delta G_{ref} = 142.1\text{kJ mol}^{-1}$, the required reformer temperature to achieve the desired flow as shown in Figure 7 is 2154 K. This is obviously too high, as most industrial equipment is made of stainless steel, which has resistance to oxidation in air up to 1373 K.[49] Therefore, we need to investigate changing the feed amounts to see if it is possible to achieve the desired extent at a more realistic temperature.

Looking at Eq. 33, there are only four variables with which to manipulate: e_{ref}, P, $N^0_{CH_4,ref}$ and $N^0_{H_2O_{(g)},ref}$. We desire e_{ref} to be equal to 0.5504 to achieve the desired reaction extent and $N^0_{CH_4,ref} = 0.551$, because methane is only a species in Eq. 10 (does not appear in Eqs. 9 or 11), so changing its amount will directly affect the overall process mass balance, shifting it away from our target. Therefore, P and $N^0_{H_2O_{(g)},ref}$ are the only two variables are our disposal. We will assume that the process occurs at ambient pressure, to start, so $N^0_{H_2O_{(g)},ref}$ will be the variable that is used.

The problem is to determine the amount of steam that must be fed to the reformer to achieve the desired reaction extent. The amount of steam fed is the amount required for the reaction (0.551 mol) plus the amount of excess steam required to drive the reaction to the desired extent. The amount of moles (total) required to drive the reaction to the desired extent at a given temperature is shown in Figure 8.

One can see that as the temperature decreases, the number of moles required to drive the reaction to the desired extent increases. Below a temperature of about 1300 K, the number of moles of steam required increases dramatically, suggesting that low-temperature operation would require large separation operations to remove the steam from the hydrogen and carbon monoxide produces and recycle streams to maintain the overall process mass balance, which are often costly and should be avoided. Notice also that at the Carnot temperature (959 K), the amount of steam recycle is very large, and, thus, operation at this point is not desirable. Therefore, it is desired to operate at a high temperature to minimize the amount of water recycle. On the other hand, the higher the temperature, the more specialized the materials become and for steam/methane feed ratios below 2, carbon deposition is observed,[50] so a steam feed of double the stoichiometric amount is chosen to minimize the steam recycle but prevent carbon deposition. The resulting temperature to achieve the desired conversion at this steam recycle amount is 1314 K. The resulting flow around the reforming unit is shown in Figure 9.

There is, however, a difficulty associated with operating the reformer at this temperature (1314 K) rather than at the reaction Carnot temperature (959 K). The difficulty is that now additional work than necessary will be carried in with the heat to bring the unit to temperature, thus, changing the overall process work balance ($\Delta G_{\text{process}} \neq 0$). How much

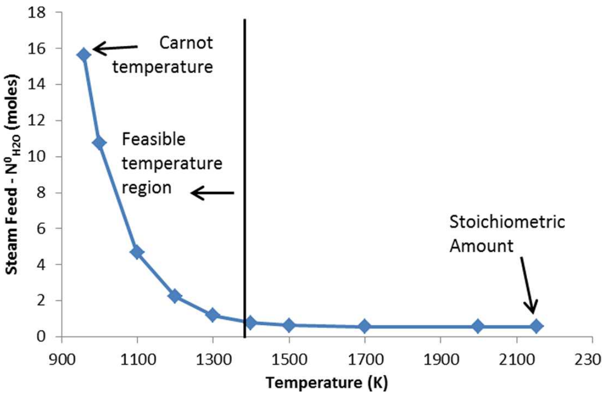

Figure 8. Required steam feed to the reformer to achieve e_{ref} = 0.5504 at P = 1 atm.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

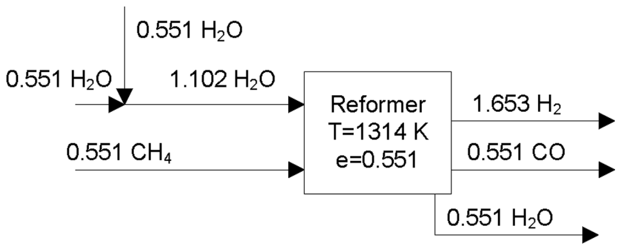

Figure 9. Flows around the steam reformer unit to achieve the desired reaction extent with a minimal steam excess.

extra work is added can be calculated with the following equation.

$$W_{\text{add}} = \Delta H_{rxn}\left(1 - \frac{T_0}{T}\right) \tag{34}$$

When providing the required amount of heat ($Q = \Delta H_{rxn} = 206.1$ kJ mol^{-1}) at T = 1314 K, an additional 17.3 kJ mol^{-1} of work is added to the unit, compared with if the same amount of heat were added at T = 959 K. This means that there is an additional amount of work available for other purposes. This will be discussed further later.

The procedure can be followed for each of the remaining independent mass balances, as shown briefly later.

Biomass Gasification. Operation of the biomass gasification unit is similar to the steam reforming unit in that steam is used as the control variable to produce the desired amounts of hydrogen and carbon monoxide from a given amount of carbon source (biomass). The only difference is that biomass is a solid material, so it does not appear in the equilibrium calculation. The resulting expression for the equilibrium constant is given in Eq. 35 as follows

$$K = P^{1.75}\frac{1.0526 e_{\text{gas}}^{2.05}}{\left(0.75 e_{\text{gas}} + N^0_{CH_{1.5}O_{0.7},\text{gas}} + N^0_{H_2O,\text{gas}}\right)^{1.75}\left(N^0_{H_2O,\text{gas}} - 0.3 e_{\text{gas}}\right)^{0.3}} \tag{35}$$

Once again an extent is chosen to be slightly less than that desired to avoid numerical discontinuities, in this case e_{gas} = 0.999*0.388 = 0.3876. With stoichiometric feed amounts, the required temperature to achieve the desired extent is 594 K, which is reasonable. However, as stated, it is desired to operate at the Carnot temperature, because at that temperature the heat carries in the required work with it, so the Gibbs energy change of the overall process is unaffected by the operating temperature. As a result, the number of moles of incoming steam is varied until the temperature at which the desired gasification reaction extent is achieved equals the Carnot temperature of the biomass gasification process (550 K). The required amount of steam is 0.123 mol, or an excess of 0.007 mol. Therefore, the resulting flow around the biomass gasification unit is as shown in Figure 10.

WGS. Determining the flow around the WGS unit is very much dependent on the preferences of the designer. One can either send all products from the reformer and gasifier directly to the WGS unit, then separate out the carbon monoxide and hydrogen, or separate the steam from the product streams of the reformer and gasifier, sending only the necessary amount of hydrogen to the WGS unit and the remainder of the hydrogen and carbon monoxide directly to the synthesis reaction. The former policy (everything to the WGS) requires only one separation (steam out of the WGS unit), whereas the latter policy requires three separation steps (steam removal from the product of the reformer, gasifier and WGS unit). Due to the costs associated with separation steps, the policy with fewer separation steps will be explored further.

The reaction equilibrium can be determined in a similar way, but by also taking advantage of the fact that a 2:1 H_2:CO molar ratio is required for the synthesis unit, or as a product from the WGS unit. Therefore, the number of moles of hydrogen and carbon monoxide can be expressed as a constant ratio rather than as a function of the reaction extent. The resulting equilibrium expression is, thus,

$$K = \frac{N^0_{H_2O,WGS} + e_{WGS}}{2\left(N^0_{CO_2,WGS} - e_{WGS}\right)} \tag{36}$$

As before, the expression is undefined for stoichiometric feeds and e_{WGS} = 0.061, so e_{WGS} = 0.999*0.061 = 0.06094. In addition, the initial number of moles of steam fed to the system is a function of the amount of recycle steam required by the reformer and gasifier, in this case $N^0_{H_2O,WGS} = 0.558$ mol. With these numbers, the temperature to achieve the desired extent is −1438 K, which is obviously unreasonable. Therefore, a recycle is required. As stated, recycling steam is not an option for the WGS unit because (1) steam is a product, so additional steam would push the reaction in the reverse direction and (2) the amount is already fixed by the reformer and gasifier unit. Therefore, from Eq. 36, the amount of carbon dioxide fed to the unit is an option for a recycle stream. The amount of carbon dioxide ($N^0_{CO_2,WGS}$) required to achieve an extent of e_{WGS} = 0.06094 at the Carnot temperature of the WGS reaction (974 K) is 0.370 mol. This means an excess of 0.309 mol of carbon dioxide fed to the unit and then recycled back to the unit. The flows around the WGS unit are shown in Figure 11.

F–T Synthesis. Design of the F–T synthesis unit follows the standard thermodynamic analysis used earlier, with no fuel or steam entering the unit. The resulting equilibrium expression is shown in Eq. 37 as follows

$$K = \frac{1}{P}\frac{\left(N^0_{CO,\text{syn}} + N^0_{H_2,\text{syn}} - e_{\text{syn}}\right)e_{\text{syn}}^2}{\left(N^0_{H_2,\text{syn}} - 2e_{\text{syn}}\right)^2\left(N^0_{CO,\text{syn}} - e_{\text{syn}}\right)} \tag{37}$$

e_{syn} = 0.999 to avoid the discontinuity, and the resulting temperature to achieve the desired extent is 396 K, which is reasonable but not equal to the Carnot temperature (683 K). In addition, there is no value of $N^0_{H_2,\text{syn}}$ when $N^0_{CO,\text{syn}} = 1$ or $N^0_{CO,\text{syn}}$ when $N^0_{H_2,\text{syn}} = 2$ (stoichiometric feeds with recycle) that achieves an extent of e_{syn} = 0.999 at T = 683 K. Therefore, recycling both components is considered (CO and H_2).

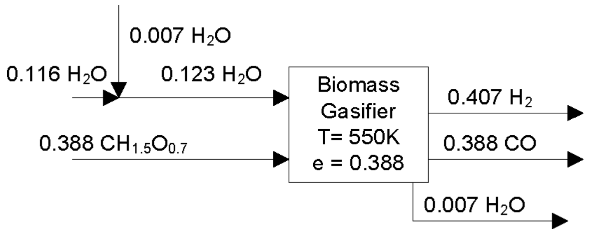

Figure 10. Flows around the biomass gasifier unit to achieve the desired reaction extent with the temperature of the unit at the Carnot temperature of biomass gasification.

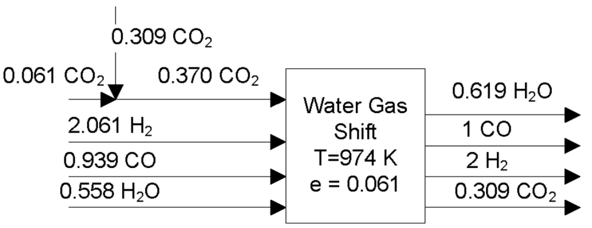

Figure 11. Flows around the WGS unit to achieve the desired reaction extent with the temperature of the unit at the Carnot temperature (T = 974 K).

Unfortunately, there is no reasonable value for the amount of recycle of each of the feed species to achieve the desired extent at the Carnot temperature. In fact, the smallest overall amount of feed needed is $N^0_{H_2,\mathrm{syn}} = 8$ mol and $N^0_{CO,\mathrm{syn}} = 3.45$ mol. The resulting separation steps to remove and recycle the carbon monoxide and hydrogen, from the fuel and steam product stream would be enormous (five times greater than the case with no recycle). Therefore, the option of recycle will not be considered, and the temperature of the unit is chosen to be 396 K. But, this choice has a work penalty associated with it due to the difference between the unit temperature and the Carnot temperature. Using Eq. 34, this work penalty is 49.6 kJ mol^{-1}, which will be addressed later in the text. The flow around the synthesis unit is shown in Figure 12.

In practice, the conversion of CO and H_2 in the F-T synthesis unit does not approach 100%, meaning that unreacted syngas will exit the unit, in addition to lower amounts of the desired products of CH_2 and H_2O. However, this is a catalyst/reactor/kinetics constraint, not a thermodynamic one, and, thus, noncomplete conversion is not considered here.

CH_2 Phase Change. Phase change reactions are straightforward, and the unit temperature is determined by the boiling point of the species. For the CH_2 phase change unit, this temperature is taken as the average boiling point of octane to dodecane, or 445 K. Notice that the Carnot temperature is 429 K. As the operating temperature is larger than the Carnot temperature, there is additional work that could possibly be recovered from the unit, with the exact amount determined by Eq. 34. This amount is 0.2 kJ mol^{-1}. The flows around the CH_2 phase change unit are shown in Figure 13.

H_2O Phase Change. The same procedure is followed for the steam to water phase change. This will occur at the boiling point of water (373 K). Again, the Carnot temperature is slightly less, so there is additional work that can potentially be recovered. This amount is 0.3 kJ mol^{-1}. The flows around the unit are shown in Figure 14.

Draw process flow map with mass integration and process temperatures

Now all the process streams (including recycles) and unit temperatures are known, so an updated mass integrated flow map can be drawn. This process flow map is shown in Figure 15.

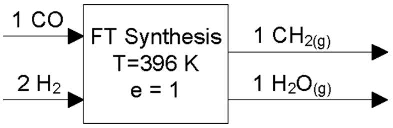

Figure 12. Flows around the synthesis unit to achieve the desired reaction extent for T = 396 K.

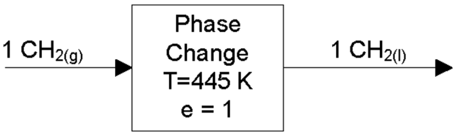

Figure 13. Flows around the CH_2 phase change unit at T = 445 K.

Once again, the overall process mass balance remains unchanged (identical to Eq. 8), and each unit now has a specified extent and operating temperature.

Identify separation steps and work requirements

Notice that three separation steps have been included in Figure 15: (1) removing the carbon dioxide from the WGS product stream to recycle back to the WGS unit, (2) removing the steam from the syngas feed to the synthesis reactor to add to the steam recycle and (3) removing steam from the F–T products to be sent back to the steam reformer and biomass gasifier. These separations require work and will, thus, affect the overall process work requirements. In addition, there are also mixing points throughout the process flow map, which have their own work of mixing associated with them.

The work of mixing is given by Eq. 38.

$$\Delta G_{mix} = nRT \sum_i x_i ln x_i \tag{38}$$

where n is the total number of moles in the stream, T is the temperature of that stream in K and x_i is the mole fraction of each component i in the stream. The work of separation is given by the negative of the work of mixing, only separating the desired component from the stream, that is, carbon dioxide from the WGS exit stream in separator (1). Ideal and perfect separations are assumed, which is an ambitious simplification, but it offers a starting point for operation. For example, the stream leaving the WGS unit has a composition $\left(CO_2, H_2O_{(g)}, CO, H_2\right) = (0.309,\ 0.618,\ 1.000,\ 2.000)$ for a total flow rate of 3.927 mol and the first separation unit only removes the carbon dioxide, or $\Delta G_{sep} = -3.927\ moles * \ 0.008314 \frac{kJ}{molK} * 974\ K * \left(0.08 * \ln(0.08) + 0.92 * \ln(0.92)\right) = 8.8\ kJ$. Therefore, 8.8 kJ will be required to separate 0.309 mol of carbon dioxide from the remainder of the stream. The same procedure can be repeated for the other two separation units to determine the additional work required. This information is shown in Table 5.

The same can be done for the streams exiting each of the units to calculate the work of mixing. This information is shown in Table 6. Again, notice that the work of mixing is negative (work producing), and the work of separation is positive (requires work).

One can see that there is a surplus of work to compensate for the separation steps as well as contribute to the other work deficiencies within the process.

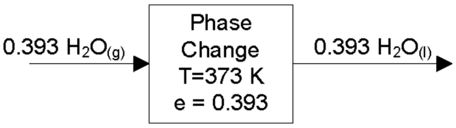

Figure 14. Flows around the H_2O phase change unit at T = 373 K.

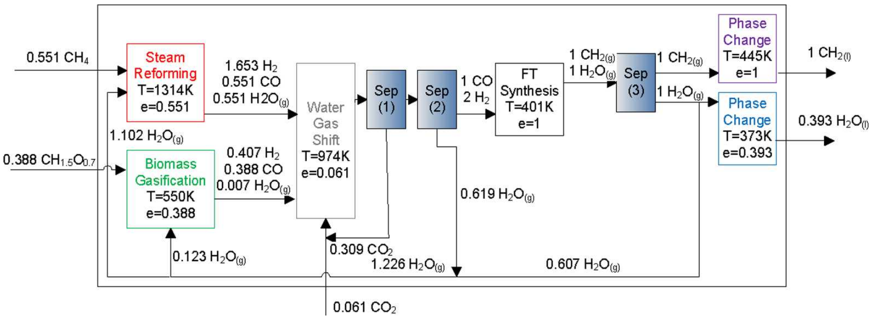

Figure 15. Mass integrated process flow sheet for the revBGTL process with unit temperatures and recycles to achieve each desired reaction extent.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Identify all work excesses/deficiencies

Balancing mass and energy in a process is straightforward and consistent: in = out. Work, on the other hand, does not balance, and, thus, processes that appear to be efficient from a mass and heat perspective may not be so from a work perspective. Once the overall target mass balance was chosen (Eq. 8), the mass and energy balances ($\Delta H_{\text{process}}$) remained unchanged. However, the choice of unit operating temperature and number of separation steps has an effect on the work requirements of the process, which will be looked at in more detail here.

The work requirements of each of the units shown in Figure 15, as well as the operating temperatures of those units and the T_{Carnot} of the six independent mass balances representing reactions are shown in Table 7. Remember that the overall process target is $\Delta G_{\text{process}} = 0$, so each of these values of ΔG_{add} is added to the overall process target.

For all units where $T \neq T_{\text{Carnot}}$, $\Delta G_{\text{add}} \neq 0$. If $T > T_{\text{Carnot}}$, then $\Delta G_{\text{add}} > 0$, or the unit has additional work that can potentially be recovered. On the other hand, if $T < T_{\text{Carnot}}$, then $\Delta G_{\text{add}} < 0$, or the unit requires additional work to proceed. For the overall process, $\Delta G_{\text{add}} = -14.9$ kJ mol^{-1}, meaning that, as written, the process is feasible and can possibly provide an additional 14.9 kJ mol^{-1} of work for another purpose. However, this assumes that there exists technology that can convert low-quality work into high-quality work, by, for example, utilizing the excess work generated in the synthesis unit operating at 401 K to provide the work required in the gasifier unit operating at 1314 K. This is infeasible, and additional work must be added through burning additional methane/biomass or by operating some of the units at a pressure greater than unity. Either approach is possible, but we will only investigate providing the required work through burning additional methane. Thus, all negative values in Table 7 corresponding to work streams exiting the unit will be neglected as unrecoverable, and the necessary work will be provided from a methane combustion unit operating alongside the process described earlier. This unit requires 76.4 kJ mol^{-1} of additional work, which corresponds to combusting 0.095 mol of methane with 0.190 mol of oxygen. The resulting process with the corresponding heat and work flows is shown in Figures 16 and 17, respectively.

Combining the overall process mass balance represented by Eq. 8 with the methane combustion process mass balances results in the following overall process mass balance

$$0.646\boldsymbol{CH}_4 + 0.388\boldsymbol{CH}_{1.5}\boldsymbol{O}_{0.7} + 0.19\boldsymbol{O}_2 \Rightarrow 0.034\boldsymbol{CO}_2 + 0.583\boldsymbol{H}_2\boldsymbol{O} + 1\boldsymbol{CH}_2 \quad (39)$$

Now carbon dioxide is a product, oxygen is a reactant and the carbon efficiency of the overall process has dropped from 107 to 97%. This is still attractive compared with the CTL and BTL individual processes and does utilize biomass, a potentially renewable fuel source, but the process exists outside of the ideal region in Figure 5, as carbon dioxide is now a product.

This analysis demonstrates that the production of liquid fuel with substantially reduced carbon dioxide emissions is possible. However, the analysis has made some simplifications about the process, which must be addressed. Specifically, we have assumed that:

- Only one reaction occurs within each box. As stated earlier, the process box is simply a representation of how much of each reaction is required to achieve the overall process mass balance. Varying extents of each reaction, especially WGS, may also occur in other units in the real process flow sheet, but at this point they have been neglected.
- Each feed is pure. A common source of methane is natural gas, which contains small amounts of higher hydrocarbons and other impurities. The same holds true for biomass, which also contains traces of sulfur and nitrogen. Each of these impurities will have to be accounted for in the overall process mass balance. However, at this stage in the analysis, the contribution of these impurities is small (<10% by weight),[10] and the goal is to target ideal operation as a benchmark for comparison between potential routes to liquid fuel.

Table 5. Work of Each of the Separation Units for the revBTGL Process Flow Sheet in Figure 15

Separation Unit	Composition				Mole Fraction to Separate		ΔG_{sep} (kJ)
1	CO_2 0.309	$H_2O_{(g)}$ 0.619	CO 1.000	H_2 2.000	CO_2 0.08	from $H_2O_{(g)}$,CO, H_2 0.92	8.8
2		$H_2O_{(g)}$ 0.619	CO 1.000	H_2 2.000	$H_2O_{(g)}$ 0.17	from CO, H_2 0.83	13.4
3			$H_2O_{(g)}$ 1.000	$CH_{2(g)}$ 1.000	$H_2O_{(g)}$ 0.50	from $CH_{2(g)}$ 0.50	4.6
						Total	**26.8**

Table 6. Work of Each of the Mixing Location for the revBGTL Process Flow Sheet in Figure 15

Mixing Location	Composition				ΔG_{sep} (kJ)
Exiting reformer		$H_2O_{(g)}$	CO	H_2	−28.6
		0.551	0.551	1.653	
Exiting gasifier		$H_2O_{(g)}$	CO	H_2	−2.7
		0.007	0.388	0.407	
Exiting WGS	$C0_2$	$H_2O_{(g)}$	CO	H_2	−37.6
	0.309	0.619	1.000	2.000	
Exiting synthesis			$H_2O_{(g)}$	$CH_{2(g)}$	−4.6
			1.000	1.000	
			Total		**−73.6**

Table 7. Work of Each of the Units for the revBGTL Process Flow Sheet in Figure 15

Unit	T (K)	T_{Carnot} (K)	ΔG_{add} (kJ mol^{-1})
Reformer	1314	959	−17.3
Mix, ref	1314	–	−28.6
Gasifier	550	550	0.0
Mix, gas	550	–	−2.7
WGS	974	974	0.0
Mix, WGS	974	–	−37.6
Sep 1	974	–	8.8
Sep 2	974	–	13.4
Synthesis	401	683	49.6
Mix, syn	401	–	−4.6
Sep 3	401	–	4.6
H_2O phase	373	370	−0.3
CH_2 phase	445	429	−0.1
	Total		−14.9

- All processes/separations are perfect. Obviously, separations and efficiencies of each individual unit will not be 100% efficient, and this must be dealt with by including impurities within each stream (including unreacted feed material). However, at this level of detail the goal is to determine what processes offer the most potential for further investigation and identify major sources of chemical inefficiency, rather than attempt to include all minor efficiencies associated with units that may not be necessary. Either way, our analysis demonstrates how well a process could perform with more ideal separations, that is, membranes and 100% conversion.
- All reactions are controlled by thermodynamics, not kinetics. Admittedly reaction equilibrium and catalyst performance may be more important than some thermodynamic limitations (such as the F–T synthesis reaction), but this assumption is necessary to compare processes from an equipment independent viewpoint. We have shown that it is possible to achieve close to 100% conversion in each unit through manipulation of feed flow rate and temperature, but kinetic and thermal limitations may dominate and limit conversion at a value less than 100%, affecting the overall process mass balance. This also has implications for the separation processes.
- Heat and work integration technology is available. It is assumed that technology exists to transfer heat and work from one process to another with 100% efficiency. This is obviously a simplification, and future work should address technological limitations and incorporate realistic inefficiencies.
- *Hydrogen shortage*. We have assumed liquid fuel is a CH_2 monomer, but additional hydrogen would be required to terminate the monomer chains in the diesel/petrol range. This will result in less WGS or more gasification/reforming, which will affect the overall process mass balance.
- *Ambient pressure*. We have assumed the process will occur at ambient pressure, which is unlikely given the current normal operating conditions for some of the units, reforming and synthesis in particular. However, we have shown that, in theory, it is possible to achieve the desired conversion at ambient pressure, so further work is required to investigate this possibility.

Relaxing any of these assumptions affects all balances over the process (mass, heat and work) and, thus, the design process is highly iterative with each additional complication included. The next step in the design process is to develop a comprehensive process flow sheet on a process simulator, such as ASPEN Plus,[10,20,26] to relax the above assumptions and determine the effect of process inefficiencies on the overall process performance. All that being said, this analysis still provides a methodology to evaluate potential processes and develop process flow maps with readily available thermodynamic information with simple linear mathematics in a matter of days, rather than on the order of weeks with complex mathematics and elaborate simulation tools. In addition, the designer now has confidence that the selected process is the most promising of similar alternatives, adding credence to the results of subsequent analyses.

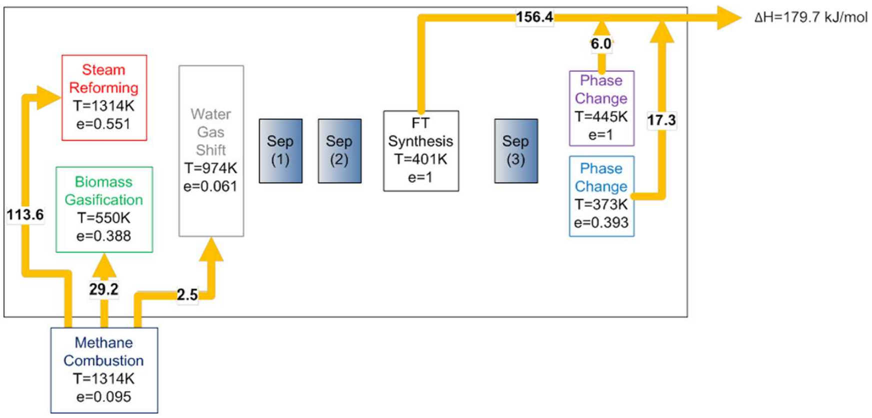

Figure 16. Heat integrated process flow map for the revBGTL process as shown in Figure 15 with supplemental heat provided by methane combustion.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

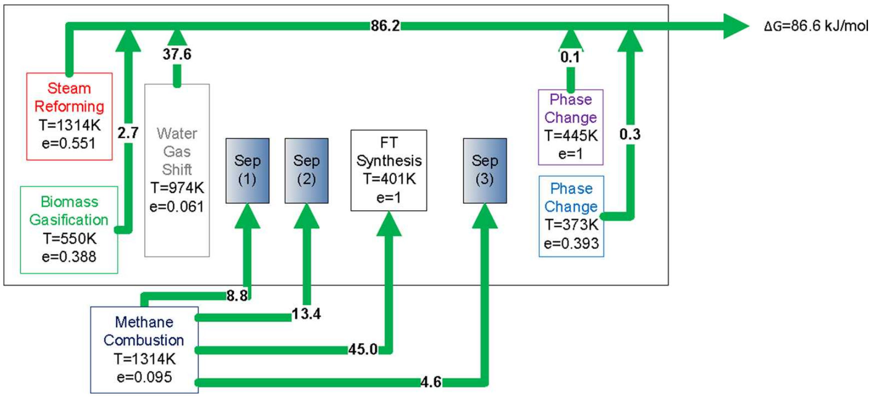

Figure 17. Work integrated process flow map for the revBGTL process as shown in Figure 15 with supplemental heat provided by methane combustion.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Therefore, this approach and a more detailed simulation approach are cooperative, with one providing a simple and quick approach to make decisions early and reduce the parameter space, whereas the more detailed design includes all relevant units and develops a proper process flow sheet. We have shown here that you can formulate a BGTL process to maximize chemical potential of the feed with minimal CO_2 emissions inherent in the design.

Summary

In summary, we have investigated seven processes for producing synthetic liquid fuels using varying feed stocks: coal, natural gas, biomass and combinations thereof. The methodology presented here is a straightforward means of identifying processes that are less worthy of further investigation (CTL and BTL) and focus on those that do show promise, such as GTL, BGTL and CGTL. Targets are derived to which engineers can compare existing and future designs to identify and remove sources of inefficiency as a result of irreversibilities. Utilization of our approach can drastically alter the perception of synthetic fuels as being undesirable from an environmental perspective, especially the production of liquid fuels from coal. Combining feed stocks can also help to introduce a renewable resource into the manufacturing progress, stimulating further research in the field of renewable resources and assist the transition from a fossil fuel based energy infrastructure to a more renewable based energy infrastructure. Thus, environmental impact of emerging technologies can be minimized, while also enabling developing countries, often in possession of reserves of both natural gas and biomass, to feed the needs of their burgeoning economies. We hope that our approach will enable transformation of current technology to make liquid fuels from various carbon sources (specifically coal, natural gas and biomass), that unlike the current methods that all produce large amounts of carbon dioxide emissions during the manufacturing process, produce close to zero levels of carbon dioxide. That we are able to make this significant advance is because of a breakthrough in the methods used to synthesize plant flow maps, the details of which have been demonstrated in this article. Also, this approach can assist in developing efficient processes to utilize hydrogen derived from solar power as suggested by Agrawal et al.[2] and Floudas and coworkers[26–30] in an effort to develop a completely sustainable, synthetic carbon cycle. Nature has taken thousands of years to convert plant matter to oil, and we are proposing a methodology that can help achieve the same goal in a much shorter time frame, while also utilizing other resources with a lower environmental burden.

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