PRODUCTION OF LIQUID DIESEL FUEL VIA GASIFICATION OF MUNICIPAL SOLID WASTE: PROCESS SYNTHESIS, SIMULATION, OPTIMIZATION, ENERGY INTEGRATION, AND ECONOMIC ANALYSIS

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1 EXECUTIVE SUMMARY

In this report, we evaluate a proposed process for converting municipal solid waste (MSW) to liquid transportation fuels. The aim is to maximize the profitability of the process, under the stipulation that 5,000 barrels/day of liquid transportation fuels are produced, with the additional goal of maximizing production of diesel. A methanol synthesis approach is utilized, and the entire process is modeled in AspenPlus to a high degree of accuracy. The simplifying assumptions that are made are discussed and justified.

Following MSW pretreatment to wet refuse derived fuel (RDF), the process begins with 383,784 kg/hr of wet RDF that is dried and passed through a gasifier, in which pyrolysis reactions are used to convert the biomass in the RDF to synthesis gas at a flowrate of 18,310 kmol/hr, plus various contaminant species. After the syngas is cleaned and usable waste is salvaged in the form of solid sulfur, the syngas is passed to a methanol synthesis reactor at a rate of 9,456 kmol/hr. This syngas is mixed with an H_2 stream from a pressure-swing absorption (PSA) unit and a vapor recycle stream designed to increase conversion to methanol in an equilibrium-modeled reactor. The total feed to the methanol synthesis reactor is 50,386 kmol/hr. The crude methanol product is sent to a degasser distillation column to produce a purified product stream of water and methanol at a flowrate of 4,990 kmol/hr, of which 1,191.55 kmol/hr is methanol. This stream is then converted to olefins and, subsequently, liquid transportation fuels using a methanol-to-olefins (MTO) and mobile olefin-to-gasoline-distillate (MOGD) approach. After separating the product diesel and gasoline streams and recycling light gases for combustion, the process yields 73.4787 kmol/hr of diesel and 17.1317 kmol/hr of gasoline. The volumetric flowrate of liquid diesel and gasoline is 4442.40 barrels/day and 557.75 barrels/day, respectively, for a total liquid transportation fuel product flowrate of 5000.15 barrels/day. An acceptably high proportion of 88.85% diesel in the product liquid transportation fuels is achieved.

Heat exchange network synthesis is performed in order to minimize the annual cost of utilities needed to meet the energy needs of the process and to minimize the number of heat exchangers needed. The process features 23 hot streams, 14 cold streams, and 5 available utilities, resulting in 27 temperature intervals. An LP transshipment model is developed and solved in GAMS, indicating two subnetworks and a minimum annual utility cost of $83,346,477/year after electricity cost is included. An MILP model is solved in GAMS using the residuals and utility heat loads reported by the LP model, yielding a minimum of 36 matches across both subnetworks. The heat exchanged for each match is used to determine the size and cost of the 36 heat exchangers needed.

Economic analysis is performed in order to assess the profitability of the proposed process and highlight the greatest contributions to capital

investment and manufacturing cost, along with further areas for possible research. The total direct cost of all units is determined using cost functions from the Problem Statement and literature sources, a base module cost approach for heat exchangers using area calculated from heater duties, or Aspen PEA for units other than heaters where the cost functions are not available. Indirect cost is assumed to be 32% of total direct cost. The calculated total capital investment is $1,409,579,809. This value is then used, in conjunction with utility calculations, to determine manufacturing costs, including direct and indirect costs. The total manufacturing costs are $362,656,466/year, assuming a tipping fee of $70 per metric ton of MSW. Net profit after taxes is assessed using Guthrie's Method, resulting in a projected net profit after taxes of -$219,535,070/year. Net Present Value is calculated to be -$2,458,086,291. The proposed process is not profitable for a number of reasons that will be discussed later, including the fact that due to the high input rate of RDF, manufacturing costs are higher than proceeds from sales. Parametric analysis indicates that the process is expected to break even annually at a tipping fee of $160/ton for MSW.

The recommended steps for future work are to focus on improving the carbon conversion from the 8.37% achieved. Although the process is not currently profitable, it is possible that by further optimizing the carbon conversion and reducing the necessary feed rate of wet RDF to the process, it will be profitable. However, if those improvements require inclusion of different process units, it is possible that the different operating cost of those units will still lead to a process that is not economically feasible. As gas prices rise and the need for alternate fuel sources becomes more dire, it is possible that the proposed process will be viable.

2 INTRODUCTION

The process of converting municipal solid waste (MSW) to liquid transportation fuels (LTF) has been discussed in a previous report [8]. A first iteration to simulate the proposed process has been completed, including an economic analysis to assess preliminary feasibility [9]. Producing LTF via alternative methods is an important problem due to the increasing transportation fuel burden in the US [14], and the increasing dependence on the volatile global oil market [1]. MSW is a commercially viable biomass source because it is negatively priced and has a heating content of 11.73 MMBtu/ton [15]. Two process alternatives have been proposed for LTF production, one involving methanol synthesis and another using Fischer-Tropsch synthesis [8]. Methanol synthesis is projected to be preferable for maximizing production of diesel transportation fuels on the scale of 5,000 barrels/day [7], and is discussed in detail in this report. The alternative Fischer-Tropsch process is included and briefly discussed in the Appendix. The background considerations for each process units

have been discussed at length, and are also included in the Appendix. In this report, we implement several optimizations to the previously discussed steady state AspenPlus process simulation [8]. Additionally, heat integration of the entire process is conducted to minimize costs of utilities and heat exchangers, and a complete economic analysis is carried out to more accurately assess the profitability of the entire proposed process.

Representative units for the simulation are chosen for each process unit, with reasonable operating parameters derived from various literature sources. Operating parameters include temperature, pressure, split fractions, occurring reactions, molar flowrates, distillation column tray numbers and reflux ratios, and more. This report will first briefly lay out the problem statement, along with the objectives used to guide design decisions. The process approach will then be described in detail, including AspenPlus units used, operating parameters, and total steady state flowrates through the various units, as well as the species flowrates of the most important species involved. Process optimizations will be discussed in detail, including sensitivity analysis of the methanol synthesis reactor operating temperature. Heat integration calculations will be presented, including the hot and cold streams used to model the process, the utilities available, the minimum annual cost of utilities for the plant, the minimum number of stream matches, and the details of the corresponding heat exchangers needed. Important safety considerations will then be discussed to outline possible issues with implementing the process from a practical perspective. Finally, in the economic analysis, the cost functions and costs based on inlet and outlet flowstreams for each unit will be described, along with cost considerations for utilities and raw materials used. Economic analysis results of the entire process will be reported. Finally, the conclusions reached regarding the calculated profitability of the process will be discussed, and areas for future research indicated.

3   PROBLEM STATEMENT AND OBJECTIVES

The primary objective is to model a process for converting MSW to LTF that is maximally profitable. The process is designed based on based on various process considerations discussed in literature, in addition to carrying out heat integration to minimize utility costs and optimizing important units. The target LTF production of the process is 5,000 barrels of LTF per day while maximizing diesel production. An input flowrate of RDF is chosen and units are sized appropriately to accommodate this desired output. The cost of utilities following heat integration, credits based on raw materials, and total capital investment for all units are taken into account. Fixed and operating costs are compared to the gross income from the LTF and all usable byproducts, and the net annual profit is calculated and reported in addition to other metrics of profitability.

4 DESCRIPTION OF APPROACH

This section will describe in detail the AspenPlus process units used to simulate the proposed process and the resultant flowrates of all streams through each unit. The molar flowrates of relevant species and operating conditions of all units will be reported as well. The entire process flow diagram is shown in Figure 13 on page 48. Each overarching section is justified in the following sections in terms of the reasons for its inclusion. Specific units are discussed as subsections within their overarching section.

4.1 Municipal Solid Waste Pretreatment

Following treatment of MSW at a RDF facility (not modeled), a feed stream of raw RDF is input to the process at a flowrate of 383,784 kg/hr. The units for this section are displayed in Figure 1. This flowrate is calculated retroactively after determining the efficiency of RDF to LTF conversion in the proposed process and scaled such that 5,000 barrels of LTF per day are produced. The feed stream conditions are standard conditions of 25°C and 1 bar. This is fed into a dryer unit, implemented as an AspenPlus User2 model. The dryer unit reduces the moisture content of the raw RDF from 28% to 8.8%, as specified in the Problem Statement [7], producing outflow streams of 302,988 kg/hr of dry RDF and a wastewater stream of 4,484.9 kmol/hr of pure water, which is purged. The dry RDF serves as the feed stream to the gasification section.
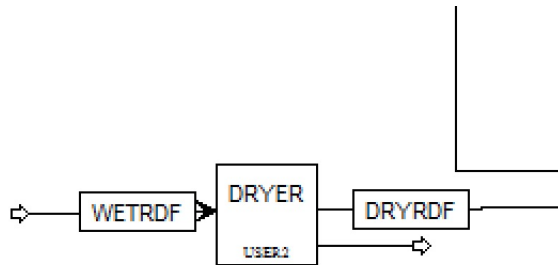
Figure 1: Pretreatment of Wet RDF Diagram.

4.2 Gasification

The gasification section is necessary for converting the dried RDF into synthesis gas to be used to form methanol, along with a variety of contaminants to be removed, such as ash, char, nitrogen compounds, and sulfur compounds. This is done using a pressurized, oxygen–blown fluidized–

bed gasifier [2, 8], in which pyrolysis reactions occur to convert the carbon compounds present in the RDF to various C_1–C_2 hydrocarbons. The necessary steps taken to form syngas from the input stream of dry RDF are outlined below. A diagram of the gasification section is shown in Figure 2.
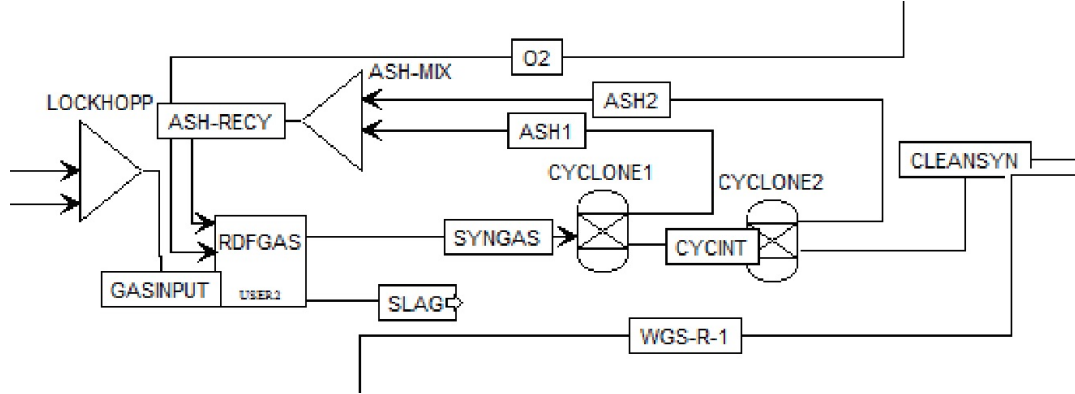
Figure 2: Diagram of Gasification Section.

4.2.1 Lockhopper

The 302,988 kg/hr input stream of dried RDF is first fed into a lockhopper, along with a stream of 30,298.8 kg/hr of compressed CO_2 recycled from the Rectisol unit. The recycle stream is used so that CO_2 does not need to be purchased and so less CO_2 is vented from the Rectisol unit. The CO_2 feed is recycled at a rate of 10wt% / dry RDF, as specified in the Problem Statement [7]. As no reactions or changes to conditions are occurring, the lockhopper is modeled simply as a mixer operating at 1100K and 1 bar. The resultant stream of 333,286 kg/hr of mixed RDF and CO_2 is fed into the gasifier.

4.2.2 RDF Gasifier

The gasifier is implemented as a User2 model. The input streams are 333,286 kg/hr of mixed RDF and CO_2 from the lockhopper, a pure oxygen stream of 6,908 kmol/hr, and an ash/char recycle stream of 201.436 kg/hr. The oxygen stream is necessary to enable gasification via pyrolysis, and the flowrate is experimentally determined to ensure complete gasification. The recycle stream flowrate is the result of steady state operation of the gasifier and cyclone units generating the recycle stream, to be discussed below. The gasifier effluents are a 537,996 kg/hr syngas stream (18,310.4 kmol/hr, excluding the nonconvential ash and char species) and a 16,386.1 kg/hr slag stream, composed of 99% of the ash input to the gasifier [7]. The slag stream is purged. The 17 components in the syngas outflow stream are CO_2, CO, H_2, H_2O, CH_4, C_2H_2, C_2H_4, C_2H_6, N_2, NH_3, HCN, NO, N_2O, H_2S, Ar, Char, and Ash [7]. The conversion of the RDF, CO_2, O_2, and ash/char recycle input streams to each of these

components is calculated using the equations and specifications given in the Problem Statement [7]. The calculations are implemented in the Excel spreadsheet for the AspenPlus User2 model. The molar outflow rates of each component in the syngas are displayed in Table 1. The gasifier is modeled as operating at 1100K and 1 bar, the same conditions as the input streams.

Table 1: Composition of Raw Syngas Gasifier Effluent

Species		Flow Rate (kmol/hr)
H_2O	Water	4,946.55
O_2	Oxygen	0
CO_2	Carbon Dioxide	7,781.59
H_2	Hydrogen	1,481.62
CO	Carbon Monoxide	2,359.94
CH_4	Methane	900.86
C_2H_2	Acetylene	477.14
C_2H_4	Ethylene	280.02
C_2H_6	Ethane	25.79
N_2	Nitrogen	23.08
NH_3	Ammonia	3.92e-06
HCN	Hydrogen Cyanide	5.20e-5
NO	Nitric Oxide	0.34
N_2O	Nitrous Oxide	2.39
H_2S	Hydrogen Sulfide	31.02
Ash		165.51 (kg/hr)
Char		35.92 (kg/hr)

4.2.3 Cyclones

The gasifier syngas effluent is passed through primary and secondary cyclones in order to remove all of the remaining solids. The cyclones are both modeled as separators with ash and char recycle stream split fractions of 0.99 for the first cyclone and 1 for the second cyclone, as specified in the Problem Statement [7]. The ash/char streams from the two cyclones are mixed, resulting in a total of 201.44 kg/hr of ash/char that is recycled back to the gasifier. The remainder of 18,310.4 kmol/hr of syngas vapor that is now more pure is fed to the syngas cleaning section. The cyclones both operate at 1100K and 1 bar, the same operating conditions as all other units in this section.

4.3 Synthesis Gas Cleaning

This part of the proposed process is necessary in order to remove residual byproducts and contaminants from the syngas. The target ratio of H_2/CO

in the syngas is 2 [1]. Syngas effluent from the cyclones at a flowrate of 18,310.4 kmol/hr is sent to a water–gas–shift reactor followed by a series of cleaning and waste recovery units, as described below. At the end of this section, the final outflow of clean syngas to be fed to the methanol synthesis reactor is 9,456 kmol/hr, and will now contain only water, CO_2, H_2, CO, CH_4, and nitrogen species. The units for the syngas cleaning section are shown in Figure 3.
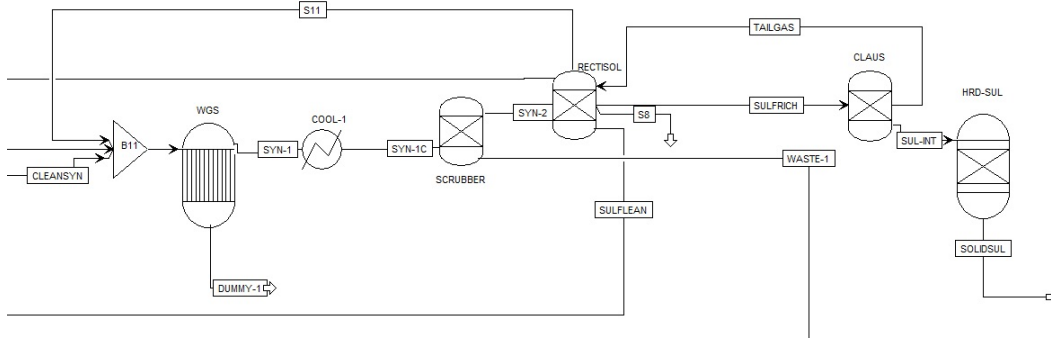
Figure 3: Flowsheet for Syngas Cleaning Units.

4.3.1 *Water–Gas–Shift Reactor*

A sour water–gas–shift reactor (WGS) is employed to increase the H_2/CO ratio, which will later be beneficial to improve methanol output in the methanol synthesis reactor [16]. This is discussed further in the optimization section. The WGS reactor operates at 26 bar and 350°C. The operating temperature is increased to 350°C from 300°C, which was the operating temperature in the past iteration [9]. The reactor runs the forward WGS reaction, displayed in equation 1. The reactor is forced towards the forward reaction by the addition of a 4107.71 kmol/hr CO_2 recycle stream from the Rectisol unit and a 77.0855 kmol/hr H_2 recycle stream from the PSA unit, discussed later. This is done to optimize later production of methanol.

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad (1)$$
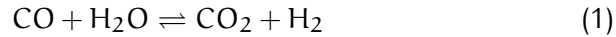
The WGS is modeled in AspenPlus as an REquil. Equation 1, the WGS reaction, is the only reaction occurring in the reactor. The input and output flowrates of the species involved in the WGS reaction are reported in Table 2 on the next page. The resultant Ribblett ratio at the methanol synthesis reactor inlet is 0.3904. The 22,495 kmol/hr of product gas is cooled to 49°C before being sent to the sour syngas scrubber.

Table 2: Composition of WGS-Active Species in Reactor Inlet and Outlet

Species	Inlet (kmol/hr)	Outlet (kmol/hr)
CO	2359.94	654.84
H_2O	4946.55	3241.44
CO_2	11889.30	13594.40
H_2	1558.7	3262.81

4.3.2 Sour Syngas Scrubber

The sour syngas scrubber is important in order to clean the syngas before methanol synthesis. It removes all tar, particulates, and NH_3 still present in the syngas [7]. This is modeled in AspenPlus as a separator, with split fractions such that all NH_3, C_2H_2, C_2H_4, and C_2H_6 are directed to a waste stream, and all other species remain in the syngas effluent. The two-carbon species are diverted to the waste stream because they will not take part in methanol synthesis. Instead, they are diverted to the biological digester and combined with other waste streams to produce CH_4 and CO_2, which can be safely disposed. The result is a syngas effluent that is sent to the Rectisol unit and a waste stream of 783 kmol/hr containing only the aforementioned species.

4.3.3 Rectisol Unit

The Rectisol unit is a dual-capture methanol absorption system that is necessary to further purify the syngas by removing all of the H_2S and 90% of the CO_2. Taking the 21,712 kmol/hr of syngas inlet plus a tail-gas CO_2/H_2S recycle stream from the Claus recovery system (discussed below), the Rectisol unit produces a sulfur-rich stream, three pure CO_2 streams, and a syngas effluent intended for the methanol synthesis reactor. Multiple sulfur streams are used in order to recycle CO_2 as needed to several previous units, as discussed further in the optimization section. The Rectisol unit is implemented as a separator in AspenPlus, with split fractions such that 10% of the CO_2 is allowed to remain in the syngas. The division of the rest of the CO_2 is determined via a design specification maintaining a molar ratio of 3:1 CO_2 to H_2S in the sulfur-rich stream [7]. The remainder of the CO_2 goes to three pure CO_2 streams, one of which is recycled back to the lockhopper, one of which is purged, and one of which is recycled back to the WGS reactor. The WGS recycle stream is added to promote further CO production. The resulting outlet streams are 7,429.01 kmol/hr of pure CO_2 vented, 4,107.71 kmol/hr of pure CO_2 recycled to the WGS reactor, 688.46 kmol/hr pure CO_2 recycled back to the lockhopper, 130.62 kmol/hr of sulfur-rich stream in the aforementioned ratio of CO_2:H_2S that is sent to the Claus recovery system, and 21,712.2 kmol/hr of clean syngas that can now be sent to the methanol synthesis reactor.

4.3.4 *Claus Recovery System*

The Claus recovery system is used in order to convert some of the sulfur compounds to more useful solid sulfur [7]. This unit is modeled as a separator, in which 95% of the input H_2S is separated to a waste stream, and the rest of the H_2S and CO_2 is recycled back to the Rectisol unit in order to recover the remainder of the sulfur. The inlet to the unit is 130.62 kmol/hr of CO_2 and H_2S from the Rectisol unit. The resulting outlet streams are 31.023 kmol/hr of pure H_2S and 99.599 kmol/hr of a tailgas recycle stream composed of the balance of H_2S and CO_2. The pure H_2S stream is converted to a purge stream of 31.023 kmol/hr of pure H_2 and 31.023 kmol/hr of solid sulfur, which is sold. This is done using a RYield reactor operating at 49°C and 1 bar.

4.4 Methanol Synthesis

The purpose of the methanol synthesis section is to take the inlet syngas species from the syngas cleaning section and form methanol via the methanol synthesis and WGS reactions. The methanol is later upgraded to the target fuel-range hydrocarbons. The inlet to this section is the 9,456 kmol/hr of clean syngas that is produced following the Rectisol unit. This syngas stream consists of water, CO_2, H_2, CO, CH_4, N_2, HCN, NO, and N_2O. The stream is first heated to 250°C to ensure that it is entirely vapor, and then compressed to 51 bar, as specified in the Problem Statement [7]. All compression units are assumed to have an efficiency of 0.72, which is the default efficiency assumed by AspenPlus. The stream is now ready to be input into the methanol synthesis reactor, described below. After a series of further steps to be discussed, the product of this section is a 4,990.33 kmol/hr methanol and water stream that can be converted to hydrocarbons. The process units responsible for methanol synthesis are diagrammed in Figure 4.

Figure 4: Diagram of Methanol Synthesis Section.

4.4.1 Methanol Synthesis Reactor

The methanol synthesis reactor operates at 200°C and 50 bar [7]. The temperature is decreased from 300°C in the previous iteration in order to improve the rate of methanol production. In addition to the 9,456 kmol/hr of clean syngas inlet, the reactor also takes a 40,396.3 kmol/hr vapor recycle stream of syngas species intended to increase yield, as well as a 534.473 kmol/hr pure hydrogen stream generated by the PSA unit (discussed later) that serves to push the methanol synthesis and WGS reactions in the forward direction. Ideally, a Ribblett ratio of 1 is desired. The Ribblett ratio is defined in Equation 2.

$$H_2/(2CO + 3CO_2) \qquad (2)$$

The current process has a Ribblett ratio of 0.39. Although this ratio is lower than the original target of 1, adjusting the H_2 recycle stream from the PSA to increase the Ribblett ratio did not improve production of methanol or recovery following the flash unit. A mixer is used to combine the streams, and the total inlet and outlet flowrates of all species to the reactor are shown in Table 3. The reactor itself is modeled as a REquil in AspenPlus, with the following reactions occurring:

$$CO + 2H_2 \rightleftharpoons CH_3OH \qquad (3)$$
$$CO_2 + H_2 \rightleftharpoons CO + H_2O \qquad (4)$$
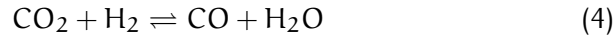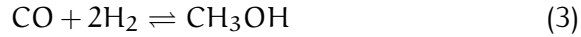
Table 3: Composition of Methanol Synthesis Reactor Input and Effluent

Species	Input (kmol/hr)	Effluent (kmol/hr)
H_2O	3294.74	3855.49
CO_2	13810.7	13249.9
H_2	16847.4	13882.1
CO	862.499	220.97
CH_4	14992.9	14992.9
N_2	384.595	384.595
HCN	7.189e-04	7.189e-04
NO	5.696	5.696
N_2O	38.0957	38.0957
CH_3OH	149.281	1351.56

The effluent is cooled to 35°C [7] and then sent to the flash unit as described below. The total molar flowrate of the cooled product from the methanol synthesis reactor is 47,981.4 kmol/hr.

4.4.2 Flash Methanol Separation

As shown in Table 3, the methanol in the effluent from the methanol synthesis reactor is only 2.82 mole% of the effluent stream. A unit is thus

needed to separate the crude methanol from the rest of the species to create a stream of higher methanol concentration. Since methanol and water are the only two species present that can hydrogen bond, this can be accomplished using a vapor–liquid equilibrium flash unit, in which the liquid stream will be highly rich in methanol and water. This is modeled in AspenPlus using a vapor–liquid flash unit operating at 35°C and 48 bar [7]. The effluent liquid stream successfully recovers 1,192.74 kmol/hr of methanol, or 88.2% of the methanol from the recycle stream. This recovery rate is reasonably high, and indicates that the Ribblett ratio of 0.39 in the inlet (defined in equation) is not a significant concern, despite being lower than the target . This configuration is optimized to reduce the excessively large recycle stream flowrate present in the previous iteration [9] and achieve maximum methanol recovery. The liquid flash effluent also contains 3,798.78 kmol/hr of water in addition to the methanol, plus trace concentrations of other species present in the synthesis reactor effluent, for a total flowrate of 5,006.6 kmol/hr. The crude methanol liquid stream will be sent to a degasser distillation column.

The vapor product from the flash separator has a flowrate of 42,974.8 kmol/hr and is mostly H_2, CO_2, and CH_4. This vapor stream is split into three streams as follows: 94% of the stream is compressed to 51 bar and recycled back to the methanol synthes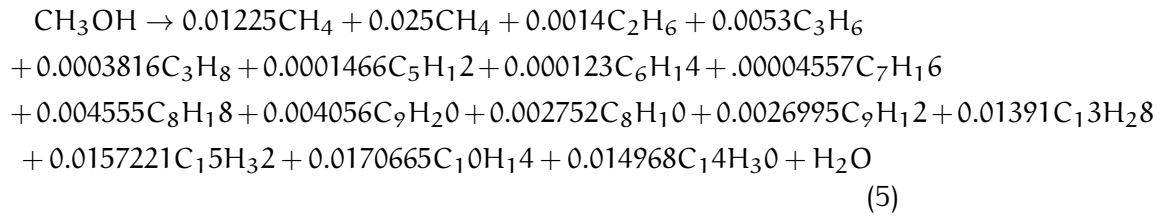is reactor in order to improve conversion of syngas species to methanol. 94% is chosen here instead of the suggested 95% [7] to ensure convergence of the recycle stream at steady state in the AspenPlus simulation. Another 5% is diverted as a purge stream to be utilized as fuel gas, specifically for the production of pure hydrogen through a PSA unit (discussed later). The remaining 1% is purged as a waste stream and sent to the external gas loop, eventually being processed by a biological digester. These ratios are again determined to allow the stream of pure H_2 from the PSA to converge when recycled back to the methanol synthesis unit.

4.4.3 Degasser Distillation Column

The degasser distillation column is used to further purify the crude methanol/water stream with extremely minimal loss of methanol. Prior to entry into the column, the inlet stream is heated to 400°C, expanded to 5 bar using a series of two turbines in series in order to recover electricty, and then cooled back to 60°C, as specified in the Problem Statement [7]. This is necessary to achieve a vapor–liquid equilibrium in the inlet stream. The degasser is modeled as a RadFrac. It includes 30 stages and a partial–vapor condenser. The reflux ratio is 1.25, and the bottoms rate is determined through a design specification enforcing 99.9% recovery of methanol in the inlet stream to the bottoms stream. The resulting bottoms flowrate is 4,990.33 kmol/hr, while the distillate flowrate is 16.2716 kmol/hr. The distillate is recycled to the PSA unit for production of H_2,

and the bottoms, which is now effectively pure methanol and water, is ready for conversion to hydrocarbons.

4.5   Methanol to Hydrocarbons

The purpose of the methanol to hydrocarbons section is to convert the methanol from the methanol synthesis section into fuel-range hydrocarbons, which are the target molecules of the entire process. A methanol-to-olefins (MTO) process is used combined with a Mobil olefins-to-gasoline process (MOGD) [8]. As the molar distribution of methanol carbon to fuel product carbon that results from using this process is known, indicated in the Problem Statement [7], and discussed again in a previous report outlining the proposed process [8], a combined MTO-MOGD reactor is used to model this step. This is possible because, given the carbon distributions, we can calculate the resulting proportion of hydrocarbon products, assuming 100% conversion of methanol to hydrocarbons, as specified [7]. These units are still considered separately in the economic evaluation. Before entering the MTO-MOGD reactor, the purified methanol/water inlet stream is first heated to 400°C and 1.2 bar [7]. The inlet stream for this section, produced from the degasser, is 4,990.33 kmol/hr. The process flowsheet for the methanol to hydrocarbons section is displayed in Figure 5.

Figure 5: Methanol to Hydrocarbons and Light Gas / Gasoline Separation.

4.5.1   *MTO-MOGD Reactor*

This combined reactor is necessary to model the conversion of methanol to a variety of hydrocarbons, including hydrocarbons in the desired gasoline and diesel range. This is implemented as a RStoic reactor because the molar distribution of the products is known. The reactor operates at 375°C and 1 bar [7]. The stoichiometric equation representing the reaction of methanol to hydrocarbons is shown in equation 5 on the following page. The flowrate of each species in the outlet to the reactor is shown in Table 4 on the next page.

$$CH_3OH \rightarrow 0.01225CH_4 + 0.025CH_4 + 0.0014C_2H_6 + 0.0053C_3H_6$$
$$+ 0.0003816C_3H_8 + 0.0001466C_5H_12 + 0.000123C_6H_14 + .00004557C_7H_16$$
$$+ 0.004555C_8H_18 + 0.004056C_9H_20 + 0.002752C_8H_10 + 0.0026995C_9H_12 + 0.01391C_13H_28$$
$$+ 0.0157221C_15H_32 + 0.0170665C_10H_14 + 0.014968C_14H_30 + H_2O$$

$$(5)$$

Table 4: Composition of MTO-MOGD Reactor Effluent

Species		Effluent (kmol/hr)
H_2O	Water	4990.33
CH_4	Methane	14.5965
C_2H_4	Ethylene	29.7887
C_2H_6	Ethane	1.66817
C_3H_6	Propylene	6.3152
C_3H_8	Propane	0.454694
C_5H_{12}	n-Pentane	0.174681
C_6H_{14}	n-Hexane	0.14656
C_7H_{16}	n-Heptane	0.0542987
C_8H_{18}	n-Octane	5.4275
C_9H_{20}	n-Nonane	4.83291
C_8H_{10}	p-Xylene	3.27914
C_9H_{12}	1,2,3-Trimethylbenzene	3.21658
$C_{13}H_{28}$	n-Tridecane	16.5744
$C_{15}H_{32}$	n-Pentadecane	18.7336
$C_{10}H_{14}$	1,2,4,5-Tetramethylbenzene	20.3355
$C_{14}H_{30}$	n-Tetradecane	17.8351

The outlet stream of hydrocarbons and water with compositions as described above is now ready to enter the LPG-Gasoline separation section.

4.6   Separation of Gasoline and Light Gases

This section is necessary because the water and hydrocarbon streams need to be separated into product components, wastewater, and light gases to be recycled. This is accomplished using a series of knock-out units, a de-ethanizer, and columns for absorption and splitting. The actual units will all be taken into account during economic analysis. However, since the intermediate conditions are not known, it is appropriate to model this section as a series of 3 separators. The flowsheet for this unit is shown in Figure 5 on the preceding page. The inlet stream to this section is 5,133.76 kmol/hr of hydrocarbons and water, with compositions as shown in Table 4. The first separator is a MTO fractionation unit (MTO-F), and results in a water stream of 4,990.33 kmol/hr with trace

CO_2, HCN, and N_2O. In the previous iteration, this stream was sent to the biodigester for processing into biogas. In this iteration, the water stream is heated to 53.7891°C and is recycled back the PSA WGS unit to force the WGS reaction to produce more H_2. The PSA section is discussed further below. The MTO-F also produces a recycle stream of 16.7193 kmol/hr of C1–C3 species that are combined with other light gases in an internal gas loop configuration, and later sent via an external gas loop to a combuster. Finally, the MTO-F produces a 126.714 kmol/hr stream of the remaining hydrocarbons. The next two separators are used to produce a stream of pure product gasoline-range hydrocarbons, pure product diesel-range hydrocarbons, and light gases to be sent to the waste combustion unit. The total flowrates of the product and light gas streams, as well as the component flowrates in each stream, are shown in Table 5.

Table 5: Composition of LTF Product and Light Gas Streams

Diesel Product Stream		
Species		Flowrate (kmol/hr)
$C_{13}H_{28}$	n-Tridecane	16.5744
$C_{15}H_{32}$	n-Pentadecane	18.7336
$C_{10}H_{14}$	1,2,4,5-Tetramethylbenzene	20.3355
$C_{14}H_{30}$	n-Tetradecane	17.8351
Total		**73.4787**
Gasoline Product Stream		
Species		Flowrate (kmol/hr)
C_5H_{12}	n-Pentane	0.174681
C_6H_{14}	n-Hexane	0.14656
C_7H_{16}	n-Heptane	0.0542987
C_8H_{18}	n-Octane	5.4275
C_9H_{20}	n-Nonane	4.83291
C_8H_{10}	p-Xylene	3.27914
C_9H_{12}	1,2,3-Trimethylbenzene	3.21658
Total		**17.1317**
Light Gas Stream		
Species		Flowrate (kmol/hr)
C_2H_4	Ethylene	29.7887
C_3H_6	Propylene	6.3152
Total		**36.1039**

The target for the process is 5,000 barrels / day of liquid transportation fuels. Using the following conversion:

$$\frac{5000 \text{fluidbarrels}}{\text{day}} \times \frac{119.240471 \text{Liters}}{\text{barrel}} \times \frac{1 \text{day}}{24 \text{hrs}} \times \frac{1 \text{hr}}{60 \text{m}} = \frac{414.03 \text{Liters}}{\text{min}} \tag{6}$$

The target output flowrate of LTF is 414.03 L/min. The product LTF streams in the proposed process are the gasoline–range and diesel–range hydrocarbon streams, for which the outlet volumetric flowrates are shown in Table 6.

Table 6: Volumetric Flowrate of Product Gases

Product Stream	Flowrate (L/min)	Flowrate (barrels/day)
Diesel	367.855	4442.40
Gasoline	46.1852	557.75
Total	414.04	5000.15

The product diesel and gasoline fuel streams are at 170°C and 80°C, respectively, and 1 bar. The combined LTF production rate is 5000.15 barrels/day, of which 88.8% is diesel. This is an indication that the proposed process is reasonably successful at maximizing the production of diesel under the constraint of 5000 barrels/day.

4.7 Wastewater Treatment

Wastewater treatment is essential in order to safely process all non–useful byproducts from the proposed process into CH_4, CO_2, H_2, and NH_3, which are biogas species that can be safely vented along with water. This is done using a biological digestor, implemented as a RYield reactor operating at 35°C and 1 bar. The units in this section are diagrammed in Figure 6.
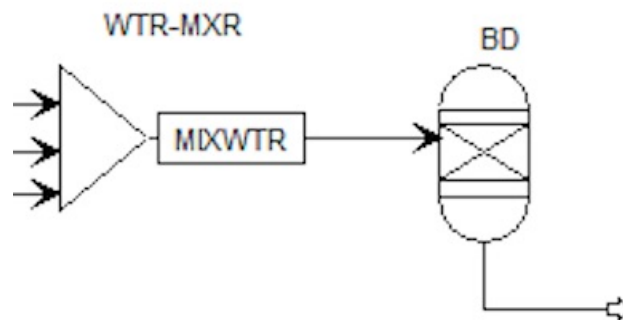

Figure 6: Flowsheet of the Wastewater Treatment Section.

The inlet streams to the biodigester are a mixture of all waste streams containing undisposable species. These include the waste stream from

the PSA (discussed later), the purge stream consisting of 1% of the vapor stream from the flash separator following the methanol synthesis reactor, and the waste stream from the sour scrubber. The yields specified for the reactor unit are calculated by a element mass balance on the inlet streams and a design specification requiring that 65% of the inlet carbon exit the biodigester as CH_4, as indicated in the Problem Statement [7]. The result of treating the 7,756. kmol/hr inlet waste stream is a 8,570.36 kmol/hr outlet stream of biogas and water that can safely be purged. The composition of the inlet and outlet streams for the biodigester are displayed in Table 7.

Table 7: Composition of Biodigester Inlet and Outlet

Species	Inlet (kmol/hr)	Outlet (kmol/hr)
Water	4985.18	4194.69
CO_2	816.046	1141.06
H_2	230.201	1055.5
CO	4.70969	0
CH_4	900.855	2119.12
C_2H_2	477.144	0
C_2H_4	280.023	0
C_2H_6	25.7916	0
N_2	23.0816	0
NH_3	3.92391e-06	59.9954
HCN	5.20036e-05	0
NO	0.342115	0
N_2O	2.39346	0
CH_3OH	10.7218	0

4.8   Combustion of Light Gases

Those light gas species that are not recycled in an internal gas loop configuration must be processed by an external gas loop configuration. In the proposed process, light gases are directed to a combustion unit to provide heat for the process. The combustion unit is modeled as a RYield unit with an inlet stream of 52.8232 kmol/hr of light gases (C_1-C_3 hydrocarbons) and 150.138 kmol/hr of pure O_2 to ensure complete combustion. The resulting stoichiometric reaction produces an outlet stream of 111.689 kmol/hr of water and 95.3861 kmol/hr of CO_2 that can be vented. The yields for the reactor are calculated via mass balance on the inlet light gas and oxygen streams. The combuster flowsheet diagram is shown in Figure 7 on the following page.
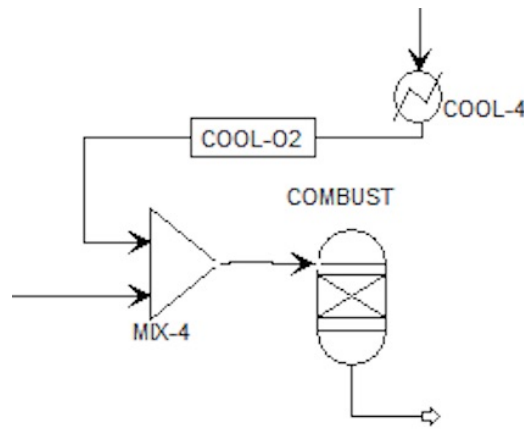
Figure 7: Diagram of Light Gas Combustion Section.

4.9 Hydrogen / Oxygen Production

As the proposed process uses a H_2 feed stream to improve methanol production in the methanol synthesis reactor and oxygen streams to ensure complete gasification in the gasifier and combustion in the combuster unit, it is necessary to include units for efficiently generating oxygen and hydrogen. Hydrogen production is accomplished via a pressure-swing adsorption unit (PSA), which uses purge streams to produce 611.558 kmol/hr of pure H_2 by the method described below. Oxygen production occurs using an air separation unit (ASU) that produces 7058.25 kmol/hr of O_2, as described below. The PSA is shown in Figure 8 and the ASU is displayed in Figure .
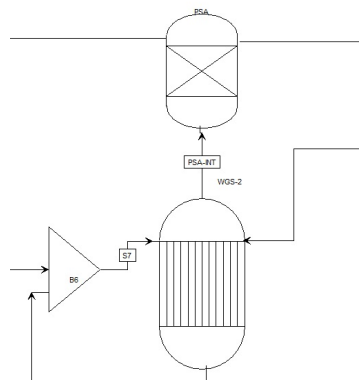

Figure 8: Diagram of Pressure-Swing Adsorption Unit.

4.9.1 *Pressure-Swing Adsorption Unit*

The PSA unit makes use of syngas species in the 16.2716 kmol/hr degasser distillate stream and in the 2148.74 kmol/hr purge stream from the flash unit vapor outlet stream that follows the methanol synthesis reactor. It also has an inlet stream of 4,990.33 kmol/hr of pure water from the
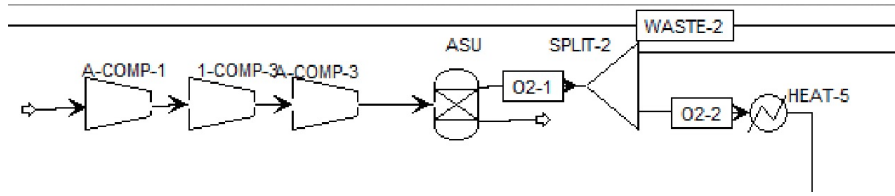
Figure 9: Diagram of Air Separation Unit.

MTO-F unit in order to increase production of H_2 in the WGS reaction by forcing it to run in the forward direction. These streams are first sent to a WGS reactor, whose purpose is to increase the amount of H_2 in the effluent. The inlet and outlet flowrates of species involved in the WGS reactor are indicated in Table 8.

Table 8: Composition of WGS-Active Species in PSA Reactor Inlet and Outlet

Species	Inlet (kmol/hr)	Outlet (kmol/hr)
CO	11.0512	2.5000
H_2O	4993.166	4984.61
CO_2	675.129	683.68
H_2	694.389	702.94

The products from the WGS reactor are sent to a PSA unit, implemented as a separator with split fractions such that a pure H_2 stream is produced with 87% recovery of H_2. The result is a pure hydrogen stream of 611.558 kmol/hr to be recycled back to earlier process units and a 6,543.78 kmol/hr stream of the remaining syngas species that is sent to the biodigester for wastewater treatment. The recycle stream is split into a 534.473 kmol/hr H_2 stream recycled to the methanol synthesis reactor and a 77.0855 kmol/hr H_2 stream sent back to the WGS reactor in the synthesis gas cleaning section. H_2 is sent to the methanol synthesis reactor in order to increase the Ribblett ratio and improve methanol production. It is sent to the WGS reactor to increase production of CO, which later also improves production of methanol in the methanol synthesis reactor. The proportion of H_2 in these two recycle streams is determined in order to optimize methanol production and recovery following the methanol synthesis section.

4.9.2 *Air Separation Unit*

The ASU is responsible for producing enough O_2 to meet the demands of the gasifier and the combuster units. This accomplished by compressing air (79% N_2 and 21% O_2) at ambient conditions to 190 psia using 3 compressors in series, and then using a separation unit to produce a 99.5 wt% O_2 stream. For the current simulation, we simplify this and assume a 100% O_2 stream is possible to ensure conversion of recycle streams in the gasification section. 33,610.7 kmol/hr of ambient air is input to the com-

pressor, resulting in a stream of 7,058.25 kmol/hr of O_2 being available for use. The nitrogen gas stream is vented, as specified in the Problem Statement [7], and can be used to reduce the explosive atmosphere around the gasifier, as discussed later in the Process Safety section. Of the O_2 available, 6,908.12 kmol/hr is heated to 1100K to match RDF conditions and directed to the gasifier to ensure complete gasification. An additional 150.138 kmol/hr of O_2 is sent to the combuster, an amount that is stoichiometrically determined in order to ensure complete combustion. The inlet amount of air required is calculated such that no O_2 needs to be vented, an improvement over the previous iteration of the process simulation [9].

5 OPTIMIZATIONS

After the initial iteration of the process simulation was completed to establish a baseline for the process, a number of optimizations are explored to improve the profitability of the process and the accuracy of the simulation. In particular, a CO_2 recycle stream is added from the Rectisol unit to both the Lockhopper and the syngas cleaning WGS unit, the amount of air input is scaled down to avoid unnecessary venting of O_2, some of the H_2 from the PSA unit initially intended for the methanol synthesis reactor is diverted back to the first WGS unit as well, and all waste streams with extremely high water content are rerouted back to the PSA unit. The proportions in which the limited amount of CO_2 and H_2 available are recycled to the various units is optimized to maximize production of diesel and gasoline. Additionally, a range of temperatures is tested for the methanol synthesis reactor, the syngas cleaning WGS unit, and the PSA WGS unit, with temperatures chosen such that LTF production is maximized. A sensitivity analysis is conducted on the operating temperature of the methanol synthesis reactor in order to optimize conversion of carbon from MSW to LTF.

5.1 Methanol Synthesis Reactor and Recycle Stream

The primary optimization implemented to increase the economic feasibility of the simulated process is to lower the temperature of the methanol synthesis unit from 300°C to 200°C. The methanol synthesis reactor features the water–gas–shift reaction and the methanol synthesis reaction. The inlet and outlet flowrates of the involved species in the prior iteration and in this iteration are shown in Table .

Although the change in flowrate for the inlet species is due in part to other optimizations leading to a decreased total flowrate throughout the process, the necessary inlet flowrate of active species to achieve the desired LTF production is decreased from 128,600.025 kmol/hr to 34,823.121 kmol/hr, an enormous improvement. At this new temperature,

Table 9: Composition of WGS-Active Species in PSA Reactor Inlet and Outlet (kmol/hr)

Species	Prior Inlet	Prior Outlet	Current Inlet	Current Outlet
H_2O	5714.58	6714.47	3294.76	3855.45
CO_2	10148.9	9149.04	13820.2	13259.5
H_2	108646	105199	16845.5	13880.2
CO	3812.16	3588.39	862.661	221.102
CH_3OH	278.385	1502.04	149.327	1351.58

the increase in methanol is 805% after the streams pass through the reactor, compared to a 440% increase in the previous iteration. Additionally, in order to allow the recycle stream consisting of vapor products from the flash separator to converge, the split fractions are adjusted. 94% of the vapor products are currently recycled back to the methanol synthesis reactor, compared to 90% in the previous process model. However, the decrease in operating temperature, along with the other optimizations implemented, has allowed for a decrease in the flowrate of this recycle stream from 122,642 kmol/hr to 40,403.8 kmol/hr, a significant improvement for the sake of minimizing operating costs for the units involved.

The operating temperature of 200°C is determined according to a sensitivity analysis carried out to maximize the conversion of carbon in the entire process from MSW to LTFs. The results of the sensitivity analysis are displayed in Table 10.

Table 10: Carbon Conversion Based on Temperature of Methanol Synthesis Unit

Temperature (°C)	Carbon Conversion (%)
200	8.37
225	1.67
250	7.84
275	7.38
300	6.69

5.2 PSA Unit

In the prior iteration of the process, the WGS reactor in the PSA unit actually decreased the flowrate of H_2 by 2.4% [9], instead of improving it as intended. To remedy this, the pure water waste stream from the MTO-F unit that had previously been directed to the biodigester is now recycled back the WGS reactor in the PSA unit, pushing the equilibrium reaction to produce more H_2. With this improvement, the WGS reactor succesfully increases the H_2 flowrate by 1.2%, with flowrates as described in the PSA unit section above. Additionally, the amount of H_2 recycled

from the PSA to the methanol synthesis reactor is decreased from 7,144.3 to 534.47 kmol/hr. This is partially due to the lower vapor gas recycle stream, meaning that a smaller amount of syngas is available for H_2 recovery, and partially due to H_2 being diverted to the syngas cleaning WGS unit, as described below. The decrease in recycled H_2 does not decrease methanol production from the methanol synthesis reactor despite a Ribblett ratio of 0.39, lower than the target of 1. Recovery of methanol in the liquid effluent of the flash unit is 88.2%, further indicating that the low Ribblett ratio is not a great concern.

5.3   Carbon Dioxide Recycle

In the previous process iteration, the CO_2 inlet needed by the lockhopper for RDF gasification was being implemented as a feed stream of pure CO_2. The process is now improved to recycle CO_2 from the Rectisol unit back to the lockhopper at a rate that maintains the desired CO_2 input rate of 10 wt% by weight of dry RDF. This decreases the amount of carbon vented in order to improve carbon conversion from MSW to LTF. Additionally, a recycle stream of 4,107.71 kmol/hr of CO_2 from the Rectisol unit is sent back to the syngas cleaning WGS reactor to promote increased production of CO and later production of CH_3OH. The remainder of the CO_2 from the Rectisol unit is vented as before.

5.4   ASU Unit

A large inefficiency in the previous proposed process was that an excess of air was being input to the ASU unit, resulting in 999.6 kmol/hr of O_2 being vented. This issue is now addressed, and the inlet amount of air feed is reduced from 68,933.3 kmol/hr to 33,610.7 kmol/hr so that no O_2 is being vented. This improvement allows for usage of only 2 ASU units, compared to 14 units needed in the previous process. The O_2 produced is entirely used by the RDF gasifier to ensure complete gasification and by the LPG combuster to ensure complete combustion.

5.5   WGS for Syngas Cleaning

Previously, the WGS reactor in the syngas cleaning section operated at 300°C and had a H_2/CO ratio of 11.7, far greater than the target ratio of 2. The unit reduced the flowrate of CO by 87.2%, a significant hindrance to downstream production of methanol. This is rectified by increasing the operating temperature to 350°C and adding H_2 and CO_2 recycle streams from the PSA and Rectisol unit, respectively, all of which serve to increase production of CO. In the current process, the H_2/CO ratio is now 4.98 and the WGS reactor only decreases the CO flowrate by 72.3%, a marked improvement over the prior version.

5.6 Process and Economic Outcomes

The optimizations implemented succeed in decreasing the amount of RDF fed to the process by 48.14 wt%. The amount of air fed to the process is decreased by 51.24%. Finally, the CO_2 feed is no longer needed, as it is now implemented as a recycle stream from the Rectisol unit. The carbon conversion for the proposed process is 8.37%. Further work should focus on improving the carbon conversion, which will further reduce the amount of inlet feeds needed and improve the economic viability of the process.

The economic feasibility of the process is greatly improved by these temperature, scaling, and recycle stream optimizations. A comparison of relevant economic metrics before and after the improvements is shown in Table 11.

Table 11: Comparison of Economic Metrics Before and After Optimizations

Metric	Before	After
NPV	-$45,792,075,210	-$4,784,371,914
Net Profit after Taxes	-$2,415,967,109	-$219,535,070
Capital Investment	$8,652,739,147	$1,409,579,809
Manufacturing Cost	$2,553,659,868	$362,656,466

6 HEAT INTEGRATION

In order to minimize utility costs and the number of heat exchangers needed in the process, heat integration analysis is performed using GAMS. Hot and cold streams are derived from all process units that require a heat duty. If there is no temperature change across the process unit, a temperature difference of 1°C is assigned. For units that have multiple inlet streams at different temperatures, mixers are added in AspenPlus to combine the streams into a single inlet stream. The heat load Q, inlet temperature T_i, and outlet temperature T_o, of each stream is given by the AspenPlus simulation, allowing for calculation of the heat capacity F_{cp} as shown in Equation 7.

$$\frac{Q}{(T_o - T_i)} = F_{cp} \tag{7}$$

The available utilities, along with their prices, are shown in Table 12 on the following page.

Dividing the entire process into hot and cold streams with the afore-mentioned criteria yields 23 hot streams and 14 cold streams. The inlet and outlet temperatures and heat capacities (F_{cp}) of the hot streams are indicated in Table 13 on the next page, and those of the cold streams are

Table 12: Available Utilities

Utility	Inlet Temperature (°C)	Outlet Temperature (°C)	Cost ($/kW year)
Fuel	927	927	160
HP Steam	227	227	140
MP Steam	157	157	120
LP Steam	107	107	80
CW	17	32	20

shown in Table 14 on the following page. The process unit labels in the AspenPlus simulation and the temperature interval diagram labels that correspond to each stream are also shown in the tables.

Table 13: Hot Process Streams

Process Name	Inlet Temp (°C)	Outlet Temp (°C)	F_{cp} (Cal/sec °C)	TI Label
WGS	685.50	350	82485.68	H1
ASU	497.43	496.43	397	H2
COOL-4	497.43	375	329.79	H3
MTO-MOGD	400	375	188444.52	H4
TURB-1	400	311.23	49.17	H5
COOL-6	375	170	3475.87	H6
COOL-7	375	80	455.46	H7
MTO-F	375	374	948	H8
MOGD-F	375	374	504	H9
GAS-SEP	375	374	79	H10
COOL-8	375	53.79	57349.91	H11
COMBUST	375	35	14138.76	H12
COOL-1	350	49	69004.96	H13
TURB-2	311.23	204.545	51.34	H14
PSA	300	299	22473	H15
BD	236.42	35	127890.99	H16
COOL-3	204.54	60	109063.90	H17
COOL-2	200	35	140565.01	H18
DEGASSER-QC	60	40.5566	28952.14	H19
SCRUBBER	49	48	271869	H20
RECTISOL	49	48	4261369	H21
CLAUS	49	48	14	H22
FLASH-1	35	34	11139629	H23

A transshipment LP model is developed in GAMS to calculate the heat load and minimum cost of utilities needed in the optimal heat exchanger network, as well as the residual heats across each temperature interval, which is used in the subsequent transshipment MILP problem. First, the hot and cold streams, along with the available utlities, are partitioned

Table 14: Cold Process Streams

Process Name	Inlet Temp (°C)	Outlet Temp (°C)	F_{cp} (Cal/sec °C)	TI Label
A-COMP-1	25	121.88	273.31	C1
HEAT-2	35	400	51605.50	C2
COMP	35	41.38	357.46	C3
B5	35	53.94	9914.51	C4
HEAT-4	49	250	57621.51	C5
HRD-SUL	49	50	419383	C6
WGS-2	53.79	300	75449.20	C7
DEGASSER-QR	60	130.21	31772.19	C8
METH-RXR	107.52	200	67927.70	C9
1-COMP-3	121.88	281.96	278.38	C10
HEAT-3	130.21	400	60987.69	C11
COMP-2	250	364.44	93.88	C12
A-COMP-3	281.96	497.43	289.95	C13
HEAT-5	497.43	826.85	15804.63	C14

into temperature intervals. The resulting TIs, as well as streams and utilities, are shown in Figure 12 on page 47. The 23 hot streams, 14 cold streams, and 5 available utilities combined to yield 27 temperature intervals. The LP transshipment model consists of the objective function, an energy balance for each TI, a non-negativity statement, and a constraint on the first and last residuals, laid out by Floudas [25] and displayed in Equations 8 on the following page, 9 on the next page, 10 on the following page, and 11 on the next page, respectively. The necessary sets and indices are shown below.

- $HP_k = i$ | hot process stream i in interval k

- $CP_k = j$ | cold process stream j in interval k

- $HU_k = i$ | hot utility i in interval k

- $CU_k = j$ | cold utility j in interval k

- i : hot process stream or utility

- j : cold process stream or utility

- k : temperature interval

The definitions of the involved variables are as follows.

- QS_{ik} = heat load of hot utility i entering temperature interval k

- QW_{jk} = heat load of cold utility j entering temperature interval k

- R_k = heat residual load leaving temperature interval k

- Q_{ik}^H = heat load of hot process stream i going into temperature interval k

- Q_{jk}^C = heat load of cold process stream j going into temperature interval k

$$\min \sum_{i \in HU} C_i \sum_{k \in TI} QS_{ik} + \sum_{k \in CU} C_j \sum_{k \in TI} QW_{jk} \qquad (8)$$

$$\text{s.t.} R_k - R_{k-1} + \sum_{j \in CU_k} QW_{jk} - \sum_{i \in HU_k} QS_{ik} = \sum_{i \in HP_k} Q_{ik}^H - \sum_{j \in CP_k} Q_{jk}^C, k \in TI \qquad (9)$$

$$QS_{ik}, QW_{jk}, R_k \geqslant 0, k \in TI, i \in HU, j \in CU \qquad (10)$$

$$R_0 = R_k = 0 \qquad (11)$$

This LP transshipment heat integration problem is modeled in GAMS and solved for the aforementioned temperature intervals, hot and cold process streams, and utilities. The results are summarized in Table 15 on the following page, including heat residuals for each TI, heat loads for the utilities present, and the solved minimum cost of the utilities. The heat residuals and utility heat loads are used to solve the MILP transshipment problem, which is discussed later. The temperature boundaries for the TIs below can be found in Table 12 on page 47.

The minimum utility cost is \$7,560,507/year. This number is obtained after converting the cost of the available utilities from \$/(kW year) to \$/(cal sec) to match the units given by the AspenPlus heat load output. This annual cost is factored into the economic analysis, and represents a significant NPV improvement over the previous iteration. The residual heat from TI-1 to TI-2 is found to be 0, and all other temperature intervals are non-zero. This indicates there are two heat exchange subnetworks in the process, one that only includes TI-1, and one that includes TI-2 to TI-27.

After the LP heat integration problem is solved, the MILP transshipment heat integration problem is solved for each subnetwork to find the minimum number of matches between hot and cold streams and the heat load of each match. The necessary variables and sets are the same as in the LP problem, with the addition of the following variables. The set of hot streams is combined with the set of hot utilities and denoted H (H_k if the hot stream or utility is present in TI-K). The same is done for the cold streams and utilities, denoted C (C_k if the cold stream or utility is present in TI-K). A match between hot and cold utilities is not allowable.

- $y_{ij} = 1$ if match ij occurs and 0 if not

Table 15: LP Heat Integration Solution Summary

TI	Residual (Cal/sec)	TI	Residual (Cal/sec)
TI-1	0	TI-2	1.1874e7
TI-3	1.2696e7	TI-4	1.9611e7
TI-5	2.3572e7	TI-6	2.4653e7
TI-7	2.4698e7	TI-8	2.5919e7
TI-9	2.5518e7	TI-10	2.5187e7
TI-11	2.3783e7	TI-12	2.1390e7
TI-13	2.1639e7	TI-14	2.1862e7
TI-15	2.2168e7	TI-16	3.1070e7
TI-17	3.4505e7	TI-18	3.6454e7
TI-19	3.9811e7	TI-20	4.2985e7
TI-21	5.4146e7	TI-22	5.6213e7
TI-23	5.7723e7	TI-24	5.7622e7
TI-25	6.1108e7	TI-26	6.6639e7
TI-27	6.9590e7		

Utility	Heat Load (Cal/sec)
Fuel	2.3920e7 (Cal/sec)
HP Steam	0
MP Steam	0
LP Steam	0
CW	8.0730e7
Minimum Utility Cost	**$7,560,507/year**

- Q_{ijk} = heat exchanged in match ij at interval k

- Q_{ik} = heat exchanged for match ij over the entire subnetwork

- R_{ik} = heat residual of hot procses stream/utility i out of TI k

- U_{ij} = upper bound of the heat exchanged between hot stream/utility i and cold stream/utility j

The MILP model for the heat integration transshipment problem is then described by an objective function, a hot stream energy balance, a cold stream energy balance, an upper bound on the total amount of heat exchange allowable between two streams, a non-negativity constraint on the residuals, a non-negativity constraint on the heat exchanged, and a constraint limiting y to a binary variable. These are shown in Equations 12, 13 on the next page, 14 on the following page, 15 on the next page, 16 on the following page, 17 on the next page, 18 on the following page, respectively.

$$\min \sum_{i \in H} \sum_{j \in C} y_{ij} \tag{12}$$

$$R_{i,k} - R_{i,k-1} + \sum_{j \in C_k} Q_{ijk} = Q_{ik}^H, i \in H_k \tag{13}$$

$$\sum_{i \in H_k} Q_{ijk} = Q_{jk}^C, j \in C_k \tag{14}$$

$$U_{ij} = \min(\sum_{k \in TI} Q_{ik}^H, \sum_{k \in TI} Q_{jk}^C) \tag{15}$$

$$R_{ik} \geqslant 0, k \in TI \tag{16}$$

$$Q_{ijk} \geqslant 0, k \in TI \tag{17}$$

$$y_{ij} = 0 - 1 \tag{18}$$

Table 16: MILP Heat Exchanged for each Match

Match	Heat Exchanged (Cal/s)	Match	Heat Exchanged (Cal/s)
H1-C2	8343532	H11-C5	7928940
H1-C11	16453810	H12-C8	2230757
H1-C13	62467	H12-CW	2576423
H1-C14	2814378	H13-C7	18576420
H2-C3	397	H13-C10	44564
H3-C4	40379	H13-CW	2149507
H4-C5	3529366	H14-C4	5477
H4-C9	1181747	H15-C1	22113
H5-C1	4365	H15-C3	360
H6-C4	141901	H16-CW	25792900
H6-C6	419383	H17-C9	4948869
H6-C9	151270	H17-CW	10815770
H7-C5	123618	H18-CW	23193210
H7-C12	10743	H19-CW	562928
H8-C3	948	H20-CW	271869
H9-C3	497	H21-CW	4261369
H10-C3	79	H23-CW	11139630
H11-C2	10492480	QF-C14	2391983

The MILP transshipment model is developed in GAMS and solved for subnetwork 1 and subnetwork 2. The same 27 temperature intervals, 23 hot streams, 14 colds streams, and 5 utilities from the LP problem are used. The values of the residual heat loads across each temperature interval and the utility heat loads are taken from the solved LP GAMS model.

Figure 10: Matrix of Heat Network Matches Between Hots and Colds.

After solving the model, the minimum number of matches is found to be 36. A matrix of possible matches is shown in Figure 10, with subnetwork 1 matches shaded in yellow and subnetwork 2 matches shaded in black.

The total heat exchanged between hot streams or utilities and cold streams or utilities for each match is also calculated and shown in Table 16 on the preceding page. These values are used in the economic analysis section to determine the size and subsequent cost needed for the 36 heat exchange units needed following optimization of heat integration.

There are 401 possible matches. This consists of the 322 (23*14) possible matches between hot and cold streams, the 23 (23*1) possible matches between hot streams and Cooling Water, the lone cold utility, and the 56 (4*14) possible matches between the cold streams and the hot utilities (HP Steam, MP Steam, LP Steam, and Fuel). Of these possible matches, only 36 heat exchangers are needed to accomodate the energy exchange needs of the process. Although only 12 heat exchangers

were needed in the prior iteration without heat exchange network synthesis, the annual cost of utilities using this optimization is decreased from $192,102,224/year to $7,560,507/year. The capital investment for heat exchangers decreases from $6,747,468 to $146,944. This is discussed in more detail in the Economic Analysis section.

7 ECONOMIC ANALYSIS RESULTS

In order to determine the economic viability of the process, an economic evaluation is carried out following heat integration and optimization. The capital investment and manufacturing costs are determined in order to estimate earnings and return on investment [11].

7.1 Capital Investment

The capital investment is comprised of manufacturing capital, or total direct cost, and nonmanufacturing capital, or indirect cost [11]. The total direct costs for all units are determined either using cost functions, a bare module cost approach for heat exchangers based on unit size from heater duty, or values from Aspen Process Economic Analyzer (PEA). Cost functions are used for all units for which cost function information is available in the Problem Statement or in literature.

Total direct costs (TDC) for each unit are evaluated from the cost function parameters in the Problem Statement or literature using Equation 19 [3].

$$TDC = (1 + BOP) \times C_o \times \left(\frac{S_r}{S_o} \right)^{S_f} \tag{19}$$

The balance of plant percentage (BOP) is assumed to be 20% of the total installed cost, representing a 20% contingency cost. C_o is the base component cost, S_r is the actual flowrate through the unit, S_f is the scaling factor, and S_o is the base capacity [3]. Maximum capacities, S_{max}, are provided for several units in the Problem Statement. If the flowrate through a unit exceeds the indicated S_{max}, multiple units are included in the cost analysis as needed to handle the specified flowrate. Process improvements made since the last report helped to mitigate this problem. Previously 33 Rectisol units were required, and now the process only utilizes one. Four MSW Handling & RDF Facilities and three Gasifiers are still needed, but the overall number of units has decreased substantially.

The cost function parameters for the Claus unit and air compressor are taken from Baliban et al. 2011 [1], and the C_o value is converted from 2009 Q4 dollars to August 2014 dollars using plant cost index values from Chemical Engineering Online [10]. The cost function parameters for all other units are taken from the Problem Statement [7].

For the non–heat exchanger units for which cost function parameters are not available, the total direct costs are determined using Aspen PEA. These values are computed in 2012 Q1 dollars, which are again converted to August 2014 dollars using the Chemical Engineering Plant Cost Index [10].

The calculation of total direct cost for heat exchangers is more involved. As explained in the Heat Integration section, 36 heat exchangers are required based on the 36 matches obtained in the MILP transshipment heat integration problem. The heat duties of these matches are taken from GAMS in cal/s, and are converted to Btu/hr. A intermediate representative heat transfer coefficient of U=700 Btu/(ft^2 hr °F) is selected from Table 4.3 in Biegler et al [11]. The log mean temperature difference (LMTD) is determined based on the inlet and outlet temperatures in °F of each stream involved in the heat exchanger. Equation 20 is then used to determine the area (A) in square feet required for the given heat exchanger.

$$Q = U \times A \times LMTD \tag{20}$$

Once the area is found, the cost function in Equation 21 for a shell and tube heat exchanger of an area less than 100ft^2 [11] is used to find the base cost (BC).

$$BC = C_o \times \left(\frac{A}{S_o} \right)^\alpha \tag{21}$$

The base cost is $C_o = \$300$, the base capacity $S_o = 5.5$, and the scaling factor is $\alpha = 0.024$ [11]. The total updated installed cost is computed using the Equation 22.

$$TDC = UFBC(MPF + MF - 1) \tag{22}$$

MPF is 1 and MF is 1.83 [11], and the update factor (UF) is calculated using Equation 23, based on a present cost index of 579.8 for October 2014 and a base cost index of 113.7 for 1968, as found in [10].

$$UF = \frac{present\,cost\,index}{base\,cost\,index} \tag{23}$$

These values for total direct cost are then used in computing the capital investment for the process. Pricing heat exchangers based on their areas calculated in this manner rather than based on values from PEA, as was previously done, results in a decrease from \$1,416,180,333 to \$1,409,579,809 for the capital investment. Manufacturing capital is lowered as well, resulting in a net profit after taxes of –\$219,535,070 per year rather than –\$221,124,925 if PEA values are used.

Several assumptions are made in computing the total direct costs of all units. First, the TDC for the MSW Handling and RDF Facility is assumed to cover the dryer and lockhopper. The TDC for MSW Gasification is assumed to include the RDF gasifier, both cyclones, and the ASH–MIX unit. The cost for the two knockout units involved in light gas/gasoline separation are assumed to be included in the cost of the deethanizer. When mapping units in PEA, the default is used and settings are changed only if errors present themselves. The TDCs for all units are shown in Table 17, along with the source of the cost function and the number of units necessary.

Table 17: Costs and Number of Process Units

Unit	# Units	Cost Source	Cost (USD MM)
MSW Handling/RDF Facility	4	Problem Statement	295.98
MSW Gasification	3	Problem Statement	264.62
WGS (cleaning)	1	Problem Statement	5.33
WGS (H_2 Synthesis)	1	Problem Statement	1.73
Rectisol	1	Problem Statement	65.77
Methanol Synthesis	1	Problem Statement	36.34
Methanol Degasser	1	Problem Statement	8.92
Methanol-to-olefins	1	Problem Statement	8.26
Olefins-to-diesel-gasoline	1	Problem Statement	7.98
Deethanizer	1	Problem Statement	0.20
Absorber Column	1	Problem Statement	0.99
PSA	1	Problem Statement	30.86
ASU	2	Problem Statement	77.68
Biological Digester	1	Problem Statement	2.86
Claus Plant	1	Problem Statement	17.06
Air Compressor	3	Problem Statement	51.28
Scrubber	1	Problem Statement	6.14
Combustor	1	PEA	0.31
Compressor	2	PEA	7.17
Turbine	2	PEA	0.83
Flash Separator	1	PEA	3.00
MTO Fractionator	1	PEA	0.52
MOGD Fractionator	1	PEA	0.26
Solid Sulfur Converter	1	PEA	0.18
Heat Exchangers	36	BMC	0.09

Once the TDC for each unit is computed, these values are summed to determine the total manufacturing capital for the plant, which is $894,264,799. The nonmanufacturing capital is then determined by assuming that these costs, including buildings, services, and land [11], make up 32% of the manufacturing capital [3]. This results in a nonmanufacturing cost of $286,164,736. The manufacturing and nonmanufacturing capital together make up the total fixed capital of $1,180,429,535. The working capital is

then calculated as 19.4% of the fixed capital [11], or $229,003,330. The fixed capital and working capital together comprise the capital investment, resulting in a cost of $1,409,579,809. While still high, this is a sixfold decrease from the last reported value of $8,652,739,147, an improvement resulting from process improvements and heat integration.

7.2 Manufacturing Costs

The fixed capital is used to determine various components of the manufacturing cost. Raw materials for the plant either result in no cost or a credit, depending on the chosen cost associated with dry RDF. Direct expenses include labor, supervision, payroll, utilities, maintenance, supplies, and royalties [11]. Labor is computed as 10% of the fixed capital, supervision is assumed to be 15% of labor, and payroll is calculated as 20% of labor and supervision [11]. Maintenance is assumed to be 6% of fixed capital, and supplies are calculated as 2% of fixed capital [11]. Royalties are assumed to be part of the nonmanufacturing costs, as in Niziolek et al. [3]. Depreciation is calculated using a straight-line model, where 1/30 of the total value depreciates over each of the 30 years of the plant's life. Taxes and insurance are 3% of fixed capital. Finally, the cost for pretreatment of RDF is included in the manufacturing cost by multiplying the metric tons of RDF processed per year by $66.67/dry metric ton [7]. These costs are shown in Table 18.

Table 18: Manufacturing Costs Breakdown

Type of Cost	Cost (Millions of USD)
Labor	118.04
Supervision	17.71
Payroll	27.15
Maintenance	70.83
Supplies	23.61
Utilities	83.35
Depreciation	39.35
Taxes & Insurance	35.41
Tipping Fee (at $70/ton RDF)	-212.77
RDF Operating Cost	159.99
Total Manufacturing Cost	**362.66**

The calculations required for utilities are more extensive. To determine the cost of fuel, steam, and cooling water used, fuel at a maximum inlet temperature of 1200K is priced at $160/kWyr, high pressure steam at a maximum inlet temperature of 500K is priced at $140/kWyr, medium pressure steam at a maximum inlet temperature of 430K is priced at $120/kWyr, low pressure steam at a maximum inlet temperature of 380K is priced at $80/kWyr, and cooling water at a maximum inlet tempera-

ture of 290K and outlet temperature of 305K is priced at $20/kWyr. As described previously, a transshipment LP model is used in GAMS to determine the minimum utility cost of $7,560,507 for fuel and cold water. This represents a large decrease from the previously reported utility cost of $192,102,224 before heat integration and process improvements. The cost for electricity used in compressors is calculated by taking the power value in kW from Aspen and converting power to energy in kWhr based on how many hours each unit runs per year. Based on energy used by each compressor and produced by each turbine and an electricity cost of $0.07/kWhr, an additional $75,785,970 is spent on electricity each year, making for a total utility cost of $83,346,477 per year. All components of the manufacturing cost are summed up and calculated for several different tipping fee costs for MSW. These are given in Table 19.

Table 19: Manufacturing Costs at Different Tipping Fees

Tipping Fee per metric ton MSW	Manufacturing Cost
$0	$575,426,316
$24	$502,476,653
$47	$432,566,560
$70	$362,656,466

7.3 Net Profit After Taxes

The gross sales of the products produced are calculated from Aspen PEA. The gallons of diesel and gasoline produced each year, calculated from the diesel and gasoline output streams, are multiplied by the cost for diesel and gasoline listed by the US Energy Information Administration, which is $3.012 and $3.013/gallon, respectively [12]. The solid sulfur produced in the process is also considered as a product, priced at the cost of $105/ton listed by the National Iranian Gas Company's Sulfur Information Services [13]. The production of diesel, gasoline, and sulfur led to total gross sales of $159,023,774/year.

Net profit after taxes is determined by the calculations in Table 20 on the next page, assuming the highest tipping fee of $70/ton RDF.

7.4 Measures of Return on Investment

Several economic measures are determined from the previously found values, according to formulas in Biegler et al. [11]. The calculated values are displayed in Table 21 on the following page.

For a more reliable determination of economic feasibility, the net present value of the plant is evaluated using the formula in Biegler et al. [11], assuming an interest rate of 5%. The formula is shown in Equation 24 on the next page.

Table 20: Guthrie's Method at Various Tipping Fees $70/ton RDF (Values in USD MM)

	$0/ton	$24/ton	$47/ton	$70/ton
Gross Sales:	159.02	159.02	159.02	159.02
–Manufacturing Costs:	575.43	502.48	432.57	362.66
=Gross Profit:	–416.40	–343.45	–273.54	–203.63
–SARE Expenses (10% Gross Sales):	15.902	15.902	15.902	15.902
=Net Profit Before Taxes:	–432.30	–359.36	–289.45	–219.54
–Taxes:	$ 0	0	0	0
=Net Profit After Taxes:	–432.30	–359.36	–289.45	–219.54

Table 21: Economic Measures

Measure Name	Value
Return on Investment (ROI)	–0.156%
Payout Time	N/A
Proceeds for Dollar Outlay	–3.835
Annual Proceeds Per Dollar Outlay	–0.128
Average Income on Initial Cost	–0.156

$$NPV = -(capital\,investment) + (net\,profit\,before\,taxes) \times \frac{1-(1+i)^{-30}}{i}$$

(24)

The resulting NPV calculated is –$4,784,371,914. A second formula is used to find the present value at each year throughout the process, shown in Equation 25.

$$NPV = -(C_I + C_W) + \sum_{j=1}^{n} \frac{(R-X)_j(1-t)}{(1+i)^j} + \sum_{j=1}^{n_t} \frac{D_j t}{(1+i)^j} + \frac{C_S + C_W}{(1+i)^n}$$

(25)

Given that the manufacturing cost each year is greater than proceeds from sales, the present value decreases each year rather than increasing after the first year's capital investment. The NPV after 30 years based on this formula is –$2,458,086,291 when rate of return is set to 10%. The present value for each year in the plant's life is shown in Figure 11 on the next page.
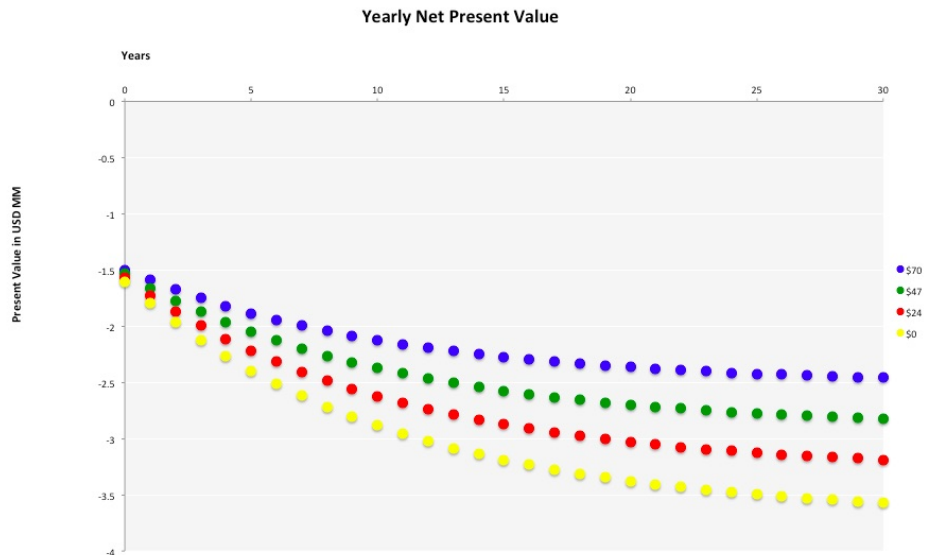
Yearly Net Present Value

Figure 11: Net Present Value over Plant Life of 30 Years

8 PROCESS SAFETY

There are multiple safety risks associated with the proposed process, and measures must be put in place to mitigate these risks. The process involves flammable and toxic chemicals, high temperatures and pressures, risks to plant employees, and risk of explosions. It is important to carry out a process hazard analysis (PHA) to analyze which portions of the process carry risks and what the causes and results of those risks might be [17]. The PHA will help employers and employees make decisions to improve process safety.

In particular, the gasifier unit involves several safety hazards, including risk of explosion, fire, and gas leaks. The unit operates at the high temperature of 1,100K and contains flammable gases, resulting in the possibility of either fire or explosion. To manage the high temperatures, heat resistant stainless steel should be used for the gasifier [18]. The room containing the gasifier should be equipped with flame detectors, and an explosive atmosphere should be avoided [19] by purging the room with nitrogen during startup [18]. One of the products of gasification is carbon monoxide, an extremely toxic gas. It is crucial to avoid gas leaks both to reduce the risk of carbon monoxide escaping into the environment and to decrease the chance of explosion [19]. The room should be equipped with carbon monoxide detectors that alarm at 25–50 ppm [18]. The gasifier should also be equipped with pressure gauges to alert operators when pressure reaches dangerously high levels, and piping should be welded rather than flanged to reduce risk of gas escape [18]. Finally, inlets and outlets from the gasifier should have anti–backfiring valves to further decrease risk of pressure and gas buildup [18].

In addition to the risk of carbon monoxide resulting from gasification, the process also produces methane and H_2S. When the concentration of methane exceeds 45%, the gas becomes very flammable. This is of particular concern in the biodigester [20]. The concentration by weight of CH_4 entering the biodigester is 8.87 wt%, and the concentration in the effluent is 20.87%, resulting in a reasonably low risk of flammability. H_2S is extremely toxic even at low levels, leading to unconsciousness, paralysis, and death, so preventing gas leaks at all points before sulfur is removed via the Claus unit is important for the safety of operators [21].

Units present in multiple stages in the process, such as compressors, can also carry risks. Compressors should include relief valves to vent excess pressure [22]. Distillation columns can also contain high pressures, and should be built with pressure relief valves and emergency shut down systems in case a vent line becomes blocked [23].

Measures should be taken to protect operators in the plant. Personal protective equipment should include hard hats, safety shoes, work gloves, safety goggles, hearing protection, portable carbon monoxide detectors, and flame retardant uniforms [24]. Employees should also be trained according to the PHA so they are aware of all risks associated with the process and can respond in case of emergency. Evacuation plans should also be put in place, as well as disaster response procedures.

9 CONCLUSIONS AND FUTURE WORK

As it currently stands, the proposed process is not profitable, with an NPV of -\$2,458,086,291. A variety of optimizations involving heat exchange network synthesis, unit operating temperatures, addition of recycle streams, and scaling of inlet streams were conducted, resulting in large economic improvements in comparison to the previous iteration. The feed rate of MSW needed to achieve 5,000 barrels/day of LTF was reduced from 740,071 kg/hr to 383,784 kg/hr, which has helped to reduce the number of process units needed. For example, only 1 Rectisol unit is currently needed, an enormous improvement from the 33 needed in the previous process simulation. The process also successfully produces an LTF product that is 88.85% diesel, which adequately addresses the design objective of maximizing diesel production.

Heat exchanger network synthesis via LP and MILP transshipment models succeeded in reducing the minimum utility cost to \$83,346,477/year, including electricity. The process features 23 hot streams, 14 cold streams, 5 available utilities (of which only Fuel and Cooling Water are necessary), and 27 temperature intervals. A minimum of 36 matches is required to meet the heat exchange needs of the process.

For future work, the process should be further optimized to improve conversion of carbon from the inlet MSW to the output LTF. The current carbon conversion is 8.37%, a value that should be increased if the pro-

cess is to be profitable. It may be possible that conducting sensitivity analyses on the operating conditions of more process units will allow for significant improvement of the carbon conversion. For example, different operating temperatures that have not been fully explored may further improve process performance. It would also be beneficial to model and test alternative approaches for different sections of the process, such as Fischer–Tropsch synthesis. However, it is important to note that although alternative approaches may achieve a higher conversion of MSW to LTF in terms of carbon, the units involved may prove to have a higher operating cost, rendering the process still economically infeasible.

Despite the current infeasibility of the process, it is important to note that process optimizations and heat integration led to significant steps forward in the profitability of the process. As it stands, the process can be expected to reach an annual net profit after taxes of 0 at a tipping fee of $160 per metric ton of MSW. As gas prices continue to rise and the importance of alternate fuel sources grows, this process of converted MSW to LTF may become more viable.

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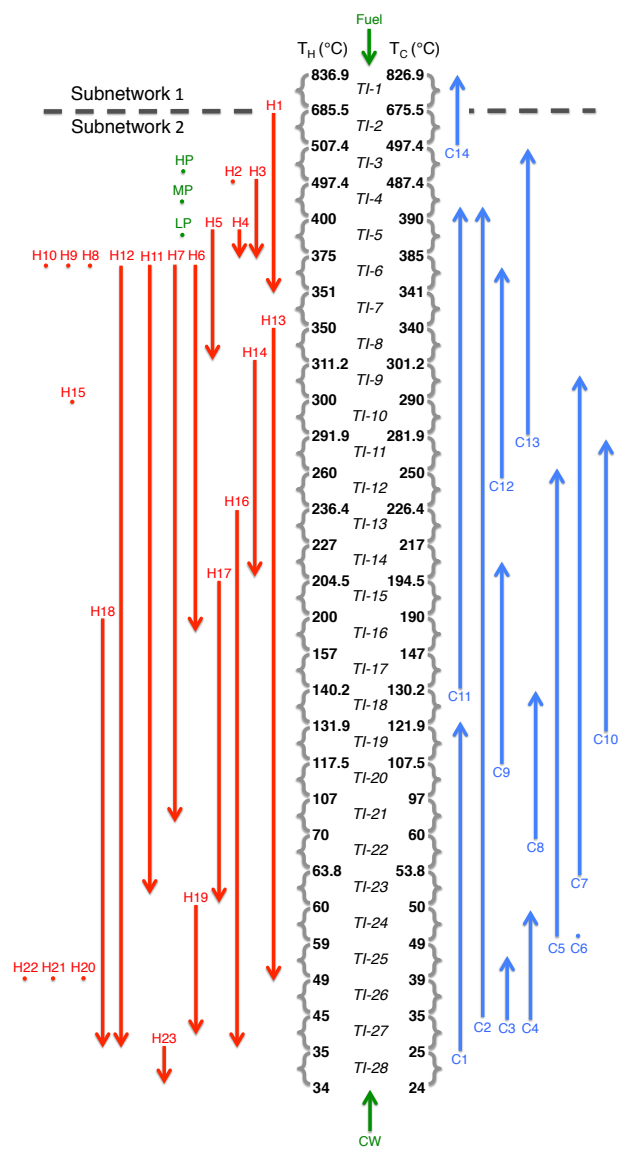
10 APPENDIX – TI DIAGRAM

Figure 12: Partitioned Temperature Intervals and Process Streams.
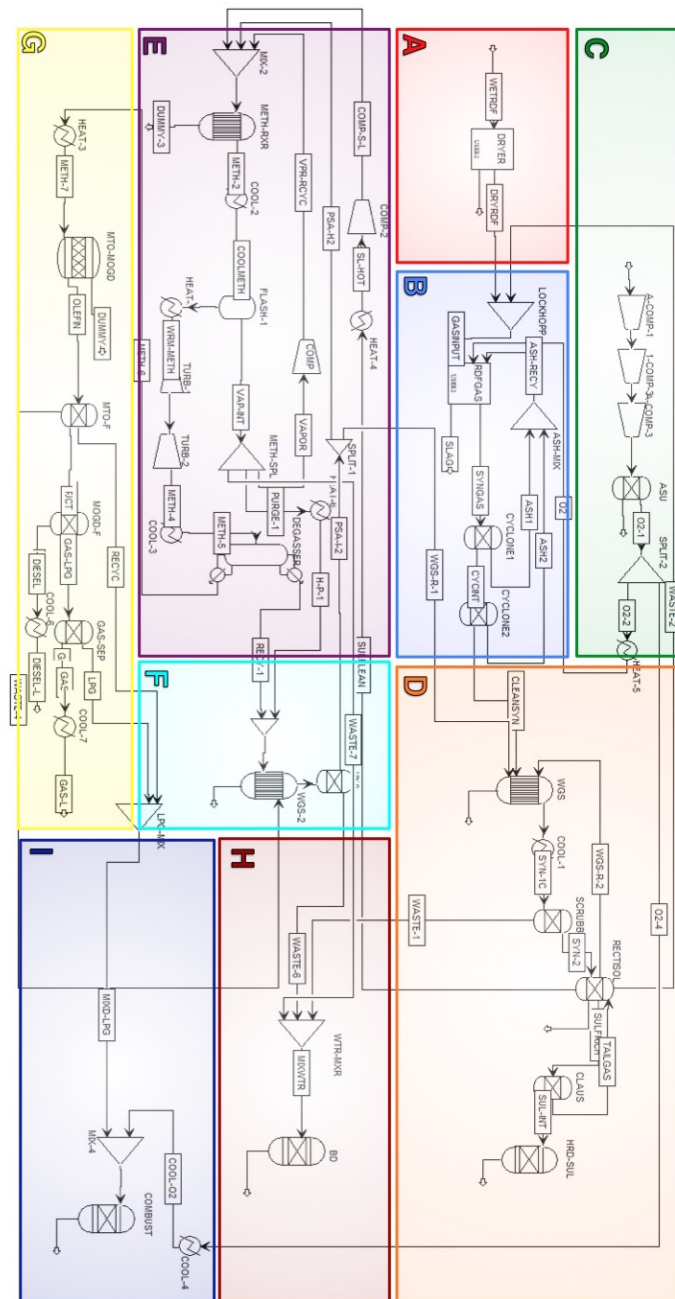
11 APPENDIX – ENTIRE PROCESS FLOWSHEET

Figure 13: Flowsheet of Entire Proposed MSW to LTF Process.

12   APPENDIX – ALTERNATE PROCESS: FISCHER– TROPSCH

As an alternative to the above methanol synthesis and conversion process, Fischer-Tropsch synthesis could be used to produce diesel and other liquid transportation fuels from municipal solid waste (Figure 14 on the following page).

The first steps of this proposed process are identical to Process 1. MSW is converted to RDF, which is input to a drier and lockhopped into the gasifier unit using CO_2. The same fluidized bed gasifier as in Process 1 is also used here, and two cyclones are used to remove solid particles in the syngas as before. A WGS reactor, scrubber, Rectisol dual-capture system, Claus recovery system, and LO-CAT iron-chelate unit are all used as described above. However, in this case the syngas from the Rectisol unit is sent on to the Fischer-Tropsch synthesis unit. The Fischer-Tropsch unit is a slurry-phase reactor utilizing a cobalt catalyst and operating at low temperatures to convert the syngas to hydrocarbons [29]. The lower temperatures allow for a higher alpha value, resulting in a higher liquid selectivity and producing more diesel-range hydrocarbons [33]. The cobalt catalyst is chosen over iron due to its higher activity and the higher per-pass conversion [16].

The hydrocarbons will leave the FT unit in a waxy liquid stream and vapor stream. The wax is sent to a hydrocracker and the vapor is sent for processing [16]. A hydrocracker takes heavy hydrocarbons, such as the waxy liquid produced in FT synthesis, and cracks them into lower mass gasoline and distillate range hydrocarbons through catalytic cracking [5]. These hydrocarbons are then separated based on their molecular weights, as in the methanol synthesis and conversion process described previously, resulting in a diesel range stream and gasoline range stream, as well as a wastewater stream.

The vapor phase is composed of hydrocarbons ranging from C_1 to C_{30+} in addition to water and oxygenated species. To treat the vapor phase, first the water-soluble oxygenates are removed and sent to wastewater treatment [14]. The stream is then sent to a three-phase separator to remove the aqueous phase from the vapor and hydrocarbon liquid [29]. The vapor is further separated to remove oxygenates, and the hydrocarbon liquids are combined with the hydrocarbons from the three-phase separator. In all of these steps, the wastewater and oxygenates are sent to the biological digester for treatment, as explained previously [16]. The hydrocarbon liquid is passed over a ZSM-5 zeolite for conversion to gasoline and distillate [14].

The ZSM-5 effluent is separated so that the water is sent to wastewater treatment, the diesel-range hydrocarbons are added to the diesel from the hydrocracker, and the gasoline is sent through a gasoline-LPG separation process as described previously [14].
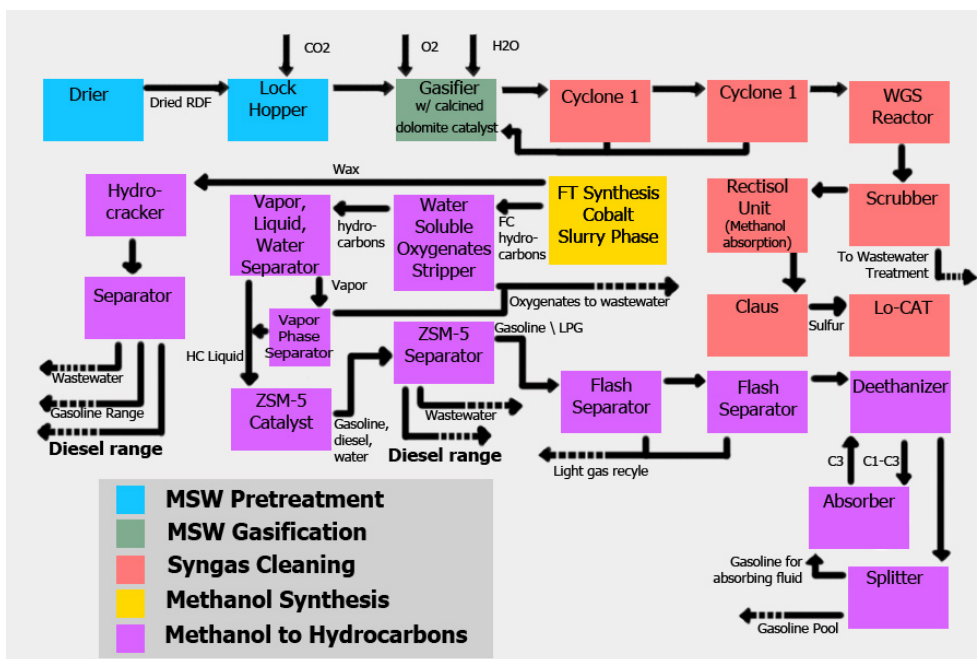
Figure 14: Diagram of diesel production via Fischer–Tropsch.

13 APPENDIX – BACKGROUND

13.1 Usefulness of MSW as a Feedstock

While coal, natural gas, and biomass have traditionally been considered in the development of synthetic fuels through either Fischer–Tropsch synthesis or methanol synthesis and conversion, municipal solid waste has a number of advantages that make it worth investigating as a feedstock.

There is a strong financial incentive to use MSW as a feedstock instead of other forms of biomass, as MSW is negatively priced with a tipping fee ranging from \$24–70. [40]. The tipping fee varies widely and is affected by state and local government regulations, the origin of arriving waste, and the method of MSW disposal (e.g. landfill or incineration) [42].

Another considerable advantage of using MSW over other types of biomass is that infrastructure already exists to collect MSW and dispose of it in landfills. Additionally, there is a trend towards a smaller number of larger landfill sites and more landfill sites being operated by waste management companies that could serve as potential collaborators on the development of a MSW-to-liquid fuels treatment facility. [42]. In 2006 there were 47 landfill sites in the US receiving at least 3,300 short tons per day of MSW, which is a rough estimate of the daily rate of raw feedstock necessary to feed an economically viable 2,000 tons-per-day wood gasifier [42].

After pretreatment, MSW must be converted into a synthesis gas by gasification, but impurities such as ash and water dilute the heating value of the biomass and are detrimental to the gasification process. If

MSW is to be a useful feedstock, ash produced during gasification must be removed from the product gas. The gas must also be dried to remove contaminating water. There is a tradeoff that must be considered between the cost of further purifying the feed and the cost of operating the gasifier [42].

13.2 MSW Pretreatment to Produce RDF

Before conversion to syngas in a gasifier, the municipal solid waste must be converted to refuse derived fuel (RDF) in order to increase the heating value and meet the size and material requirements of the gasifier. These steps, largely based on physical separation, must be carried out in order for syngas conversion to be effective.

MSW contains a number of recyclable and non–combustible materials that should be removed to facilitate conversion of the remaining combustible material for use as fuel. The product of this processing is RDF, a homogenous fuel that occurs after ferrous material is removed and shredding, screening, crushing, eddy-current separation, and air classification occur. A successful pretreatment process will convert 75-85% of MSW by weight to RDF and will retain 80-90% of the biomass's heating content [42].

First the material is shredded to reduce particle size, and then the shredded material is passed through magnets to remove ferrous metals. An eddy current separator is utilized to remove nonferrous metals; aluminum in particular can be collected and sold for $1/lb [43]. Disc screens are next used to remove larger material and an air classifier separates material by weight. The material is then shredded again to further reduce particle size, resulting in usable RDF that comprises 80% of the original feed [43].
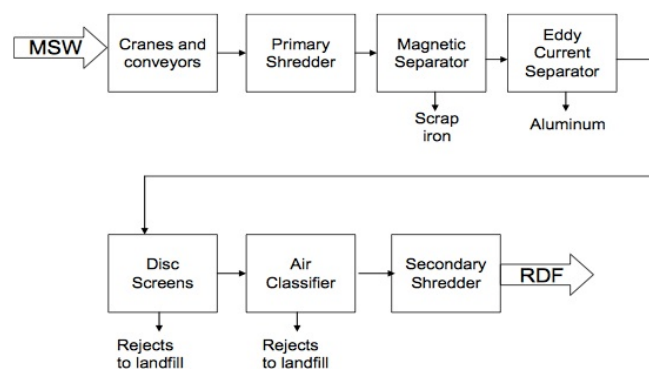

Figure 15: Diagram of MSW pretreatment process [43].

Following conversion of MSW to RDF, the RDF must be dried to reduce moisture content from 28% to 8.8% before being sent to the gasifier [7]. According to other sources, MSW can have a moisture content of up to 50% that can be reduced to 12% using rotary dryers [43]. The drying process is aided by heat from flue gas generated by combustion elsewhere in the process [16]. After drying, the RDF is passed through a lockhopper that uses compressed 10 wt% CO_2 to transfer the RDF into the gasifier [16].

13.3 MSW Gasification to Produce Synthesis Gas

MSW gasification for liquid fuels synthesis is a viable technology and has a number of advantages over MSW combustion. Pyrolysis reactions, followed by reduction and oxidation reactions using steam and/or oxygen are used to convert the RDF into synthesis gas that will be converted to hydrocarbons downstream, and a number of byproducts that must be addressed. There are four different types of gasifiers with advantages and disadvantages that will be discussed here.
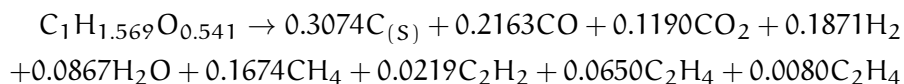
It is only recently that a simulation model has been developed for the gasification process [15]. The result of gasification is the breakdown of the long-chain polymers present in RDF to the following assortment of molecules: "$CO_2, CO, H_2, H_2O, CH_4, C_2H_2, C_2H_4, C_2H_6, N_2, NH_3, HCN, NO, N_2O, H_2S, Ar$, Char (100% carbon), and ash" [7]. The molecules of interest in this step are the H_2 and CO molecules that form through pyrolysis, oxidation, and reduction [15]. These organic molecules, along with CO_2, form synthesis gas (syngas) that can then be converted to methanol, and eventually to gasoline-range hydrocarbon polymers. The effluent stream is assumed to be in equilibrium with respect to the water-gas shift reaction (see Methanol Synthesis section) [14]. Thus, the proportion of these syngas products in the gasifier output (Nx) is constrained according to the equilibrium equation of the water-gas-shift reaction: [7]

$$N_{H_2}N_{CO_2} \rightleftharpoons K_{WGS}^{eq}N_{H_2O}N_{CO} \qquad (26)$$
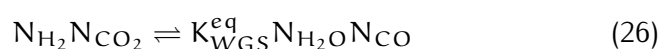
The equilibrium constant K_{WGS}^{eq} here can be calculated by running Aspen simulations at differing temperatures. The overall species flowrates can be calculated with an atomic balance on the gasifier, along with the equations for the other product species as indicated in the Problem Statement. Composition of the gasifier effluent is dependent on RDF composition, gasifier temperature, and steam/oxygen flowrate [14]. 99% of the ash input can be disposed of as slag, with the rest being captured by cyclones and recycled. Steam and/or oxygen will be used to oxidize the pyrolysis products in a ratio that will be calculated during process simulation in order to optimize eventual production of diesel-range hydrocarbons [7].

The biomass in RDF consists largely of cellulosic materials and plastic. The predominant carbon molecules present in these are as hemicellulose ($C_5H_8O_4$), cellulose ($C_6H_{10}O_5$), Lig-C ($C_{15}H_{14}O_4$), Lig-O

($C_{20}H_{22}O_{10}$), Lig-H ($C_{22}H_{28}O_9$), polyethylene ((C_2H_4)n), and polystyrene ((C_8H_8)n) [15]. Separate models are developed for the pyrolysis reaction for each of these molecules, and these models are combined based on the proportions typically present in RDF feedstock to produce the overall pyrolysis equation [15]:

$$C_1H_{1.569}O_{0.541} \rightarrow 0.3074C_{(S)} + 0.2163CO + 0.1190CO_2 + 0.1871H_2$$
$$+0.0867H_2O + 0.1674CH_4 + 0.0219C_2H_2 + 0.0650C_2H_4 + 0.0080C_2H_4$$

Although gasification is not vastly commercialized, it is an attractive option because it has been shown to perform better than combustion when subjected to economic analysis [39]. This process also results in an intermediate gas product at a higher efficiency and lower temperature than combustion that can be used in a wider range of applications [47]. A nonconvex, nonlinear model of RDF gasification has been developed that serves as the basis for further designing commercial RDF gasifiers [15]. It is desirable to produce syngas with a H_2/CO ratio greater than 1 to favor production of liquid fuels [37]. Tar buildup, the accumulation of organic material produced by partial-oxidation of the biomass, is a serious concern for any gasification process [38]. However, a calcined dolomite catalyst will be used within the gasifier, which has been shown to reduce tar content to negligible levels in the syngas when steam is introduced, as is the case here [7, 36]. An outline of the various types of gasifiers available for potential use is discussed in the following section.

There are four types of gasifiers that will be discussed: fixed bed, fluidized bed, entrained flow, and plasma. Each has advantages and disadvantages that will be assessed [42]. Larson et al. recommend using a pressurized, oxygen-blown fluidized-bed gasifier [2]. The process is oxygen-fed because, despite the costs of supplying O_2 from the air separation unit, this results in fewer cleanup steps downstream. Although MSW must be pretreated to work with fluidized bed gasifiers, this is not a problem because the feedstock will be RDF. Using this type of gasifier involves small residence times ranging from 1 second to 1 minute, which will allow us to scale up the process to support production of 5,000 barrels/day of liquid transportation fuels as specified [7].

13.3.1 *Fixed Bed Gasifiers*

Biomass is added to the top of the gasifier while ash and char are removed from the bottom. The biomass will move slowly through a fixed zone. The gasifier is relatively small and is directly heated using air or purified oxygen from an air separation unit (large-scale gasification). An up-draft gasifier can be used, in which air is introduced at the bottom and reacted gases exit at the top in counterflow to the biomass entering at the top. Gases exiting an up-draft gasifier will usually be at a temperature of about 772K. An advantage of this configuration is that char produced from slow pyrolysis of the biomass sinks towards the bottom where it is

combusted by the introduced air, releasing heat that can be used to drive endothermic drying and pyrolysis reactions [42].

The alternative fixed bed gasifier is a down-draft design, in which the moisture, pyrolysis gases, and tars produced pass out through the bottom of the vessel through the area in which air is introduced. This allows the air to combust the pyrolysis gases, tar, and some of the char in a high temperature area in which steam and CO_2 can react with the remaining char to produce more H_2 and CO. [35]. This setup produces on the order of 1000 times fewer tars in the product gas than the up-draft gasifier design [42]. Both fixed bed gasifiers are low-cost but are limited in capacity due to long biomass residence times and limits on vessel size. Up-draft gasifiers can handle higher moisture and ash content, but produce high tar content in the product gas (10–20 wt%) [35].

13.3.2 Fluidized Bed Gasifiers

Fluidized bed gasifiers make use of a heated solid that is made to bubble due to introduction of a gas at sufficient velocity to fluidize the solid and allow for free motion. MSW is introduced and mixed with the solid (hot sand), resulting in gas and small quantities of tar and char. The fluidized sand grinds up the char to small char and ash particles that must be removed by cyclone after exiting the gasifier [42]. These types of gasifiers operate at 980–1230K with residence times ranging from a second to a minute, allowing them to scale to higher capacities. However, MSW must be pretreated to remove large heavy particles, size reduced, and screened to achieve particles with uniform aerodynamic particle properties to be usable in a fluidized bed gasifier. RDF is a suitable feedstock. This setup produces quantities of tar in the range of 5.9×10^{-4} - 8.9×10^{-4} lbs/scf, comparable to fixed bed gasifiers, but results in an undesirable high aromatic content [30, 42].

13.3.3 Entrained Flow Gasifiers

Entrained flow gasifiers introduce gas at the bottom of the vessel at a high velocity, causing entrained flow in the fluidized medium and biomass occurring at the top of the vessel. Residence times range from 1–10 seconds at 1170–1670K. Entrained flow gasifiers are similar to fluidized bed gasifiers in terms of pros and cons, with the added advantage of greater throughput and disadvantage of more stringent required properties of the solid. Equipment erosion rates are also faster [42]. The RDF particles fed to entrained flow gasifiers must be a maximum of 1mm in diameter, which poses an additional constraint during the pretreatment step, but conversion to syngas is high [30].

13.3.4 Plasma Gasifiers

Gasifiers of this type use low-density ionized vapor to heat the feed stream. Extremely high temperatures are used to convert the biomass

stream to synthesis gas and slag. Arc plasmas are used for waste treatment, and a further molten metal or glass layer may be used [42]. The power requirements for plasma gasifiers are estimated at 0.34 – 4.4 MMBtu/ton of waste [6].

13.4 Synthesis Gas Cleaning

Synthesis gas contains contaminants such as tar, particulates, sulfur species, and NH_3. Before conversion to hydrocarbons either via methanol synthesis or Fischer-Tropsch synthesis, the syngas must undergo several cleaning steps to increase fuel quality and avoid catalyst poisoning downstream.

After leaving the gasifier, the raw syngas must be processed before conversion to hydrocarbons either through a Fischer-Tropsch process or methanol synthesis and conversion. First the gasifier effluent passes through two cyclones to remove solids in the vapor phase. The primary cyclone removes 99% of ash and char and the secondary cyclone removes the remaining solid particles; these are recycled and sent back to the gasifier [7]. Most syngas applications require a vast reduction in particulate matter [31]; this is certainly true for Fischer-Tropsch and methanol synthesis. A tar cracker, implemented as a bubbling fluidized bed reactor, may be used to convert tar and light hydrocarbons to CO and H_2 and to convert ammonia produced by the gasifier to nitrogen and hydrogen gas [43]. Tars are condensable organic compounds with complex chemical structures that have the "potential to foul filters, lines, or engines, as well as deactivate catalysts in...downstream processes" [31]. Thus it is important to remove tars given the extensive catalyst use downstream. According to the problem statement, the tar cracker is contained within the gasifier via the calcined dolomite catalyst, so a distinct tar cracking unit is not required.

Next the syngas is sent to a sour water-gas-shift (WGS) reactor, which will run either the forward or reverse WGS reaction depending on the desired ratio of H_2:CO [16]. The ideal ratio differs based on the method of syngas conversion; methanol synthesis and Fischer-Tropsch require different relative amounts of hydrogen and carbon monoxide. According to the Problem Statement, the WGS reactor will operate "in the presence of sulfur species, at a pressure of 26 bar, between 300-600°C, and can facilitate either the forward or reverse WGS reaction" [7]. Baliban et al. note similar operating conditions, indicating a pressure of 28 bar and 400-600°C. They also note that hydrogen can be supplied to help convert CO_2 using the reverse WGS reaction [16].

The syngas effluent from the WGS reactor is then sent to a scrubbing system that will remove remaining tar, particulates and NH_3 [7]. These are removed in a wastewater stream, which is treated as noted in section 2.10. The syngas is sent to a dual-capture methanol absorption system to remove the H_2S and CO_2. This step prevents "poisoning of the down-

stream hydrocarbon production catalysts" [16]. The removal of CO_2 helps to improve kinetics and economics downstream [4].

As Tijmensen et al. discuss, "Sulfur is an irreversible poison for the cobalt and iron catalysts...because it will stick to [the] active site" [29]. Furthermore, sulfur compounds corrode metal surfaces and if oxidized may form pollutants in the form of SO_2 [31]. Over 30 different technologies have been implemented to remove sulfur compounds from syngas [31]. The methanol absorption system implemented as a Rectisol unit can also remove NH_3 from the syngas [28]. Niziolek et al. simulate a Rectisol unit that removes 90 wt% CO_2 and 100 wt% H_2S. This effluent is then split into a sulfur-rich and CO_2-rich stream [3]. The sulfur rich stream contains 3 moles of H_2S for each mole of CO_2 and is sent to a Claus recovery system (95 wt% conversion of H_2S to solid sulfur).

Kreutz also implements a Rectisol acid gas removal system that uses methanol as an absorption fluid [4]. To recover the sulfur, the waste is sent through a sulfur recovery system. Baliban utilizes two types: a Claus recovery system to convert 95% of the H_2S to solid sulfur and a LO-CAT iron-chelate based process that when coupled with the Claus unit leads to almost 100% conversion to solid sulfur [16]. The CO_2 in the stream can be sequestered or sent back to be used in the reverse WGS reaction [28]. Finally, the clean syngas is compressed to 2000 psi and is sent to the methanol synthesis section [43].

13.5 Methanol Synthesis

In order to convert the cleaned syngas into hydrocarbons, a methanol synthesis unit can be used in conjunction with either a methanol-to-gasoline or methanol-to-olefins/distillate unit. In the methanol synthesis step, the syngas is converted to methanol in a fixed bed reactor, and once isolated will be converted to hydrocarbons.

A methanol synthesis reactor operating at 300°C and 50 bar is used, with an input of syngas that is either CO_2-rich or CO_2-lean [7]. These operating conditions are the same as those used in Baliban's study [16], while his 2012 study uses a pressure of 51 bar [3, 28]. According to Baliban et al., the ideal Ribblett ratio for this process is equal to 1, where the Ribblett ratio is defined as follows [16]:

$$H_2/(2CO + 3CO_2) \tag{27}$$

If the inlet stream is too CO_2-lean, concentration of CO_2 and H_2O in the effluent will be low, which will result in a "less energy intensive methanol purification if it is required for downstream conversion" [16]. On the other hand, when the input syngas is very CO_2-rich, the reverse WGS reaction will occur, increasing water concentration and thus the cost of methanol purification in the next step of the process [16]. An excess of CO_2 will also decrease rate of methanol production [26]. The Ribblett

ratio of 1 ensures that there is a "high overall conversion of ($CO + CO_2$) using subsequent recycle of unreacted syngas" [16].

The reactor may be a fixed bed tubular design, with catalyst in the tube and steam passing through the shell [43]. Lee et al. utilize a slurry phase reactor to carry out the synthesis reactions, owing to its good heat exchanging properties [26]. The catalyst used is a mixture of $Cu/ZnO/Al_2O_3$, specifically CuO and ZnO coprecipitated on an Al_2O_3 support [26]. The methanol synthesis reaction and the water–gas–shift reaction are assumed to be operating at equilibrium as follows:

$$CO + 2H_2 \rightleftharpoons CH_3OH \qquad (28)$$
$$CO_2 + H_2 \rightleftharpoons CO + H_2O \qquad (29)$$
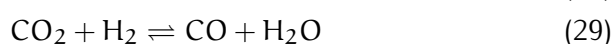
The expected per-pass conversion of CO and CO_2 to methanol is 35% [45]. One option is to dry the raw methanol product with a molecular sieve to achieve a pure methanol stream [43], but this is likely not necessary because downstream methanol processing steps will yield more water that can be later dealt with [7].

The effluent from the methanol synthesis reactor is sent to a flash separator, where over 95% of the methanol will remain in the liquid phase; inert gases will be removed from the vapor stream and the remaining 95% of vapor will be recycled back to the methanol synthesis reactor [16] in order to increase methanol yield [28]. The inert gas purge stream will be recycled and used as fuel gas. The bottoms, which contains 95% of the methanol, is heated to 200°C and 5 bar to generate electricity, and then cooled back to 60°C [3, 16]. The stream is then passed to a degasser distillation column, which recovers 99.9% of the methanol in the bottoms [16]. The distillate is recycled, while the bottoms containing methanol and water is then sent to the next unit for conversion.

13.6 Methanol to Hydrocarbons

The clean methanol from the methanol synthesis unit must be converted into hydrocarbons for use as fuel. This can be done in one of two ways, using either a methanol–to–gasoline (MTG) process, or a methanol–to–olefins (MTO) process followed by a Mobil olefins–to–gasoline/distillate (MOGD) process. Since the goal of this process is maximized diesel production, we utilize the MTO/MOGD process which results in a maximum of 82 wt% distillate/diesel.

Methanol can be converted to hydrocarbons using either a methanol–to–gasoline (MTG) or methanol–to–olefins (MTO) and then Mobil olefins–to–gasoline/distillate (MOGD) process [16]. These processes were developed by Mobil in the 1970's and 1980's, and use a ZSM–5 zeolite to convert the methanol to hydrocarbons [28]. Both the MOGD unit and the MTO unit generate steam to handle the exothermic reactions, which can

then be used elsewhere in the process [28]. The MTG process produces gasoline range hydrocarbons and others with carbon content shown in Table 22. [7]:

Table 22: Effluent of MTG Unit

Species		Value
CH_4	Methane	0.008244
C_2H_4	Ethylene	0.005161
C_2H_6	Ethane	0.005294
C_3H_6	Propylene	0.01035
C_3H_8	Propane	0.04943
C_4H_8	1-Butene	0.001756
iC_4H_{10}	Isobutane	0.059262
nC_4H_{10}	N–Butane	0.031692
C_5H_{10}	1-Pentane	0.000108
nC_5H_{12}	N–Pentane	0.006497
C_6H_{12}	1-Hexane	0.006376773
C_6H_{14}	N–Hexane	0.006376773
C_7H_{14}	1-Heptane	0.000108
C_7H_{16}	N–Heptane	0.002333374
C_8H_{18}	N–Octane	0.248430849
C_9H_{20}	N–Nonane	0.248916066
C_8H_{10}	P–Xylene	0.150142053
C_9H_{12}	1,2,3-Trimethylbenzene	0.165628885

Diesel hydrocarbons have carbon contents ranging from $C_{10} - C_{15}$, so it is clear that this MTG process does not produce hydrocarbons in the appropriate range and will thus not be used [7]. However, it is still valuable to examine the products of the MTG process. Methanol is catalytically converted to the hydrocarbons "using a ZSM-5 zeolite and a fluidized bed reactor" [16]. The conversion over the catalyst proceeds autocatalytically and caused by the reaction of olefin and ethanol [48]. In addition to the hydrocarbons shown above, the process produces an effluent stream of 44 wt% water [16]. Initially the crude hydrocarbons contain by weight: 2% light gases, 19% $C_3 - C_4$, and 79% gasoline. After upgrading, the effluent is upgraded to contain 82 wt% gasoline and 10 wt% liquefied petroleum gas (LPG), and the remainder recycle gases [16].

The MTO and MOGD processes, on the other hand, do produce diesel. According to Niziolek et al, the MTO operates at 375°C and 1 bar, and the methanol is heated to 375°C and 1.2 bar prior to entering the unit [3]. However, Baliban et al. and the Problem Statement specify the methanol as being preheated to 400°C and compressed to 1.2 bar prior to entering the MTO [1,7]. Due to the high operating temperature, production of light olefins is thermodynamically favored [3].

The MTO unit is a fluidized bed reactor that may utilize a SAPO–34 catalyst to convert 100% of the methanol inlet stream to an olefin effluent [3]. Based on the process used by Baliban et al., the effluent composition will be 1.4 wt% CH_4, 6.4 wt% $C_2 - C_4$ paraffins, 56.4 wt% C_2-C_4 olefins, and 35.7 wt% C_5-C_{11} gasoline [16]. According to Niziolek et al, the effluent of the MTO unit is over 95 wt% $C_2 - C_4$ olefins [3]. The difference in compositions is likely due to the lack of catalyst SAPO–34 used in Baliban et al.'s model. The composition in the Problem Statement differs and is stated to be 93 wt% olefins [7]. In all cases, the product is sent to the methanol–to–olefins fractionator (MTO-F) to separate the light gases, olefins, and gasoline exiting the MTO unit. According to Baliban et al. 2013 and Niziolek et al., $C_1 - C_3$ paraffins are recycled, gasoline is sent to a gasoline stream along with other gasoline produced during the process, water is sent to wastewater treatment, and C_4 paraffins and olefins are sent to the MOGD unit for conversion [3,16].

The MOGD unit is a fixed bed reactor running at 400°C and 1 bar that uses a ZSM–5 zeolite to convert the olefins to gasoline and distillate [3,7]. ZSM–5 was shown by Tabak et al. to be temperature and pressure dependent up to 650K, but at temperatures above 650K equilibrium constraints limit the molecular weight of the product [34]. According to Niziolek et al., the unit can run in maximum distillate or maximum gasoline mode by varying the reaction temperature and recycle composition [3]. In maximum distillate mode the effluent contains 82 wt% distillate, and in maximum gasoline mode the effluent contains 84 wt% gasoline [3]. Baliban et al. select a gasoline/distillate ratio of 0.12 in order to achieve this same goal [16].

The MOGD effluent (seen in Table) is then fractionated to separate the diesel–containing distillate from the gasoline and light gases. According to Baliban et al., the unit outputs 82 wt% distillate, 15 wt% gasoline, and 3 wt% light gases [16]. Again, the problem statement gives a different composition, shown below, that can be summarized as 8.2095 wt% light gases, 12.1061 wt% gasoline, and 79.6844 wt% distillate [7].

13.7 LPG-Gasoline Separation

Following separation from diesel, the gasoline and light gases must be separated because gasoline is a desired liquid fuel, and the light gases can be recycled back into the process to produce electricity, heat, or additional syngas.

After separation from the diesel, the gasoline and light gases, or liquefied petroleum gas (LPG), must be separated, as the gasoline is a desirable product while the LPG will be recycled. First the gasoline and LPG are passed through two flash units that remove some of the light gases. The crude hydrocarbons are then passed through more separation units, including "a deethanizer column, a stabilizer column, an absorber

Table 23: Effluent of MOGD Unit

Species		Value
CH_4	Methane	0.012250
C_2H_4	Ethylene	0.05000
C_2H_6	Ethane	0.002800
C_3H_6	Propylene	0.015900
C_3H_8	Propane	0.001145
C_5H_{12}	n–Pentane	0.000733
C_6H_{14}	n–Hexane	0.000738
C_7H_{16}	n–Heptane	0.000319
C_9H_{20}	n–Nonane	0.036512
C_9H_{12}	1,2,3–Trimethylbenzene	0.170665
$C_{13}H_{28}$	n–Tridecane	0.180795
$C_{15}H_{32}$	n–Pentadecane	0.235831
$C_{10}H_{14}$	1,2,4,5–Tetramethylbenzene	0.170665
$C_{14}H_{30}$	n–Tetradecane	0.209552

column, a splitter column, and an LPG alkylate splitter to separate the LPG from the gasoline fractions" [16]. The de-ethanizer removes $C_1 - C_2$ hydrocarbons [28], which are then sent to an absorber that removes remaining C_3 species using a lean oil recycle stream [28]. The $C_1 - C_2$ species are recycled while the C_3 species return to the de-ethanizer. The heavier hydrocarbons are sent to a stabilizer column for alkylation; if butane species were present as they are in the MTG process, these would be removed, but the MTO/MOGD process does not produce butane [28]. The de-ethanizer removes $C_1 - C_2$ hydrocarbons [28], which are then sent to an absorber that removes remaining C_3 species using a lean oil recycle stream [28]. The $C_1 - C_2$ species are recycled while the C_3 returns to the de-ethanizer. The heavier hydrocarbons are sent to a stabilizer column for alkylation; if butane species were present as they are in the MTG process, these would be removed, but the MTO/MOGD process does not produce butane [28].

The gasoline range hydrocarbons leaving the de-ethanizer are sent to a splitter column, which sends some gasoline back to the absorber column to help remove C_3 hydrocarbons and the rest to the gasoline stream [7]. "Light and heavy gasoline fractions are recovered from the column top and bottom, respectively" [28]. These steps result in all of the hydrocarbons being separated into light gases, gasoline, and diesel according to the split fractions in Table [7]:

Table 24: Hydrocarbon Split Fractions

Species		Light Gas	Gasoline	Diesel	Waste Water
H_2O	Water	0	0	0	1
CH_4	Methane	1	0	0	0
C_2H_4	Ethylene	1	0	0	0
C_2H_6	Ethane	1	0	0	0
C_3H_6	Propylene	1	0	0	0
C_3H_8	Propane	1	0	0	0
C_5H_{12}	n-Pentane	0	1	0	0
C_6H_{14}	n-Hexane	0	1	0	0
C_7H_{16}	n-Heptane	0	1	0	0
C_9H_{20}	n-Nonane	0	1	0	0
C_8H_{10}	p-Xylene	0	1	0	0
C_9H_{12}	1,2,3-Trimethylbenzene	0	1	0	0
$C_{13}H_{28}$	n-Tridecane	0	0	1	0
$C_{15}H_{32}$	n-Pentadecane	0	0	1	0
$C_{10}H_{14}$	1,2,4,5-Tetramethylbenzene	0	0	1	0
$C_{14}H_{30}$	n-Tetradecane	0	0	1	0

13.8 Light Gas Recycling

The light gases produced by methanol synthesis and conversion or Fischer-Tropsch synthesis should be recycled in order to reduce waste and make use of the energy available in these byproducts.

The light gases generated by either methanol synthesis and conversion or Fischer-Tropsch synthesis may be recycled in one or several ways. These consist of H_2, CO, CO_2, H_2O, $C_1 - C_2$ hydrocarbons, and inert species [14], and may be recycled back to the methanol synthesis or Fischer-Tropsch synthesis unit via an internal gas loop [16]. Some of the light gas stream must be purged to prevent build-up of inert species [3]. Since the light gases contain unreacted H_2 and CO, the recycle stream may serve to increase per-pass conversion [14]. The benefit of this route is a higher yield of liquid transportation fuels with minimal cost to recompress the gases [16]. The purged gases enter an external gas loop and can be directed either to a turbine to recover electricity or to a combustion unit to produce heat [7], with conditions as specified in the Problem Statement. The effluent gases from the gas turbine and combustion unit pass through a CO_2 separation unit (Rectisol unit) to allow for CO_2 recycling before being vented to the atmosphere [14]. Only a compressor or heat exchanger are necessary for this recycle stream to transfer the unreacted syngas to the reactor inlet, a reduction in the number of necessary process units that will help to reduce capital costs [14]. The proportion of light gas that is recycled versus purged is a design consideration to be optimized [14].

Another possibility is to send the light gases to an autothermal reformer that will convert the hydrocarbons into a hydrogen-rich syngas [16], which can then be added to the syngas stream entering the methanol or Fisher-Tropsch synthesis unit [3]. Alternatively, the light gases could also be combusted to supply heat to units such as the drier and gasifier [3].

13.9 Hydrogen/Oxygen Production

There are two options for H_2 and O_2 production. The first is to produce H_2 via pressure swing adsorption system of the syngas, while an air separation unit (ASU) produces 99.5 wt% O_2. The second is to use an electrolyzer fed water to produce both H_2 and O_2.

To produce O_2 using an air separation unit (ASU), air is first compressed to 190 psia then passed to the ASU operating at 90f and 125 psia. 99.5 wt% O2 is produced by the ASU, and the N_2 rich effluent is vented. The effluent O_2 is then compressed and either mixed with O_2 from the electrolyzer or passed to the various O_2 requiring process units [27].

To produce H_2 from syngas, the syngas is preheated and then passed to water-gas shift reactor (WGS). CO_2 is removed from the effluent of the WGS after which the remaining gas is purified using a pressure swing adsorption system [3]. Purge gas from this process can be burned with electricity then exported as a product. Two alternate arrangements are explored by Larson et al.: in one H_2 production is maximized with little exported electricity, and in the other the water-gas shift is lessened to export approximately equal amounts of H_2 and electricity [2]. The other option that can be used in conjunction with those listed above is to generate O_2 and H_2 through electrolysis in an electrolyzer [3, 27]. O_2 not consumed in the diesel production process can be sold as product.

13.10 Wastewater Treatment

Wastewater for the system will be treated by utilizing a biodigester (BD) and sour stripper (SS) in combination to effectively remove acid gases and hydrocarbons. The BD's purpose is to operate either aerobically or anaerobically to convert undesired hydrocarbons and acid gases into biogases: CH_4, CO_2, H_2, NH_3, and Ar which can be recycled to the process for combustion.

13.10.1 *Process Wastewater Handling*

The biodigester (BD) can act as a primary waste removal unit if acid gas concentrations are sufficiently low. Based on simulation data from Baliban et al. 2011, acid gas concentrations are sufficiently low in the effluents of hydrocarbon recovery unit (HRC), wax hydrocracker (WHC),

and distillate hydrotreater (DHT); therefore these streams can be combined and either passed directly to the BD or first through the SS and then to the BD [1].

Due to acid gas concentrations, the effluents from acid gas flash unit (AGF), Claus flash unit (CF), and aqueous effluent from Fischer–Tropsch hydrocarbon production must first be passed through the SS. Effluent from SS may either be sent away as outlet or sent to the BD to produce biogas. Sour gas from the SS is compressed and recycled back into the process [1].

Wastewater also comes from the post-combustion knockout units including: fuel combustor flash (FCF) and gas turbine flash unit (GTF). These are combined and can be sent to the SS and then the BD, directly to the BD, or directly as outlet wastewater [1].

Biogas from the BD can be sent to to the Claus combustor (CC), while the treated water can be recycled back into the process to the electrolyzer, cooling tower, deaerator, or directly discharged as outlet wastewater [1]. The biogas can also be fractionated to isolate CH_4 and sent to an autothermal reformer (ATR) to produce additional CO and H_2 which can be recycled back into the process [16].

13.10.2 *Utility Wastewater Handling*

Steam is required for use within the biomass gasifier (BG), autothermal reactor (ATR), and water–gas–shift reactor (WGS). The steam cycle must incorporate blowdown streams to prevent the build-up of solids which hinder heat transfer. Reverse osmosis (RO) is employed to remove solids from blowdown streams collected from the cooling tower, or from a combined stream of all process boilers. Following RO the effluent may be sent to a deaerator, back to the cooling tower, or as output from the system [1].