

Methane to Gasoline

1. Introduction

The goal of this project is to design a process for methane to methanol to gasoline, which would produce 100,000 barrels per stream day (BPSD) of gasoline. The motivation for this project is to use the new, abundant resource of shale gas methane other than for a heating fuel. In addition to the production of gasoline, substantial quantities of other liquid fuels, petrochemicals, and electricity can be produced from this process.

2. Results

2.1 Overall Process Design

The block flow diagram (BFD) for the entire MTG process is shown in Figure 2.1-1. The process flow diagrams (PFDs) corresponding to each of the blocks are provided with description in the respective plant sections. The natural gas and oxygen are fed into Unit 100 where they are reacted to produce syngas, energy, wastewater, and carbon dioxide. The syngas mixture was set to a 2:1 mixture of carbon monoxide and hydrogen before being fed in to Unit 200. The syngas is reacted in Unit 200 to produce methanol and energy. The methanol is then fed into Unit 300 and further reacted to produce gasoline, LPG, propylene, ethylene, energy, and wastewater. The wastewater from the process would be sent to an off-site facility for treatment prior to being discharged to the environment. The excess energy from the entire process would be used to heat boiler feed water to produce high-, medium-, and low-pressure steam, which would then be run through turbines to produce electricity, which could be used on site in the process or be sold to the power grid.

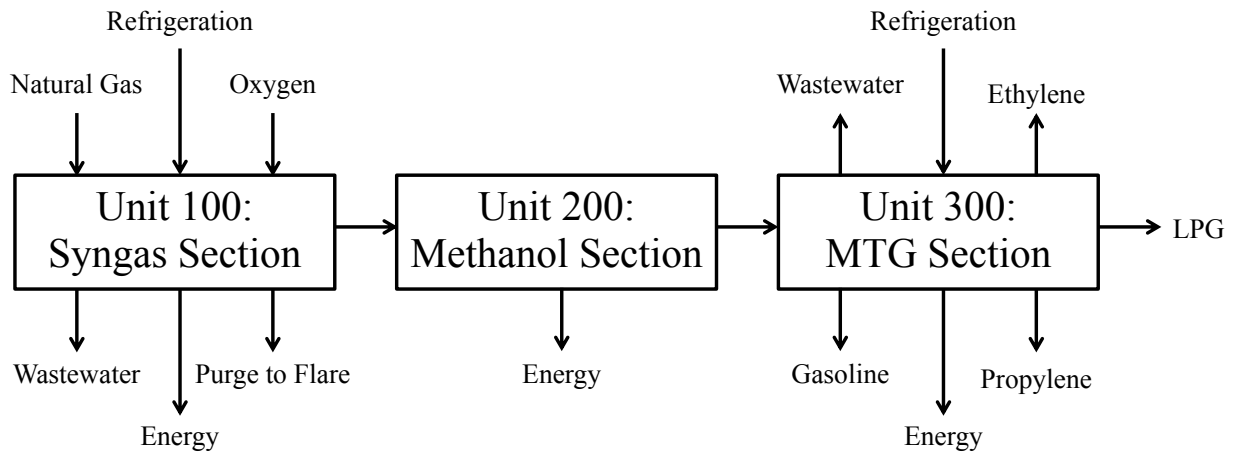


Figure 2.1-1: The BFD for the Methanol-to-Gasoline Process

The overall manufacturing cost summary for the proposed MTG production process is given in Table 2.1-1. This table details the itemized annual cost of the raw materials, products, and utilities along with the corresponding cost per unit. The electricity value given in the table is the net amount generated after the process needs are met.

Table 2.1-1: Manufacturing Cost Summary for Units 100, 200, and 300

Raw Material	Annual Feed (tonne/y) (MSCMD)*	Cost (\$/tonne) *(\$/MSCM)	Cost (\$million/y)
Natural Gas	32,000*	103.52* ^[1]	1,178,000,000
Pure Oxygen	11,690,000	66.61 ^[2]	779,000,000
Products	Annual Production (tonne/y) (BPSD) [^] (1000m ³ /y) ^{&}	Cost (\$/tonne) (\$/bbl) [^]	Cost (\$million/y)
Ethylene	199,000	1,278.68 ^[3]	(481,000,000)
Propylene	376,000	1,499.14 ^[3]	(298,500,000)
LPG	37,500 [^]	112.56 [^] ^[4]	(1,496,000,000)
Gasoline	100,000 [^]	123.62 [^] ^[6]	(4,383,000,000)
Wastewater	9,800 ^{&}	41.00 ^{&} ^[5]	400,000
Utilities	Energy Consumption (GJ/y) (MWh) [#]	Cost (\$/GJ) (\$/kWh) [#]	Cost (\$million/y)
Electricity	670,000 [#]	00.06 [#] ^[5]	40,060,000
High-Pressure Steam	5,120,000	00.00 ^{\$}	-
Medium-Pressure Steam	2,020,000	00.00 ^{\$}	-
Low-Pressure Steam	7,790,000	00.00 ^{\$}	-
Cooling Water	95,990,000	0.354 ^[5]	34,980,000
Refrigeration (5°C)	2,010,000	4.43 ^[5]	8,910,000
Refrigeration (-20°C)	2,000,000	7.89 ^[5]	15,750,000

() - Denotes a negative value, \$ - No cost, since all energy needs were produced from process

2.2 Unit 100: Syngas Plant Section

Unit 100 is the synthesis gas (syngas) production section of the plant. Figure 2.2-1 displays the PFD for Unit 100. In the feed section of the process, 59,750 kmol/h of natural gas, available at 25°C and 6.6 bar, are fed to the process. The methane feed would be compressed to 35 bar using staged compression and then mixed with the recycle stream, Stream 31. Stream 31 would be compressed to 35 bar by C-105 and heated to 216°C via E-113, E-114, E-115, and E-116.

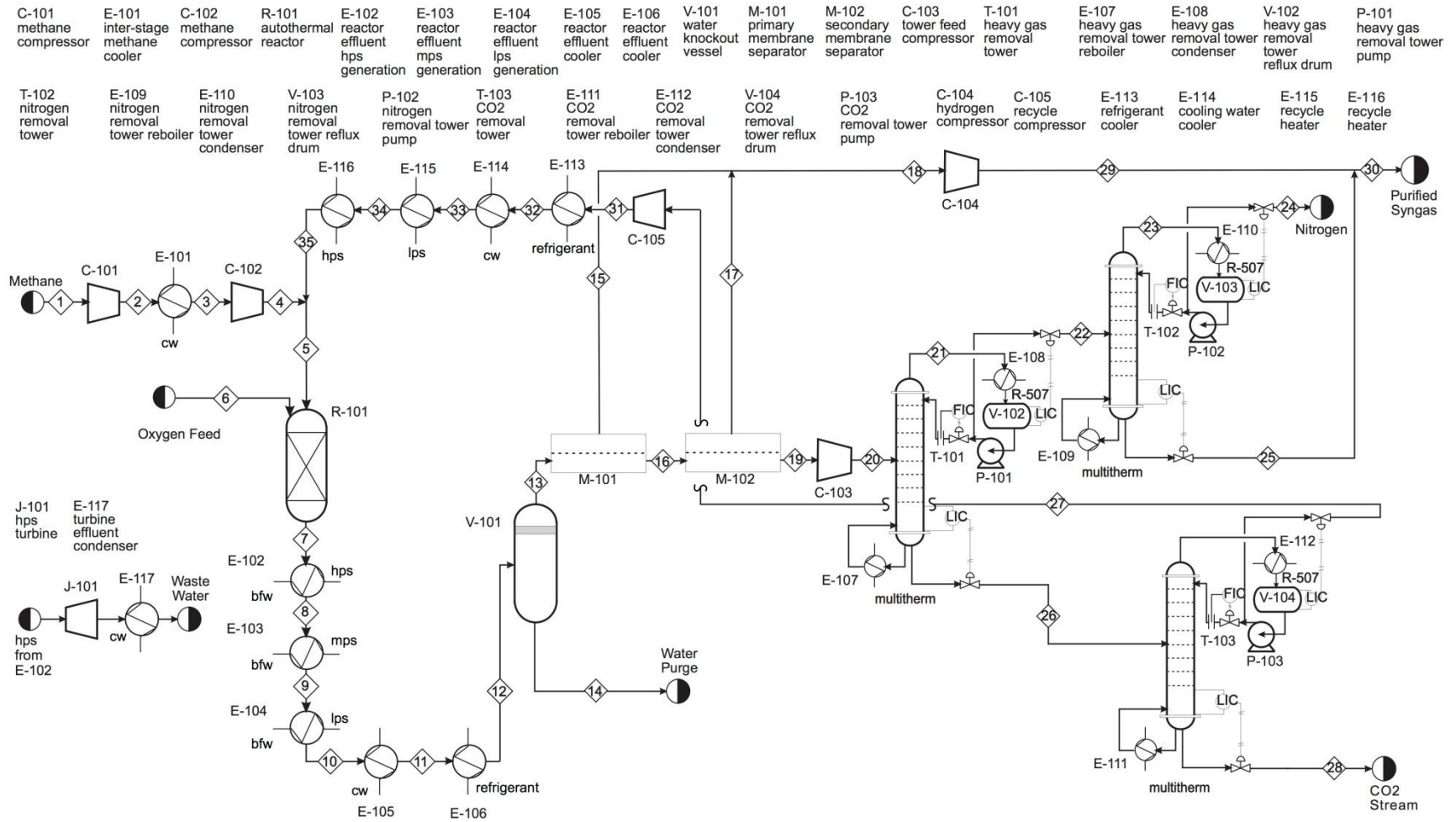


Figure 2.2-1: Unit 100 Syngas Plant

Stream 5, would then be fed to R-101 with the oxygen feed, Stream 6, of 42,980 kmol/h. This oxygen feed would be available at 25°C and 35 bar from an accompanying oxygen plant. The oxygen would be fed in a stoichiometric amount to combust 11.4% of methane and other heavier hydrocarbons contained in the natural gas feed. The combustion raises the temperature within R-101 to 1400°C and generates water needed for the steam reforming reactions. The water-gas shift reaction, along with other side reactions, produces the syngas consisting of hydrogen and carbon monoxide required for Unit 200.

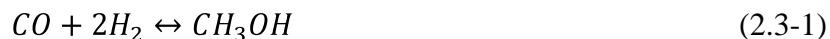
Through R-101, the endothermic water-gas shift reaction reduces the temperature from 1400°C down to 837°C. The reactor effluent would then be cooled to 10°C for the separations section. This is accomplished by using a series of heat exchangers, E-102, E-103, E-104, E-105, and E-106. High-, medium-, and low-pressure steam would be generated in E-102, E-103, E-104 using boiler feed water. These three exchangers cool the effluent to 170°C. The effluent would be further cooled to 10°C using cooling water in E-105 and low-temperature refrigerant in E-106.

The syngas reactor outlet in Stream 12 would be fed to the water knockout vessel, V-101, where water is designed to be purged from the system in Stream 14. Stream 13, which would contain mostly unpurified syngas and heavy recycle gases, is designed to be fed to two membrane separators in series, M-101 and M-102, and hydrogen would be removed from Stream 19. The membrane retentate would then be prepped and fed to T-101 by C-103. In T-101, the heavy recycle gases are designed to be removed in the bottom product at -48°C and carbon monoxide and nitrogen are to be sent to T-102 at -78°C for further separation. Before being recycled to the syngas reactor, R-101, carbon dioxide would be removed from Stream 26 using T-103. Nitrogen is to be removed from Stream 22 in T-102 at -151°C and carbon monoxide in

Stream 25 would be mixed with hydrogen in Stream 29 at -28°C and 40 bar. Stream 30 is designed to contain 148,000 kmol/h of 2:1 ratio hydrogen and carbon monoxide syngas to be sent to Unit 200 for further processing. A detailed stream table for Unit 100 is given in Table 2.2-1.

2.3 Unit 200: Methanol Plant Section

Figure 2.3-1 shows the process flow diagram for the methanol reactor section of the plant. Carbon monoxide and hydrogen gas enter the process through Stream 1 at 160°C and at 29 bar. The mixture is compressed to a pressure of 65 bar through a series of compressors and then combined with the recycle stream prior to the second compressor. The syngas is fed to R-201 and converted to methanol by the reaction shown in Equation 2.3-1.



A cooling loop removes the heat generated by the reactor and preheats boiler feed water to 125°C . The reactor effluent is used to preheat additional boiler feed water in E-203 and is then cooled to 35°C . The methanol is separated from the unreacted syngas through a flash vessel, and the syngas is recycled to the reactor. The methanol product exits Unit 200 as a liquid at 35°C and 63 bar.

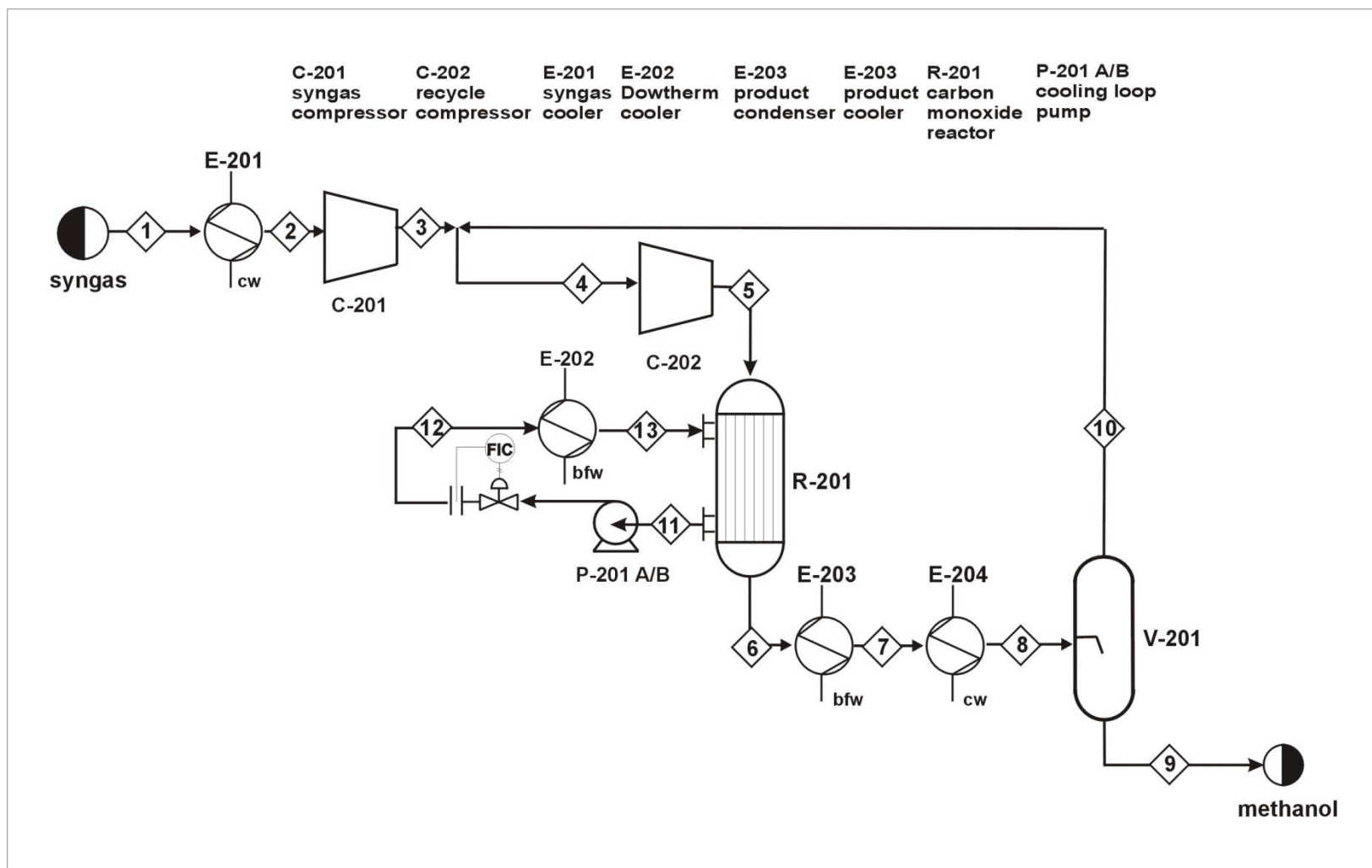


Figure 2.3-1: Process Flow Diagram for Unit 200 the Methanol Reactor Section

2.4 Unit 300: Methanol-to-Gasoline Plant Section

A process flow diagram of the MTG section is given in Figure 2.4-1. R-301 converts 95% of the incoming methanol feed to liquefied petroleum gas (LPG) and gasoline range products. It was determined that using the reactor effluent to vaporize the incoming methanol feed was the most cost effective method of preheating before the reactor. The MTG reactor was modeled as an isothermal fluidized bed with heat exchange. A detailed analysis of how reaction rates were fitted to experimental data can be found in Appendix A. Catalyst deactivation was not considered at this stage of the design. Optimal reactor operating conditions were determined to be 360°C and 5 bar. R-301 was designed as a 60 ft x 20 ft x 11 ft rectangular vessel with 20 ft heat exchanger tubes spanning the width of the vessel. The reactor would require ~25,000, 2” diameter heat transfer tubes with flowing Dowtherm to provide the necessary heat transfer area. The heat transfer tubes optimal spacing was determined to be 1.5” from wall-to-wall. An optimal Dowtherm temperature was found to be ~175°C. This moderately-hot stream can be used to preheat boiler feed water for steam generation in other sections of the plant.

The MTG reactor effluent is cooled to 50°C in E-302, and the unreacted methanol and waste water are separated using a three-phase separator, V-301. The methanol in Stream 25 is further separated from the waste water through a distillation column, T-307, and the distillate is recycled to the reactor inlet. The gas phase exiting V-301 is compressed to 26 bar and mixed with the liquid products phase, which is pumped to 26 bar in P-301. The gasoline products are separated from the LPG, propylene, and ethylene in the reactor effluent stream using a series of distillation columns. T-301 separates the ethylene from the other products to be sold at \$1,278.68/tonne. The ethylene is further separated from the methane in T-304. The gasoline

products are separated from the propylene, propane, and butane in T-302. Two distillation columns, T-305 and T-306, are used to separate the propylene from the propane and butane. The propane and butane streams are sold as LPG at \$112.56/bbl and the propylene is sold at \$1,499.14/tonne. The gasoline products are separated to light and heavy products using a splitter distillation column, T-303. The heavy stream contains 1,2,4,5-tetramethylbenzene (durene) and is sent to the durene reactor, R-302.

R-302 is added after the T-303 to isomerize ~70% of the durene in the heavy-gasoline stream produced from the MTG reactor. R-302 should operate at 288°C and 29 bar. It was determined that splitting the heavy gasoline stream into multiple fractions and using smaller reactors would decrease equipment costs.

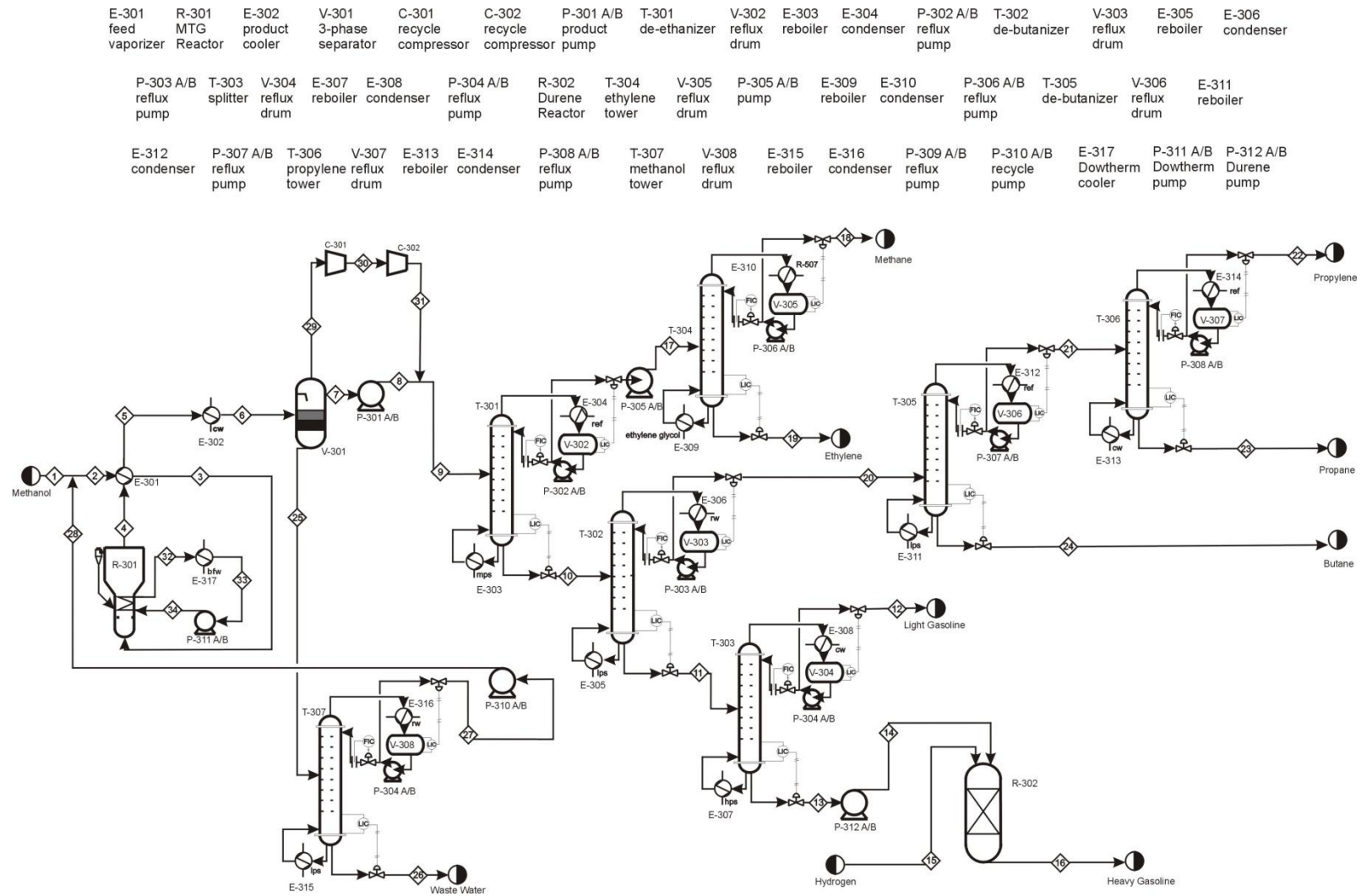


Figure 2.4-1: Process flow diagram for Methanol-to-Gasoline plant section

5. References

- [A-1] Ana G. Gayubo, P. L., *et al.*, (1996), Analysis of the kinetic models of a methanol-to-gasoline (MTG) process in an integral reactor, *The Chemical Engineering Journal*, **63** 45-51.

Appendix A - Methanol-to-Gasoline Kinetics

The MTG reactor, R-301, converts methanol, at ~99% purity, to gasoline-range products over an acid-based, zeolite catalyst (ZSM-5). Multiple kinetic models have been proposed to describe the major steps of the reaction; however, a model proposed by Schipper and Krambeck was found to describe most accurately the product composition at different reactor space times. ^[A-1] In this model, the products of the reaction are grouped under three categories: methanol/DME, light olefins, and products. The ZSM-5 catalyst is reported to produce over 150 gasoline-range products. ^[A-2] The thirty-nine most easily identifiable chemicals are given in Table A-1.

Table A-1: Major chemicals produced from MTG process

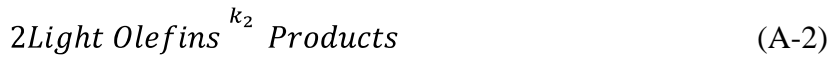
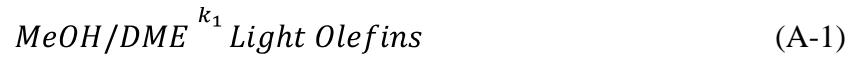
Methanol	Methylcyclohexane	Decanes
Dimethyl Ether	Methylpentanes	Benzene
Ethane	Dimethylbutanes	Toluene
Ethylene	Hexanes	Ethylbenzene
Propane	Hexenes	Xylenes
Propene	Cyclohexane	Trimethylbenzene
i-Butane	Heptanes	Methylethylbenzene
n-Butane	Heptenes	Propylbenzene
Butenes	Octanes	1,2,4,5-Tetramethylbenzene
n-Pentane	Octenes	1,2,3,5-Tetramethylbenzene
i-Pentane	Nonanes	1,2,3,4-Tetramethylbenzene
Pentenes	Nonenes	C ₁₀ Benzenes
Cyclopentane	Decanes	Naphthalenes

Due to the complexity and difficulty in modeling reactions for all 39 chemicals, a group of 16 *surrogate* chemicals was chosen to represent the properties of the actual product stream without over-complicating the reactor model. These surrogate chemicals included one chemical isomer at each chain length from C₄-C₁₀ in addition to the most common aromatic components. The list of surrogate chemicals used in reactor simulation is shown in Table A-2.

Table A-2: Simplified list of surrogate chemicals used in MTG simulation

Dimethyl Ether	n-Heptane
Methanol	n-Octane
Water	n-Nonane
Ethylene	Toluene
Propylene	Para-Xylene
i-Butane	1,2,4-Trimethylbenzene
i-Pentane	1,2,4,5-Tetramethylbenzene
n-Hexane	1,2,3,5-Tetramethylbenzene

The model by Schipper and Krambeck breaks the reaction into four steps, shown in Equations (A-1), (A-2), (A-3) and (A-4).^[A-1] In this type of model, kinetic rate expressions are fit to concentrations of groups of chemicals rather than individual chemicals.



It was found that the reaction kinetics proposed by Schipper and Krambeck could not be modeled due to the lumped concentration terms. The rate expressions for these four steps are given in Equations (A-5), (A-6), (A-7) and (A-8).

$$r_1 = 0.733 \times 10^{13} \exp \left(\frac{-139,436}{RT} \right) MeOH\ DME \quad (A-5)$$

$$r_2 = 0.127 \times 10^8 \exp \left(\frac{-73,705}{RT} \right) LO^2 \quad (A-6)$$

$$r_3 = 0.204 \times 10^{12} \exp \left(\frac{-116,986}{RT} \right) MeOH\ DME\ Products \quad (A-7)$$

$$r_4 = 0.634 \times 10^6 \exp \left(\frac{-66,274}{RT} \right) LO\ Products \quad (A-8)$$

It was determined that each reaction step had to be modified to include concentration terms of single chemicals. To accomplish this, the frequency factors for each reaction step were

modified until the rate law was consistent with data given by Gayubo.^[A-1] The finalized reaction rates are given by Equations (A-9), (A-10), (A-11) and (A-12).

$$r_1 = 4.03 \times 10^{13} \exp \frac{-139,436}{RT} \text{ DME} \quad (\text{A-9})$$

$$r_2 = 5.92 \times 10^7 \exp \frac{-73,705}{RT} C_3^2 \quad (\text{A-10})$$

$$r_3 = 9.95 \times 10^{10} \exp \frac{-116,986}{RT} C_3 C_4 \quad (\text{A-11})$$

$$r_4 = 3.96 \times 10^5 \exp \frac{-66,274}{RT} \text{ DME } C_4 \quad (\text{A-12})$$

The modified reaction rates were determined by comparing them to experimental data. The best fit was determined by calculating a squared error (*SE*) for data collected at various space times. The *SE* can be calculated using Equation A-13.

$$SE = \sum_1^5 (\text{Expected}_i - \text{Observed}_i)^2 \quad (\text{A-13})$$

Experimental data were available for space times varying from 0.01 to 0.1 at two reaction temperatures: 325°C and 375°C. A plot of experimental reaction products weight fractions (solid lines) vs. reaction product weight fractions determined with modified rate expressions (dotted lines) at 325°C is shown in Figure A-1.

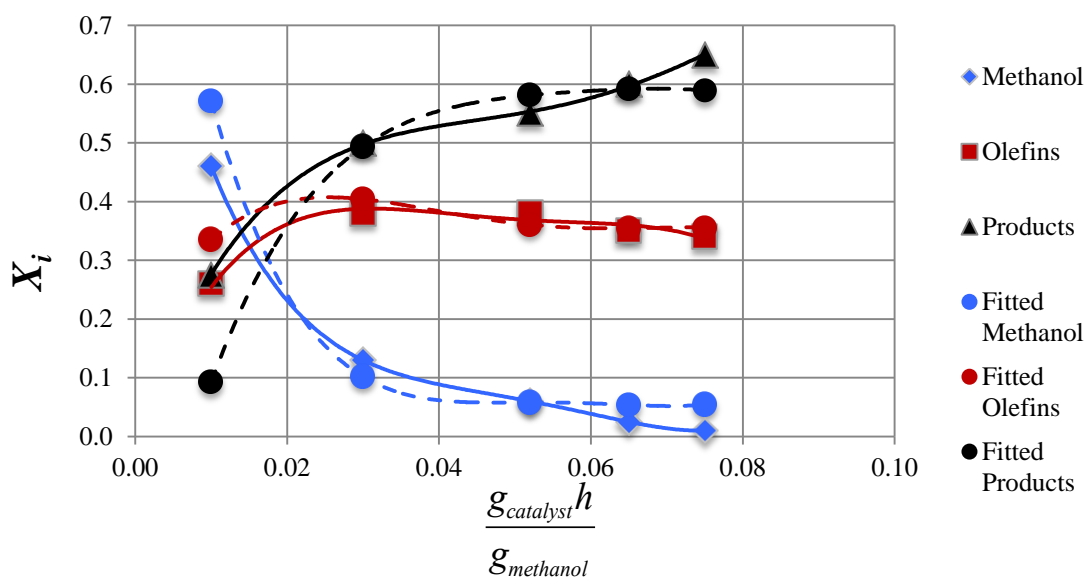


Figure A-1: Kinetic data at 325°C

A plot of experimental reaction products weight fractions (solid lines) vs. reaction product weight fractions determined with modified rate expressions (dotted lines) at 375°C is shown in Figure A-2.

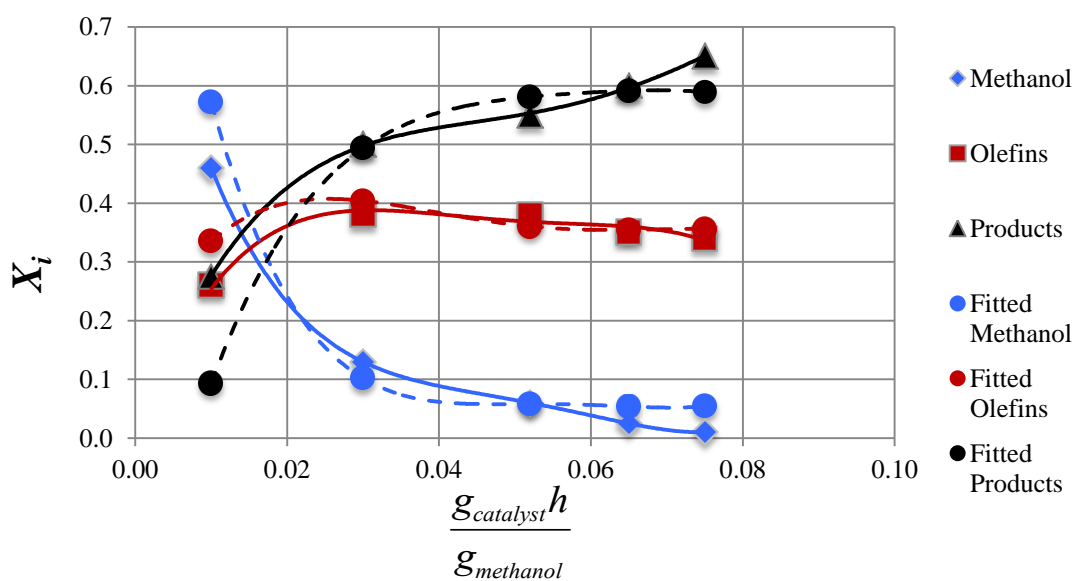


Figure A-2: Kinetic data at 375°C