

CH402 Capstone Design Problem

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1. Project Educational Objectives

- Apply unit and process design principles to the design of a chemical plant.
- Learn how to use economic, physical, and safety constraints in a process design.
- Learn how to use I/O, functions, and process flow diagrams for process design.
- Learn how to develop economic factors to assess a process design.
- Learn how to predict and respond to societal changes over time within the context of process design.
- Enhance your understanding of chemical engineering process simulators.
- Develop your communication abilities by producing oral and written reports.
- Increase your understanding of safety and environmental issues and incorporate them into your process design.

2. Introduction

The conversion of syngas (CO & H_2) to hydrocarbons using Fischer-Tropsch synthesis is a proven method for the production of liquid hydrocarbon fuels. This technology is commonly referred to as Gas-to-Liquids, or GTL. Historically, GTL processes have been used since the early 20th century, especially in countries where petroleum reserves were either unavailable or insufficient, or where natural gas and/or coal reserves were abundant. There are many currently operating GTL facilities worldwide that convert methane from natural gas to liquid fuel via syngas generation and Fischer-Tropsch synthesis [3]. The use of GTL technology in the United States is becoming particularly attractive due to the relative abundance and low cost of natural gas. The GTL pioneer Sasol has plans for at least one plant in the Gulf Coast region [9], while other companies are also either planning facilities [10] or offering small modular GTL plants [11, 12]. There are many other examples besides those listed here.

GTL technology is also attractive environmentally and financially because of the wide array of materials that can be converted into syngas feed for the GTL process. The syngas which is normally used for GTL is typically made from partial combustion of coal. However, in addition to coal, generation of syngas is possible with other carbon sources such as biomass, methane, and even municipal waste. There is considerable interest in developing new technology for the production of syngas from renewable feedstocks. While this is an interesting area of research, the primary focus of this project is the design of a GTL facility.

Your Process Design Team will provide a preliminary design for a Fischer-Tropsch Reaction unit (FTR), including reactor effluent separation facilities, as part of a planned GTL plant. Your client company has specifically requested that you design a safe, environmentally clean, thermally integrated FTR with efficient capital and operating cost utilization. In addition, your FTR is expected to effectively integrate with the other required units within the GTL plant to allow for the economically optimum diesel (C11-C20) and naphtha (C5-10, a feedstock for gasoline and chemicals) production.

3. Background

Your client company is considering a GTL plant as an option to bring to bring additional liquid fuels to the US market by utilizing gas deposits in the upper Midwest region. A simplified diagram of the GTL process the company is planning is:

As shown in the diagram, the GTL plant consists of the Syngas Unit (SU), the Fischer-Tropsch Reactor (FTR), the Gas Separator (GS), and the Hydro-Isomerization Unit (HI). The company has already completed the designs for the SU and the HI. Although the client is not asking you to design the SU and HI, they envision your design for the FTR as an opportunity to improve on the energy efficiency and operating expenses for the GTL plant as a whole.

4. Design Constraints

You must specifically address and adhere to these constraints and objectives in your design:

- 1) Safety/Environmental – Design must not pose any environmental, health or safety hazards that should have been mitigated with better equipment, instrumentation or control. Additionally, no continuous flaring/venting of hydrocarbons is permitted in the design. If necessary, hydrocarbons can be reused in the process.
- 2) Energy Efficiency & Lowest Environmental Impact – Defined as: (mass of carbon atoms in the finished products divided by the mass of carbon in methane feed) x 100%, where finished products = LPG + Naphtha + Diesel. After safety and environmental performance, energy efficiency is the most important attribute that will determine acceptance of your design by your company.
- 3) Optimum Finished Liquid Fuel Production – Appropriate cost/benefit balance is achieved.
- 4) Economic Analysis (Discounted Cash Flow Rate of Return) - Economic analysis should reflect not only the designed equipment capital investment and expense costs, but also the expense costs of the Syngas, Air Separation Plant and Hydro-Isomerization Unit. In addition, specified capital recovery costs for both the Syngas and Hydro-Isomerization units (see page 10) will need to be added to the estimated total yearly expense costs. For economic calculations assume:
 - a. Project Life of 15 years
 - b. 15 year Straight Line Depreciation
 - c. 33% Tax Rate
 - d. Projected 3% yearly inflation
 - e. The total capital investment can be estimated by multiplying the total equipment cost by 4.8. The multiplier accounts for all associated direct costs, indirect costs and working capital. You must also use the percentage of delivered equipment cost method (colorful worksheet method) for a comparison.
 - f. Total yearly operating expenses above and beyond utilities can be estimated using 3% of the total capital investment. This estimate will cover fixed charges such as

plant overhead costs, administrative costs, distribution & marketing and research & development.

- g. The FTR Unit will have a 1 month down time each year for catalyst replacement.
 - h. You may use equipment cost data from ChemCAD, textbooks, or any other public sources. All equipment costs must reference year 2013.
- 5) Feasible Design – Even though you are not providing the final design, your preliminary design should be viable as specified.
- 6) Realistic and Adequate Process Control – Control valves, instrumentation, analyzers, etc. on required equipment to provide safety and minimize personnel. It is not necessary to specify each component in detail; simply identify what they are and where in the process they are required.
- 7) Additional constraints on flow rates, selectivities, and process conditions are described below.

5. Available Facilities

Syngas Unit (SU)

The SU will be immediately upstream of the FTR. The SU is being designed to convert the 500 MSCF/D (Actual Conditions: 500 PSIG, 100 °F) of clean methane to syngas. The heat required to drive the endothermic auto-thermal reforming reaction is supplied *in-situ* by partial oxidation of methane. Steam and CO₂ are required as feeds to drive the reforming reaction to make the desired molar ratio of H₂/CO. In the SU, three primary reactions occur [1]:

- 1) Steam Reforming: $\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2$
- 2) Partial Oxidation: $\text{CH}_4 + 3/2\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2\text{O}$
- 3) Shift Reaction: $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$

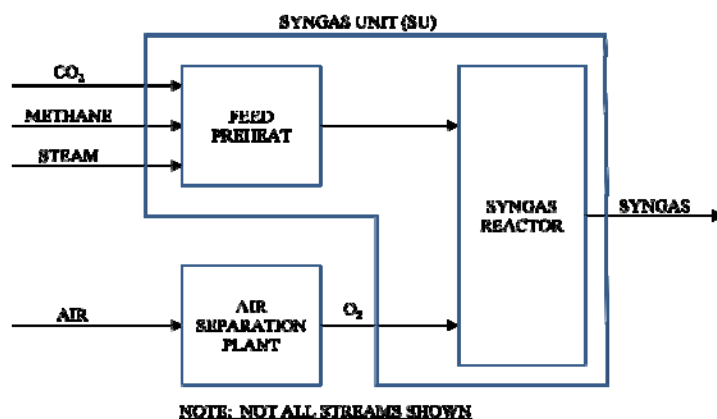
The partial oxidation reaction runs to completion; the other two reactions run to equilibrium. The heat balance determines the amount of oxygen supplied. You may assume zero heat losses for the reactor.

These reactions in combination determine the composition of the product gas from the SU. Operating pressure, temperature, and feed composition will set the overall composition of the synthesis gas. You should consider the following ranges for operating conditions:

- Temperature: 1600 - 1950°F
- Pressure: 300 - 500 PSIG
- Steam/CH₄ in Feed: 0.5 mol/mol minimum to prevent coking in feed preheater

You should target to make syngas with a H₂/CO molar ratio equal to the consumption ratio in the FTR (2:1). You will likely find that this requires supplemental CO₂ in the feed. Maximum feed

preheat temperature is 1000°F, and there will be a feed preheat furnace expected to perform at 85% efficiency (efficiency = theoretical MBTU required / actual MBTU required). 80% of the total variable energy costs for the SU are projected to be from actual preheat furnace firing duty, with the balance to be equally divided between 125 PSIG Steam and electricity. A basic flowsheet for the SU is:



Air Separation Plant (ASP)

The client was able to purchase a third-party air separation plant (ASP) to produce oxygen. The oxygen is produced as 99% pure with 1 mol% nitrogen. The ASP subcontractor has offered the following contractual terms:

- Oxygen (500 psig, 99 % purity, 75F): \$100/short ton contained oxygen.
- Energy for oxygen plant pumps and compressors to be provided by customer as:
 - Electricity Option: 1000 KW-h/short ton contained oxygen, or
 - 600 psig Steam Option: 10,000 lb/short ton contained oxygen.

The ASP is designed so that the choice of electricity or steam shall be determined by customer. Cooling water requirement is to be provided by the customer at 400 gpm per short ton/day of oxygen.

Hydro-Isomerization Unit (HI)

The HI unit for the GTL process is to be downstream of the FTR. After initial separation of products from the FTR, the distillate and heavier boiling fractions (material with greater than 350 °F boiling point) are fed to a catalytic hydro-isomerization reactor, where the paraffins are isomerized and wax is converted to lighter products. The process converts 100% of the >700 °F boiling point (b.p.) material to <700 °F b.p. material, with an overall selectivity of 1.0 wt% methane, 0.5 wt% ethane, 3.5 wt% propane, 3.5 wt% butane, 25 wt% naphtha, and the balance diesel.

Yields are expressed as overall reactor products, based on the amount of 700+ in the feed. For example:

<u>Feed</u>	<u>Basis</u>	<u>Product</u>
C1		70·1%
C2		70·0.5%
C3		70·3.5%
C4		70·3.5%
Naphtha		70·25%
Diesel	30	balance
700+	70	zero

The HI catalyst selected for this unit is very selective to >700 °F b.p. material. You are to assume that any <700 °F b.p. material in the feed to the HI will essentially pass through the HI unit and remain unconverted. The catalyst is sensitive to H₂O and CO; therefore, the liquid feed to the hydro-isomerization reactor must not have any free water above the solubility limit and the makeup gas should have a CO content no greater than 0.1 mol%.

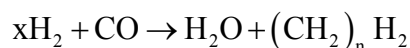
The utility and make-up hydrogen requirements for the HI Unit are:

- Fuel gas: 0.08 MBTU/bbl of feed
- Hydrogen: 300 SCF/bbl of feed
- Steam (125 PSIG): 10 lbs/bbl of feed
- Electricity: 2.5 KW-hr/bbl of feed
- Cooling Water: 300 gal/bbl of feed

6. Chemical Reaction Kinetics and Reactor Design

Chemical Reaction

In the Fischer-Tropsch Reactor (FTR), the syngas is converted to hydrocarbons and water by the following reaction:



CO Conversion Kinetics

An ultra-stable cobalt-based FTR catalyst is available for the proposed plant. In lab tests of this catalyst by a separate team of chemists, it was determined that the overall rate equation is best fit by a Langmuir-Hinshelwood form with parameters as follows [7]:

$$-r_{CO} = \frac{k \cdot T_1 \cdot P_{H_2} \cdot P_{CO}}{(1 + k_2 \cdot T_2 \cdot P_{CO})^2}$$

$$T_1 = \text{Exp} \left[-4492 \cdot \left(\frac{1}{T} - \frac{1}{473} \right) \right], \text{ T in deg K}$$

$$T_2 = \text{Exp} \left[-8237 \cdot \left(\frac{1}{T} - \frac{1}{473} \right) \right], \text{ T in deg K}$$

$$k = 0.0173 \frac{\text{gmol CO}}{\text{hr} \cdot \text{cc cat} \cdot \text{atm}^2}, \text{ where catalyst bulk density} = 0.8 \text{ g/cc}$$

$$k_2 = 4.512 \text{ atm}^{-1}$$

P_{H_2}, P_{CO} = partial pressures in vapor phase, atm

T = Reactor operating temperature

For estimation of vapor phase components in the kinetics, you may assume that the vapor phase contains 100% of the H_2 , CO, H_2O , CH_4 , N_2 components, and 0.7 moles of C_2 + hydrocarbon for every mol of CH_4 made.

The reaction temperature will be determined by the feed temperature, the heat of reaction and heat transfer out of the tube and may vary along the length of the reactor. Information on heat transfer characteristics is provided below.

Product Selectivity

You can assume the products of the hydrocarbon synthesis reaction are all alkanes. The distribution of C_5 + products is characterized by the Anderson-Shulz-Flory (ASF) probability distribution as follows:

$$\frac{W_n}{n} = \frac{(1-\alpha)^2}{\alpha} \cdot \alpha^n, \text{ or}$$

$$M_n = (1-\alpha) \cdot \alpha^{n-1}$$

where

α = ASF chain growth parameter, defined below

W_n = relative weight fraction of carbon number n

M_n = relative mole fraction of carbon number n

The ASF parameter is slightly temperature dependent and varies with the average reactor temperature as follows:

$$\alpha = 0.93 \cdot T_3$$

$$T_3 = \text{Exp} \left[250 \cdot \left(\frac{1}{T} - \frac{1}{473} \right) \right], \quad T \text{ in deg K}$$

The selectivity of methane does not follow the ASF distribution, but instead is dependent upon temperature over the range of 390-450°F as follows:

$$S_{\text{CH}_4} = \frac{r_{\text{CH}_4}}{-r_{\text{CO}}} = 0.03 \cdot T_4, \quad \text{mol/mol}$$

$$T_4 = \text{Exp} \left[-10000 \cdot \left(\frac{1}{T} - \frac{1}{473} \right) \right], \quad T \text{ in deg K}$$

The selectivity of C2-C4 alkanes are linked to CH₄ selectivity as follows:

$$S_{\text{C}_n} = 0.04 \cdot S_{\text{CH}_4}, \quad \text{mol/mol}, \quad n=2, 3, \text{ and } 4$$

For typical for cobalt-based catalysts, CO₂ selectivity is negligible.

Catalyst

The catalyst you will be using has been formulated into 1/16 inch diameter extrudates, with a packed bulk density of 0.8 g/cc and a void fraction of 0.4. Equivalent diameter is 0.08 inches. Cost is \$10/lb. The catalyst must be replaced every 4 years. The catalyst is an ultra stable formulation - with low deactivation rates - and the activity (as set by the kinetic equation) can be taken as the average activity for the life of the catalyst.

Reactor Sizing and Constraints

Because the reaction is highly exothermic you have selected a tubular fixed bed reactor cooled by boiling water. You have found that a practical limit for the size of these reactors is 20 ft in diameter and 60 ft in length. You need to determine the number of reactors needed and the optimum arrangement of the reactors (number of stages in series and number of reactors per stage).

Reactor Heat Transfer

The reaction is highly exothermic, with a heat of reaction of 70,200 BTU/lb mol CO converted. Temperature is controlled by adjusting boiling water pressure on the shell side of the tubular reactor. Normal operating conditions for both process and shell sides should be optimized to maximize process performance and minimize investment costs. You may assume, for this problem that the shell side operates isothermally.

The heat transfer coefficient is controlled by process conditions and an empirical relationship exists for the overall coefficient as follows:

$$U_o = \frac{0.385 \cdot G^{0.8}}{D^{0.2}}$$

$$U_o = \text{Overall heat transfer coefficient, } \frac{\text{Btu}}{\text{hr} \cdot \text{F} \cdot \text{ft}^2}$$

$$G = \text{Inlet gas mass velocity, } \frac{\text{g}}{\text{hr}} \cdot \frac{1}{\text{cm}^2}$$

$$D = \text{Tube diameter, cm}$$

You may consider tube diameters in a range of 3/4" to 2". Minimum spacing between tubes is 1".

Reactor Pressure Drop

Bed pressure drop should be calculated and pressure loss should be accounted for in the kinetics. Assume fluid properties are constant through the reactor and are equal to the properties at the inlet, neglecting the reaction. To account for the contribution of the liquid on overall pressure drop, assume total pressure drop is 1.5 times the gas phase pressure drop. Maximum allowable pressure drop per reactor is 50 psi.

Mass Transfer

You have found that due to the particular formulation of your catalyst that mass transfer effects are small and can be ignored.

Feed Temperature Control

The temperature of the syngas from the SU must be lowered before being fed to the FTR reactor(s). It is recommended that this is accomplished using a waste heat boiler (steam generator) in series with an air or water cooled heat exchanger.

Product Separation

You will need to design the facilities to separate the desired products in the reactor effluent from unconverted feed and water. Distillate and heavier boiling (350 °F +) fractions are solid at room temperature and must be kept above 250 °F prior to isomerization to prevent wax crystallization. Naphtha and lighter components can be collected for direct shipment without temperature concern. Water should be separated for disposal and/or reuse.

7. Utilities

The SU, HI unit, Air Separation Plant and FTR unit will all have full access to a company-owned utility grid, which can provide and (in some cases) accept any utilities

generated during the process, provided that specific conditions are met. If multiple hydrocarbon streams produced in the process are used as fuel gas, then each hydrocarbon stream will be valued at its respective BTU/lb heating value. Typical cooling water make-up rate is 0.025 gallon make-up per gallon of water circulating. The boiler feed water blowdown rate is 3% of total mass of steam produced. Boiler feed water blowdown cannot be reused for boiler/steam, but can be used as cooling water make-up. Carbon dioxide may not be returned for credit.

8. Design Report Submission Requirements

- 1) Title Page
- 2) Table of Contents
- 3) Executive Summary (w/ specific reference to design objectives)
- 4) Introduction
- 5) Summary
- 6) Discussion
- 7) Conclusions
- 8) Recommendations
- 9) Project Premises
- 10) Heat and Material Balance
- 11) FTR Unit Process Flow Diagram
- 12) Simplified GTL Plant Process Flow Diagram - Illustrating heat integration and stream flows & compositions between all units in GTL plant
- 13) Safety/Environmental Summary
- 14) Equipment Information Summary – with enough design information to cost equipment
- 15) Unit Control and Instrumentation Description
- 16) Economics - In addition to DCF, include a summary of operating costs, utility requirements and energy efficiency
- 17) Engineering Calculations,
- 18) References

9. Additional Information:

- 1) Standard conditions are 60F and 14.7PSIA.

- 2) Your company uses US Customary Units of Measure (see utility costs).
- 3) Unit prefixes: G = 10^9 , M = 10^6 , K = 10^3
- 4) Short ton = 2000lb; bbl = barrel of liquid at standard conditions = 42 gal
- 5) Ambient: 75°F (Avg), Min/Max Dry Bulb Temp = 20/90, Avg. Windspeed = 10mph.

Feed Costs:

- Methane Feed: \$2000/MSCF

Capital Recovery:

- Syngas unit: \$400M/yr
- HI unit: \$100M/yr

Utility Values:

- 600#, 490F HP Steam: Cost: \$5/klb consumed, Credit: \$4/klb produced
- 125#, 353F MP Steam: Cost: \$4/klb consumed, Credit: \$3/klb produced
- 20#, 260F LP Steam: Cost: \$3.5/klb consumed Credit: \$2.5/klb produced
- Electricity: Cost: \$0.04/KW-h consumed, Credit: \$0.03/KW-h produced
- Fuel Gas: Cost: \$3/MBTU consumed, Credit: \$2/MBTU produced
- Hydrogen: Cost: \$0.06/lb consumed
- Carbon Dioxide: 100% pure (500PSIG & 100F): Cost: \$400/MSCF consumed
- Steam Condensate (at least 99.9% v/v pure): Credit: \$2/klb produced
- Process/Cooling Tower Water (at least 95% v/v pure): Cost: \$0.5/kgal consumed, Credit: \$0.35/kgal produced
- Waste Water Treatment (at least 75% v/v pure): Cost: \$6/kgal produced

Hint: Steady-state design may not require all utilities. You may ignore transient start-up requirements for preliminary design.

Product Prices:

Product is to be transported to existing storage tanks and then loaded on to vessels for transport. The planned price structure and standard liquid densities for finished products are:

- LPG (C3, C4) – regardless of composition: \$0.30/lb
- Naphtha (C5 - C10); 45 lb/ft³: \$75/bbl
- Diesel (C11 – C20); 53 lb/ft³: \$90/bbl

Pseudocomponents:

For simulation purposes in ChemCAD, you may consider lumping some of the product species together as pseudocomponents. The following properties are provided for suggested lumped species:

Pseudocomponent Properties					
Carbon Range	C21-C25	C26-C29	C30-C35	C36-C47	C48+
MW	322.6	386.5	454.9	572.2	861.7
SG @ 60 °F	0.801	0.810	0.818	0.827	0.839
NBP, °F	714.3	799.9	877.7	982.5	1155.2

10. References

This section is not intended as a complete or comprehensive set of references, but only to get you started. You are expected to expand upon this list considerably.

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