

Fluid Catalytic Cracking

Presented To:

Marco J. Castaldi, Ph.D.

Sheldon M. Horowitz

From:

Basir Miah

Christian Pena

Jameel Hammad

Slah Yehya

The City College of New York
Grove School of Engineering
Department of Chemical Engineering

May 7, 2021

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Executive Summary

Fluid catalytic cracking (FCC) is a chemical process employed in petroleum refineries. This process simulation converts gas oil (GO) to commodity products such as dry gas (DG), liquified petroleum gas (LPG), gasoline (GLN), light cycle oil (LCO), and slurry. GO is processed at a rate of 1,604,448 gal/day and converted to produce petroleum products at varying capacities: DG at 3,717,792 gal/day, LPG at 324,864 gal/day, GLN at 648,000 gal/day, LCO at 251,424 gal/day, and slurry at 67,392 gal/day.

The simulation yields of DG, GLN, LPG, LCO, coke, and slurry are 5.9 wt. %, 48.5 wt. %, 15.8 wt. %, 17.9 wt. %, 7.9 wt. %, and 4.0 wt. %, respectively. Overall, simulation yields are consistent with product yields commonly reported in industry. The conversion of gas oil is approximately 95 wt. % and the riser residence time is 2.71 seconds. A catalyst-to-oil ratio of 6.4 was employed.

According to cost estimates as well as price history, the total depreciable cost of this process is \$134,986,461.46. Using a capital recovery factor of 0.33, the annual capital cost was calculated to be \$44,545,532.28 per year. The total cost of raw material needed for the process is \$2,203,211.41 per day and the total revenue is \$2,473,539.53 per day. When accounting for the total cost of materials, capital cost, operation and maintenance costs, and total revenue associated with this process, the project ROI was calculated as 3.68 % with a payback period of 4.6 years.

Introduction

Petroleum refineries utilize fluid catalytic cracking units to further process and refine gas oil into valuable commodity products such as dry gas (DG), gasoline (GLN), liquefied petroleum gas (LPG), and light cycle oil (LCO). Approximately 500 catalytic cracking units are being used worldwide, processing 13 million barrels of GO per day.¹ The following table highlights *some* petroleum product applications in the modern economy:

Table 1. FCC petroleum products and their applications

Petroleum Product	Application	Ref.
Dry Gas (DG)	<ul style="list-style-type: none">• Refrigerant in compressors	(2)
Liquefied Petroleum Gas (LPG)	<ul style="list-style-type: none">• Kitchen cooking appliances	(3)
Gasoline (GLN)	<ul style="list-style-type: none">• Fuel source for vehicles, boats, and small, mid-sized aircraft	(4)
Light Cycle Oil (LCO)	<ul style="list-style-type: none">• Fuel source for larger commercial automobiles	(5)

Overall Mass and Energy Balance

Gas oil, at a mass flow rate of 37 kg/s, is catalytically converted to produce dry gas, liquified petroleum gas, gasoline, light cycle oil, and slurry at a rate of 2 kg/s, 6 kg/s, 18 kg/s, 7 kg/s, and 2 kg/s, respectively. Combusting coke and igniting carbon monoxide (to generate CO₂) requires drawing in 32 kg/s of air at ambient conditions. Steam exits the process at a rate of 5 kg/s and functions as a heating utility. Catalyst is both added and withdrawn from the process at a rate of 1 kg/s. Compressing overhead vapor distillate and pumping water requires a total power input of 5 MW. The rate of heat addition (i.e., reboiler heat input in the high-pressure column) is 1 MW. Lastly, 43 MW of heat is removed by the condenser in the main fractionator and 6 MW of heat is removed by the condenser in the high-pressure column (i.e., a total of 49 MW of heat is removed). Figures 1 and 2 show the overall process mass and energy balances, respectively.

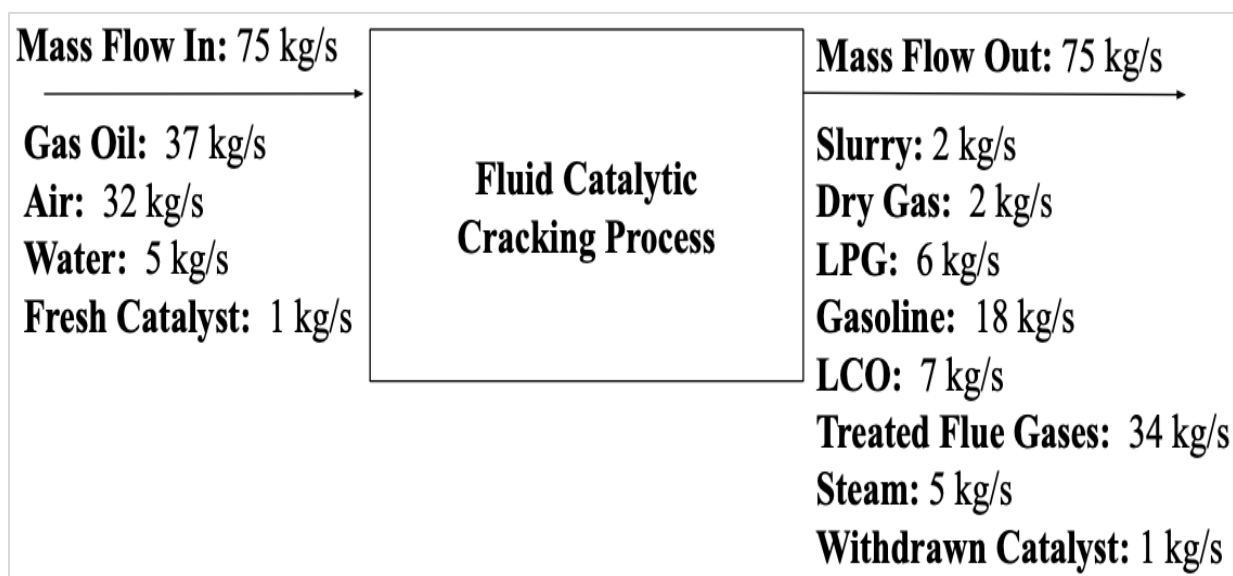


Figure 1. Overall mass balance

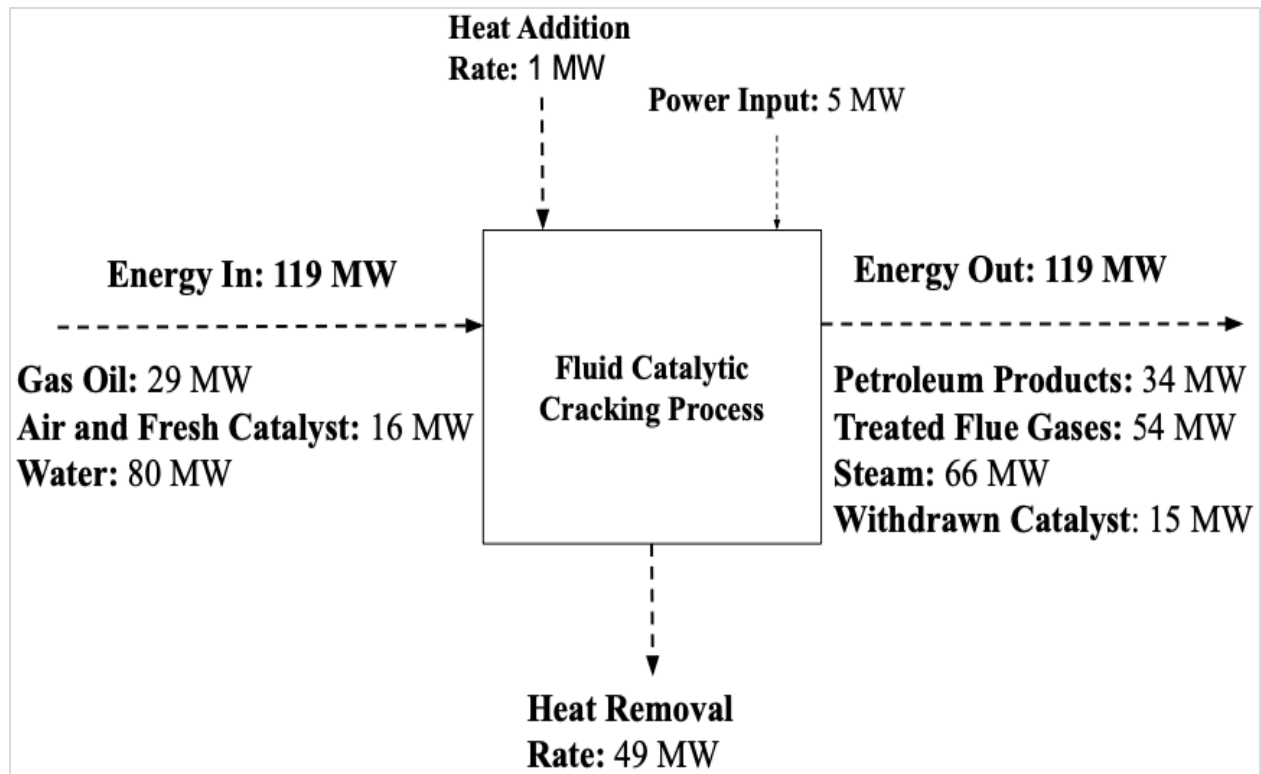


Figure 2. Overall energy balance

Process Description

Gas oil, at a temperature of 422 °C, is fed at 37 kg/s and is mixed with superheated zeolite catalyst (669 °C) flowing at 236 kg/s. Liquid gas oil vaporizes causing the catalyst particles to fluidize and the gas oil - catalyst mixture travels upward, entering the riser (vertically oriented plug-flow reactor) at a uniform temperature of 565 °C. Catalytic cracking of gas oil into smaller hydrocarbons (straight-chain paraffins, olefins) and coke (carbon-rich component) occurs inside the riser. Hydrocarbon product vapors (34 kg/s) and coked catalyst (238 kg/s) emerge from the riser at 486 °C and are mechanically separated by a single gas-solid cyclone separator. The separation efficiency of the cyclone is relatively high (100 %), hence solid-phase components do not flow downstream. Hydrocarbon product vapors flow upward into the main fractionator to be separated into sellable petroleum products. Meanwhile, the coked catalyst flows downward where it is mixed with air before entering the regenerator.

Hydrocarbon product vapors (486 °C, 34 kg/s) enter the main fractionator (through the base of the 16-stage column) and are separated into gasoline, light cycle oil, an overhead vapor distillate consisting of dry gas and liquified petroleum gas, and a bottoms product consisting of mostly unreacted gas oil. There are two liquid side streams; one side stream withdraws gasoline-rich liquid from stage 6 (99.8 wt. % gasoline at 17.8 kg/s) and the second side stream withdraws light cycle oil-rich liquid from stage 14 (98.7 wt. % light cycle oil at 6.65 kg/s). The bottoms product consists of unreacted gas oil, light cycle oil, trace amounts of gasoline and flows at 2 kg/s (i.e., the bottoms product is considered slurry). The overhead vapor distillate (-35 °C, 1 bar) flows at 8 kg/s and requires further separation (i.e., 27 wt. % dry gas and 73 wt. % liquified petroleum gas). A compressor is employed to pressurize the vapor distillate to an outlet pressure of 29 bar. Lastly, the compressed vapor enters a 30-stage column operating at 29 bar where it is separated into dry gas (99.9 wt. %) and liquified petroleum gas (99.9 wt. %).

Coked catalyst and air enters the regenerator at 441 °C and undergoes oxidation, yielding combustion products (CO₂ and CO) and releasing heat. Flue gases and regenerated catalyst (i.e., coke burned off) emerge from the regenerator at 669 °C and are separated by a single cyclone separator. Hot flue gases flow upward and into the CO boiler to undergo further treatment and are utilized in a heat recovery scheme. Air, at ambient conditions, is added to the CO boiler at a flow rate of 8 kg/s in order to completely combust carbon monoxide. Heat released from the coke combustion reactions is absorbed by the catalyst, raising its temperature to 669 °C. Approximately 1 kg/s of regenerated catalyst is purged, and 1 kg/s of fresh catalyst is fed to the regenerator. Flue gases exiting the CO boiler are processed in a heat exchanger where saturated steam is produced via evaporation of pressurized water. Steam produced in the flue gas treatment process is used as a heating utility to warm the atmospheric air being drawn (from 25 °C to 32 °C).

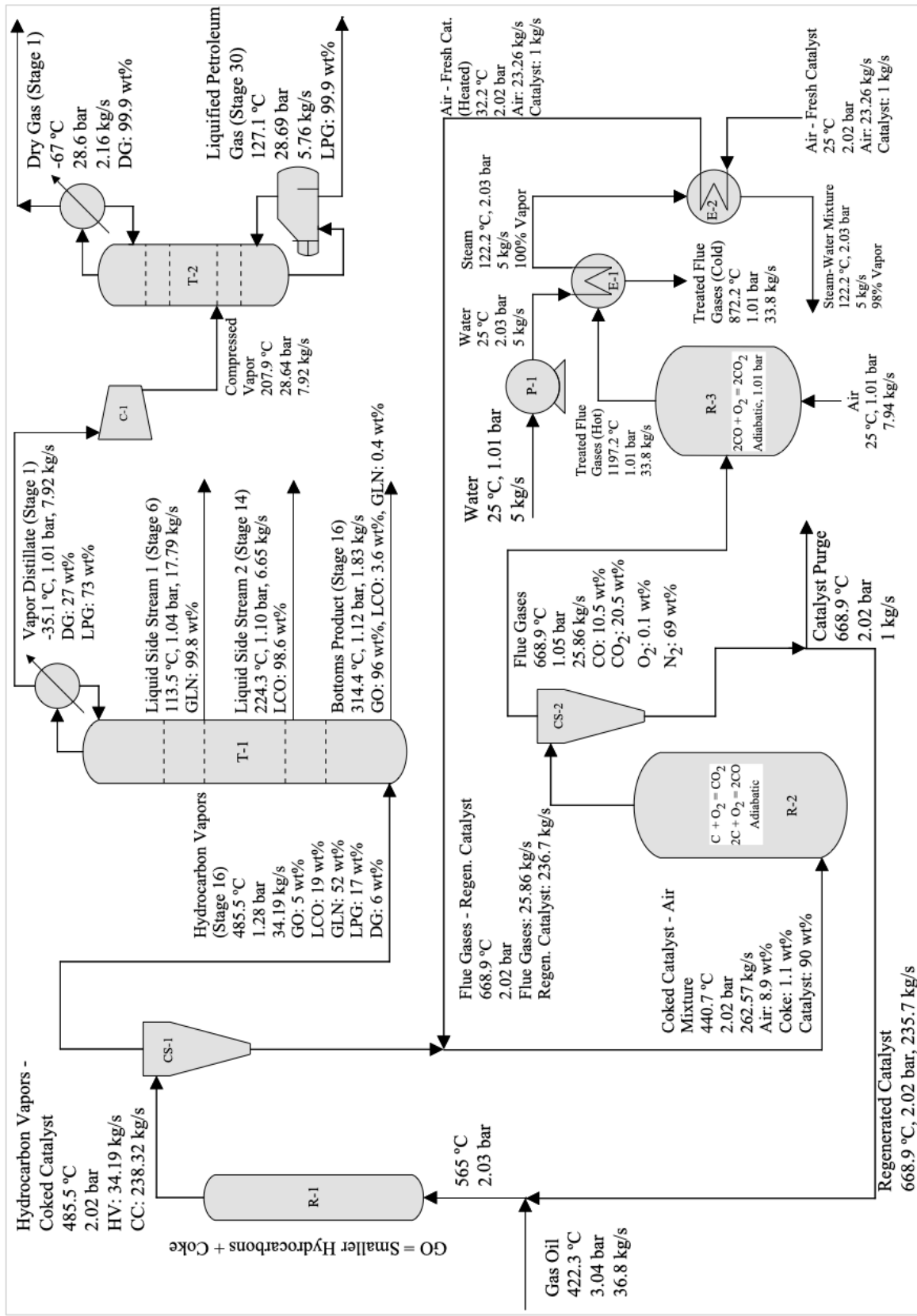


Figure 3. Process flow diagram

Table 2. Equipment specifications

Equipment	Simulation Model	ID	Specifications	
Plug-Flow Reactor (Riser) <i>Vessel for the catalytic cracking of gas oil into smaller chain hydrocarbons and coke</i>	RPlug	R-1	Inlet Temperature	565 °C
			Outlet Temperature	485.5 °C
			Inlet Pressure	2.03 bar
			Outlet Pressure	2.02 bar
			Length	23 m
			Diameter	1.5 m
			Residence Time	2.71 sec
			Volume	40.64 m ³
			GO Feed Rate	36.8 kg/s
			Heating Duty	0
			GO Conversion	95 wt. %
			Material of Construction	Carbon Steel
			Purchased Cost	\$10,057,647.05
			Bare Module Cost	\$47,673,247.04
Plug-Flow Reactor (Regenerator) <i>Vessel for the combustion of coke and regeneration of zeolite catalyst</i>	RPlug	R-2	Inlet Temperature	440.7 °C
			Outlet Temperature	668.9 °C
			Inlet Pressure	2.021 bar
			Outlet Pressure	2.02 bar
			Length	26.19 m
			Diameter	8.8 m
			Residence Time	46.54 sec
			Volume	1,593 m ³
			Heating Duty	0
			Coke Conversion	100%
			Material of Construction	Carbon Steel
			Purchased Cost	Included in R-1
			Bare Module Cost	Included in R-1
Gas-Solid Cyclone Separator <i>Mechanically separate hydrocarbon product vapors from catalyst and coke</i>	Cyclone	CS-1	Separation Efficiency	100 %
			Inlet/Outlets Temperature	485.5 °C
			Inlet Pressure	2.02 bar
			Vapor Outlet Pressure	1.28 bar
			Solid Outlet Pressure	2.02 bar
			Inlet Flow Rate	272.5 kg/s
			Vapor Outlet Flow Rate	34.19 kg/s
			Solid Outlet Flow Rate	238.3 kg/s
			Diameter	1 m
			Material of Construction	Carbon Steel
			Purchased Cost	\$306,433.58
			Bare Module Cost	\$1,452,495.18

Table 2. Equipment specifications (continued)

Equipment	Simulation Model	ID	Specifications	
Gas-Solid Cyclone Separator <i>Mechanically separate flue gases from regenerated catalyst and unconverted coke</i>	Cyclone	CS-2	Separation Efficiency	100%
			Inlet/Outlets Temperature	668.9 °C
			Inlet Pressure	2.02 bar
			Vapor Outlet Pressure	1.05 bar
			Solid Outlet Pressure	2.02 bar
			Inlet Flow Rate	262.5 kg/s
			Vapor Outlet Flow Rate	25.86 kg/s
			Solid Outlet Flow Rate	236.7 kg/s
			Diameter	1 m
			Material of Construction	Carbon Steel
			Purchased Cost	\$1,254,721.29
			Bare Module Cost	\$5,947,378.892
Furnace (Sub-unit of CO Boiler) <i>Furnace in which the flue gas is burned in order to convert carbon monoxide into carbon dioxide for cleaner emissions</i>	REquil	R-3	Inlet Temperature	668.9 °C
			Outlet Temperature	1197.2 °C
			Inlet Pressure	1.049 bar
			Outlet Pressure	1.013 bar
			Inlet/Outlet Flow Rate	33.81 kg/s
			Heating Duty	0
			O ₂ Conversion	82.8 mol %
			CO Conversion	99.9 mol %
			Equilibrium Constant	1.06×10 ¹¹
			Material of Construction	Carbon Steel
			Purchased Cost	Included in COB
			Bare Module Cost	Included in COB
Furnace (Combustion Reactor) <i>Flue gas is burned in order to convert carbon monoxide into carbon dioxide for cleaner emissions</i>	RPlug	COB ^a	Inlet Temperature	850 °C
			Outlet Temperature	892.63 °C
			Operating Pressure	1.035 bar
			Length	10 m
			Diameter	4.3 m
			Residence Time	1.17 sec
			Volume	145.4 m ³
			Inlet/Outlet Flow Rate	39.74 kg/s
			Heating Duty	0
			CO Conversion	100%
			O ₂ Conversion	98.3 %
			Material of Construction	Carbon Steel
			Purchased Cost	\$1,065,408.73
			Bare Module Cost	\$5,050,037.38

Table 2. Equipment specifications (continued)

Equipment	Simulation Model	ID	Specifications	
Heat Exchanger <i>Heats the air stream that is fed to the regenerator using heat from saturated steam</i>	MHeatX	E-2	Cold Inlet Temperature	25 °C
			Cold Inlet Pressure	2.02 bar
			Hot Inlet Temperature	122.2 °C
			Hot Inlet Pressure	2.03 bar
			Cold Outlet Temperature	32.2 °C
			Cold Outlet Pressure	2.02 bar
			Hot Outlet Temperature	122.2 °C
			Hot Outlet Pressure	2.03 bar
			Cold Inlet/Outlet Flow Rate	24.26 kg/s
			Hot Inlet/Outlet Flow Rate	5 kg/s
			Material of Construction	Carbon Steel
			Purchased Cost	\$5,360
			Bare Module Cost	\$25,406.4
Heat Exchanger (Sub-unit of CO Boiler) <i>Heats water using hot flue gases, producing saturated steam</i>	MHeatX	E-1	Cold Inlet Temperature	25.2 C
			Cold Inlet Pressure	2.03 bar
			Hot Inlet Temperature	1197.2 C
			Hot Inlet Pressure	1.01 bar
			Cold Outlet Temperature	122.2 C
			Cold Outlet Pressure	2.03 bar
			Hot Outlet Temperature	827.7 C
			Hot Outlet Pressure	1.01 bar
			Cold Inlet/Outlet Flow Rate	5 kg/s
			Hot Inlet/Outlet Flow Rate	33.81 kg/s
			Material of Construction	Carbon Steel
			Purchased Cost	Included in COB
			Bare Module Cost	Included in COB
Water Pump <i>Pumps water into the heat exchanger (E-1)</i>	Pump	P-1	Inlet/Outlet Temperature	25 °C
			Inlet Pressure	1.01 bar
			Outlet Pressure	2.03 bar
			Inlet/Outlet Flow Rate	5 kg/s
			Efficiency	50.54 %
			Net Work Required	1 kW
			Head Developed	10.39 m
			Material of Construction	TYPE-304 Stainless Steel
			Purchased Cost	\$40,000
			Bare Module Cost	\$189,600

Table 2. Equipment specifications (continued)

Equipment	Simulation Model	ID	Specifications	
Compressor <i>Raises the pressure of overhead vapor distillate leaving the main fractionator</i>	Compressor	C-1	Type	Isentropic
			Isentropic Efficiency	72 %
			Mechanical Efficiency	100 %
			Inlet Temperature	-35.1 °C
			Inlet Pressure	1.01 bar
			Outlet Temperature	207.9 °C
			Outlet Pressure	28.64 bar
			Inlet/Outlet Flow Rate	7.92 kg/s
			Net Work Required	4726.65 kW
			Material of Construction	TYPE 304 Stainless Steel
			Purchased Cost	\$26,000
			Bare Module Cost	\$123,240
Main Fractionator <i>Separate hydrocarbon product vapors into saleable petroleum fractions</i>	PetroFrac	T-1	Number of Stages	16
			Feed Stage	Stage 16
			Condenser	Partial
			Distillate (Stage 1) Rate	7.92 kg/s
			Sidestream (Stage 5) Rate	17.79 kg/s
			Sidestream (Stage 13) Rate	6.65 kg/s
			Bottoms (Stage 16) Rate	1.83 kg/s
			Condenser Heating Duty	43.25 MW
			Reflux Ratio	11.32
			Boilup Ratio	40.36
			Distillate Temperature	-35.1 °C
			Bottoms Temperature	314.4 °C
			Top Stage Pressure	1.01 bar
			Pressure Drop	0.007 bar/stage
			Material of Construction	Carbon Steel
			Purchased Cost	\$3,750,000
			Bare Module Cost	\$17,775,000

Table 2. Equipment specifications (continued)

Equipment	Simulation Model	ID	Specifications	
Distillation Column <i>High-pressure column that separates the overhead vapor distillate product, exiting the main fractionator, into LPG and DG</i>	PetroFrac	T-2	Number of Stages	30
			Feed Stage	Stage 7
			Condenser	Partial
			Reboiler	Kettle
			Distillate Rate	2.16 kg/s
			Bottoms Rate	5.76 kg/s
			Condenser Heating Duty	6.1 MW
			Reboiler Heating Duty	1.14 MW
			Reflux Ratio	5.59
			Boilup Ratio	1.15
			Distillate Temperature	-67 °C
			Bottoms Temperature	127 °C
			Condenser Pressure	28.6 bar
			Reboiler Pressure	28.8 bar
			Material of Construction	Carbon Steel
			Purchased Cost	\$70,000
			Bare Module Cost	\$331,800

^amodel seen in the separate Aspen file titled “CO Boiler May_7”

Riser Reactor

Hydrocarbon Components: Reactants and Products of Catalytic Cracking

Components were selected based on their molecular structure (short- and long-chain paraffins and olefins) and normal boiling points. The boiling range of gas oil is between 330 - 550 °C.⁶ Components n-Octacosane and 1-Octacosene were used to model gas oil (normal boiling range is between 430 and 431.6 °C). Gas oil consists of paraffins, olefins, naphthenes, and aromatics. To simplify the modeling process, only paraffins and olefins were considered. Dry gas was modeled using C₂ hydrocarbons and H₂. LPG is typically composed of C₄ hydrocarbons. In this simulation, 1-Butene and n-Butane were used to model LPG. Lastly, coke was modeled as elemental carbon (C). Table 3 summarizes all hydrocarbons that were used along with their normal boiling points and respective lumps. In addition, the composition of gas oil was modeled as 95 wt. % C₂₈H₅₈ and 5 wt. % C₂₈H₅₆.⁷

Table 3. Component chemical formulas, boiling ranges, and model lumps.

Compound	Formula	MW (g/mol)	Normal Boiling Point (°C)	Lump
n-Octacosane	C ₂₈ H ₅₈	394.7	431.6	GO
1-Octacosene	C ₂₈ H ₅₆	392.7	430	
n-Tetradecane	C ₁₄ H ₃₀	198.3	253.77	LCO
1-Tetradecene	C ₁₄ H ₂₈	196.3	251.1	
n-Octane	C ₈ H ₁₈	114.1	125.68	GLN
1-Octene	C ₈ H ₁₆	112.2	121.26	
1-Butene	C ₄ H ₈	56.1	-6.239	LPG
n-Butane	C ₄ H ₁₀	58.12	-11.72	
Ethane	C ₂ H ₆	30.06	-88.6	DG
Ethylene	C ₂ H ₄	28.05	-103.74	
Hydrogen	H ₂	2.015	-252.76	
Carbon	C	12.01	4000 +	CK

Catalytic Cracking Kinetics

A 6-lump kinetic scheme was adopted for modeling the catalytic cracking of gas oil. In reality, gas oil is composed of 10,000+ hydrocarbons. Researchers who study the kinetics of this reaction “lump” together thousands of hydrocarbons and simply denote the FCC feedstock as a single variable. The products of catalytic cracking (dry gas, light cycle oil, liquified petroleum gas, coke, and gasoline) are also treated as lumps. Usually, the number of lumps indicates the total number of reactants and products in the reaction (i.e., 6 components are present in a 6-lump model). Unfortunately, lumped kinetic models (and catalyst deactivate functions) are not compatible with the currently offered tools in Aspen Plus V8.8[®]. Employing a lumped kinetic model would require developing an external Fortran subroutine and synchronizing computer code with Aspen.⁹ Aspen allows users to multiply reaction kinetic parameters by multiplicative factors called activities. Using a trial-and-error approach, activity factors were incorporated into the reactions so that product yields matched literature values (i.e., model the catalyst deactivation which lowers the yield of hydrocarbon products). Eleven conventional components, whose

thermodynamic, transport, and physical property parameters are available in Aspen's database, were selected. Table 4 lists 15 reactions developed by the design team (in Table 17 of the appendix, there is a list of pre-exponential factors, activation energies, and activity parameters).

Table 4. Gas oil catalytic cracking reactions

Reaction No.	Reaction* (Lump Form)	Reaction (Explicit Form)
1	GO → LCO	$C_{28}H_{58} \rightarrow C_{14}H_{30} + C_{14}H_{28}$
2	GO → GLN	$C_{28}H_{58} \rightarrow C_8H_{18} + 2.5C_8H_{16}$
3	GO → LPG	$C_{28}H_{58} \rightarrow C_4H_{10} + 6C_4H_8$
4	GO → DG	$C_{28}H_{58} \rightarrow C_2H_6 + 13C_2H_4$
5	GO → CK	$C_{28}H_{56} \rightarrow 28C + 28H_2$
6	LCO → GLN	$C_{14}H_{30} \rightarrow C_8H_{18} + 0.75C_8H_{16}$
7	LCO → LPG	$C_{14}H_{30} \rightarrow C_4H_{10} + 2.5C_4H_8$
8	LCO → DG	$C_{14}H_{30} \rightarrow C_2H_6 + 6C_2H_4$
9	GLN → LPG	$C_8H_{18} \rightarrow C_4H_{10} + C_4H_8$
10	GLN → DG	$C_8H_{18} \rightarrow C_2H_6 + 3C_2H_4$
11	LPG → DG	$C_4H_{10} \rightarrow C_2H_6 + C_2H_4$
12	LCO → CK	$C_{14}H_{28} \rightarrow 14C + 14H_2$
13	GLN → CK	$C_8H_{16} \rightarrow 8C + 8H_2$
14	LPG → CK	$C_4H_8 \rightarrow 4C + 4H_2$
15	DG → CK	$C_2H_4 \rightarrow 2C + 2H_2$

*= Kinetic model and parameters obtained from John et al.¹⁰ *Note:* This reaction scheme does not consider the participation of naphthenes and aromatics. Reactions 1-15 are consistent with experimental observations in carbenium ion chemistry (i.e., long-chain paraffin → smaller-chain paraffin + olefin and olefin → coke)

FCC Catalyst

Typically, Zeolite (Type X, Type Y, and ZSM-5) is employed for catalytically converting gas oil into smaller-chain hydrocarbons. The catalyst is composed of Silicon, Aluminum, and Oxygen atoms joined together in a lattice arrangement. Due to Zeolite not being available in Aspen's component database, Kaolinite ($Al_2Si_2O_7 \cdot H_2O$) was chosen to model the circulating FCC catalyst. Kaolinite is the most commonly used Zeolite catalyst binder.¹¹ The primary purpose of Kaolinite is to function as a glue (i.e., a skeleton) to hold the Zeolite. Table 5 shows a particle size distribution for Kaolinite.¹² Particle size distribution (PSD) data is required for gas-solid cyclone separators to be fully operational in Aspen Plus®.

Table 5. Particle size distribution (PSD) for a typical FCC catalyst¹²

Particle Size (microns)	Weight (%)
63-75	50.69
75-100	30.17
100-120	8.80
120-160	8.82
160-200	1.52

Note: FCC catalyst was initially sieved and later screened into 5 size intervals.

Riser Optimization and Sensitivity Analysis

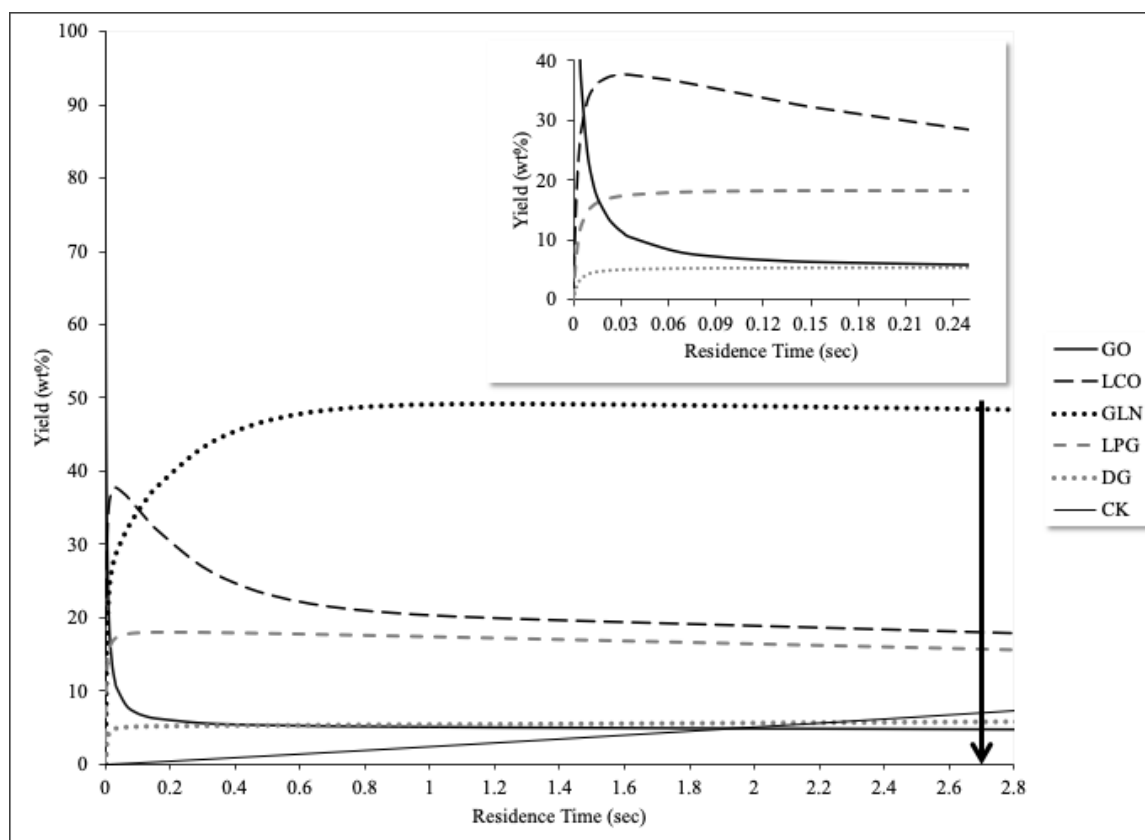


Figure 4. Effect of residence time on the yield of petroleum products. The catalyst-to-oil ratio is 6.405 and the riser diameter is 1.5 meters wide. The riser is 23 meters long and operates adiabatically. The black, bolded arrow indicates a process operating condition (i.e., target residence time of 2.7 seconds corresponds to a riser length of 23 meters and yields that are consistent with literature).

According to Figure 4, the yield (kg of petroleum product/kg of gas oil feed) of gasoline increases with increasing residence time (from 0 - 0.6 sec) and then reaches a constant value of approximately 48 wt. %. A similar trend applies to dry gas whose percent yield levels off to about 5 wt. % at a residence time of approximately 0.03 seconds. Interestingly, the yield of light cycle oil reaches a maximum value of 38 wt. % at a residence time of 0.034 seconds. For larger residence times (i.e., residence times greater than 0.034 seconds), the yield of light cycle oil

decreases monotonically and reaches a value of 17 wt. %. The yield of liquified petroleum gas increases with increasing residence time (for early residence times; 0-43 seconds) and gradually decreases. At the operating condition denoted by the bolded arrow, the yield of liquified petroleum gas is approximately 15.8 wt. %. The yield of coke increases with increasing residence time and shows no signs of flattening out. At a riser length of 23 meters, the residence time is 2.7 seconds, and the conversion of gas oil is 95.23 wt. %. At this residence time, the product yields are in-alignment with yields commonly reported in the literature.

Explanations for the inconsistent yield-residence time profile are: (1) gas oil feed flow rate and (2) riser geometry. John et al. 's (research group whose paper was referenced for kinetic parameters) simulation processed 62.5 kg/s of gas oil in a riser that is 47.1 meters long with a diameter of 1.36 meters. In our process, the gas oil feed rate is 36.8 kg/s and the riser is only 23 meters long. A catalyst-to-oil ratio of 6.405 was maintained (similar to John et al.'s simulation). In addition, the riser outlet temperature in John et al.'s simulation is 463 °C, while the riser outlet temperature in our simulation is 486 °C (i.e., approximately 23 °C higher). With regards to the catalyst temperature, the temperature of the regenerated catalyst in John et al.'s simulation is 660 °C, while the catalyst temperature in our simulation is approximately 669 °C (9 °C difference). In John et al.'s simulation, larger residence times were required to obtain conventional product yields.¹⁰ In our simulation, shorter residence times were necessary to convert gas oil and generate petroleum products at yields commonly reported in industry. Further investigation is necessary to figure out why the residence time is much shorter than commercially reported figures (i.e., the yield profiles hardly change after ~1.2 seconds and too much coke forms at 2.7 seconds). Due to time constraints, the design team has decided to settle on these yields generated by the simulator.

Table 6. Simulation and commonly reported commercial yields (measured at the riser outlet)

Component	Simulation Yield (wt. %)	Commercial Yield* (wt. %)
Gasoline (GLN)	48.5	46-51
Liquified Petroleum Gas (LPG)	15.8	12-15
Light Cycle Oil (LCO)	17.9	15-23
Dry Gas (DG)	5.9	5
Coke (CK)	7.1	4-6

*= obtained from Anchetya¹³

Overall, Table 6 shows that simulation yields are comparable to yields commonly reported in industry. Discrepancies in yields may be due to the feedstock characterization and slight differences in operating conditions (i.e., differences in temperatures, pressures, gas oil feed rate, and reactor geometry). In the simulation, gas oil consists only of long, straight-chain alkanes and short alkenes. In reality, gas oil also consists of aromatic compounds and cyclo-alkanes. Although adding more gas oil attributes would aid in getting simulation results to match commercial yields, it would greatly complicate the modeling process and significantly increase computing time (i.e., more opportunities for convergence errors). Temperatures, pressures, and flow rates were chosen and further optimized to match typical values reported in the literature.

Afterward, the activity parameters of each reaction were slightly adjusted so that calculated yields matched commercial yields. Furthermore, there exists a number of definitions for yield, and we noticed that many authors, whose work we referenced, did not explicitly state what definition of yield they used. The definition used in this report is consistent with the definitions used in Anchetya¹³ and John et al.¹⁰

Regenerator

In the simulation, the regenerator reactor (labeled R-2) was modeled with RPlug. This reactor has a single input and output. The input is the mixture of the heated air stream and the outlet of the cyclone separator following the riser reactor. The output of the reactor includes flue gases and superheated catalyst. Two primary reactions were modeled in this reactor (coke combustion reactions) and are the first two reactions listed in Table 7. The reactor was able to fully convert coke into carbon monoxide and carbon dioxide.

The reactor outlet leads to a cyclone which separates the catalyst in the regenerator from the hot flue gases. The cyclone has an inner diameter of 1 meter. The regenerated catalyst goes to enters a splitter where some of the catalyst is withdrawn and the remaining catalyst is recycled. To simulate the closed loop system, the RC-OUT has the same specifications (temperature, pressure, enthalpy, mass flow rate, etc.) as the RC-IN stream. This was done by creating a design specification that adjusts the heating duty of the heater (E-2) that heats the air stream so that the recycled catalyst stream RC-OUT has identical stream parameters as RC-IN. The flue gases that were separated in the cyclone enter the CO boiler.

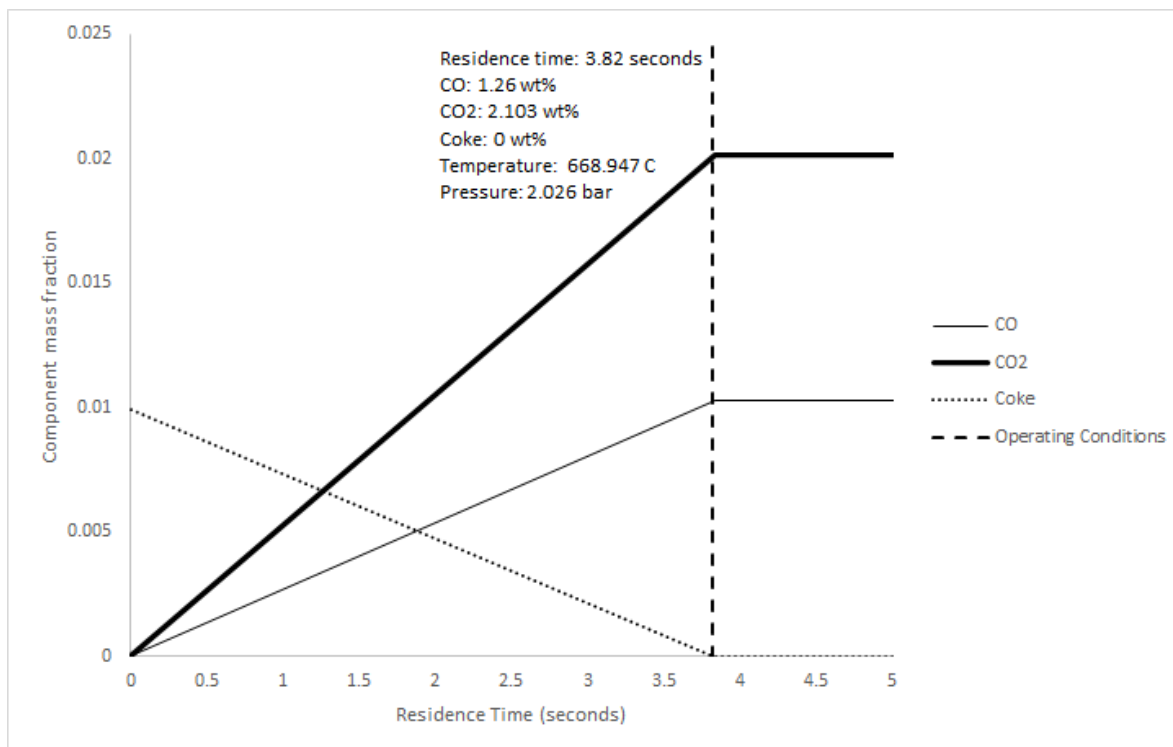


Figure 5. Effect of residence time on regenerator component mass fractions. It can be seen that at the outlet there is no more coke, and that the reaction is complete at 3.82 seconds.

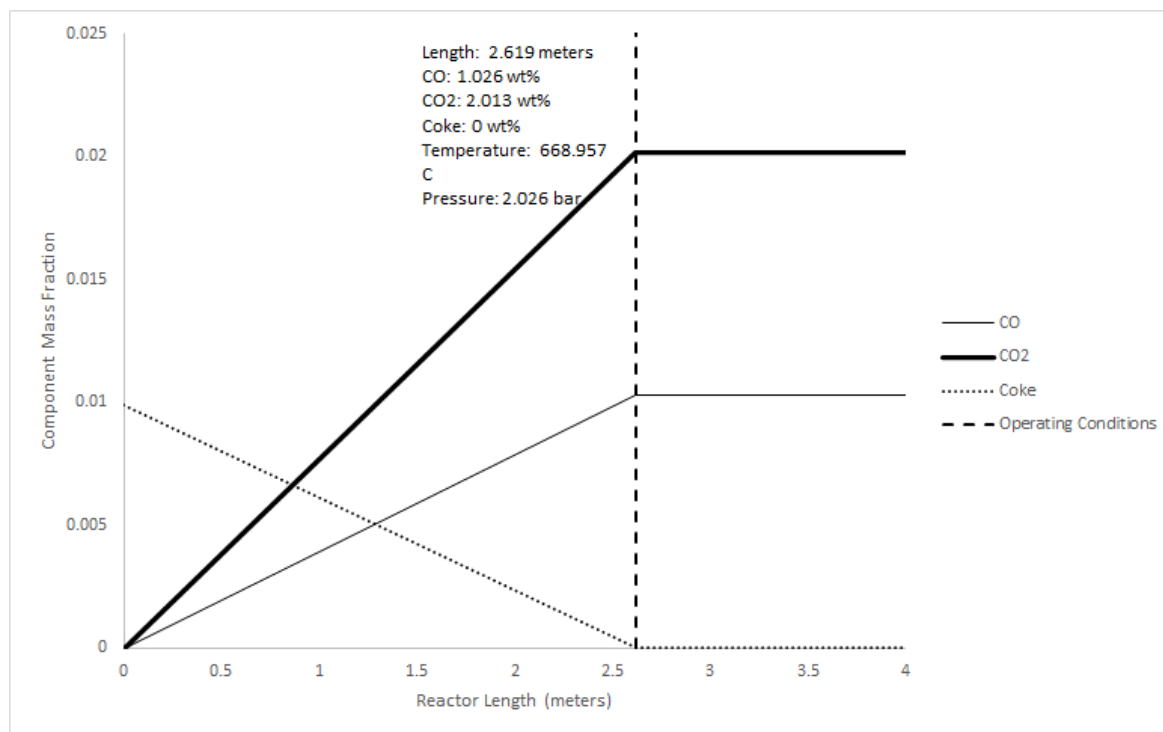


Figure 6. Effect of reactor length on regenerator component mass fractions. At the outlet there is negligible amounts of coke (~2.6 meters from the inlet)

CO Boiler

The carbon monoxide boiler was modeled with a reactor and a heat exchanger. In the simulation, the CO boiler is labeled R-3 and is simulated using an REQUIL block, operating adiabatically at 1.01 bar, with a single reaction that converts carbon monoxide into carbon dioxide. The inlets of the reactor are an airstream and the flue gases from the regenerator reactor. This reactor completely converts CO so that the flue gas outlet has negligible traces of CO.

A separate file was made to model the CO boiler as an RPLUG block that converges and gives reliable results. This was required since including it in the main flowsheet returned errors. The reactor, labeled COB, runs adiabatically with the full set of reactions in Table 7. Unlike the rest of the units in the simulation, this reactor must operate using the IDEAL property method instead of the Peng-Robinson property method. This is due to missing property parameters for monatomic oxygen (a reactant and product in several of the reactions in Table 7) that were not available in the Peng-Robinson method. The reactor is also able to completely convert CO. From this model, the reactor size and capital cost can be determined, and graphical analyses are performed, since REQUIL is unable to provide useful results needed for these conclusions to be made. This reactor was designed with the goal of achieving a residence time of 0.2 to 2 seconds, operating temperature between 427 °C and 1,093 °C, and a length to diameter ratio of 2-3.¹⁴

Although the CO boiler completely converts the carbon monoxide, it does not produce a high yield of nitrogen-based compounds in the flue gas (NO, NO₂, N₂O, and N). This is inaccurate as it is expected that a considerable amount of nitrogen-based compounds are formed during any combustion process. The reason for this inaccuracy, however, is not clear as there is an ample

amount of air in the reactor to cause these reactions as well as the high temperature that is also required to do so. The issue does not seem to be the kinetics data as they were taken from the same sources as the carbon monoxide combustion kinetics. Also, if the rate constants were adjusted in the simulator (to match literature value), there is no resulting considerable difference in the yield.

The heat exchanger (E-1) forms steam by passing cold water which receives heat from the flue gas exhaust of the CO boiler. This steam is used to heat the air stream (AIR+FC) that enters the regenerator reactor. The specifications and results of block E-1 are available in Table 2.

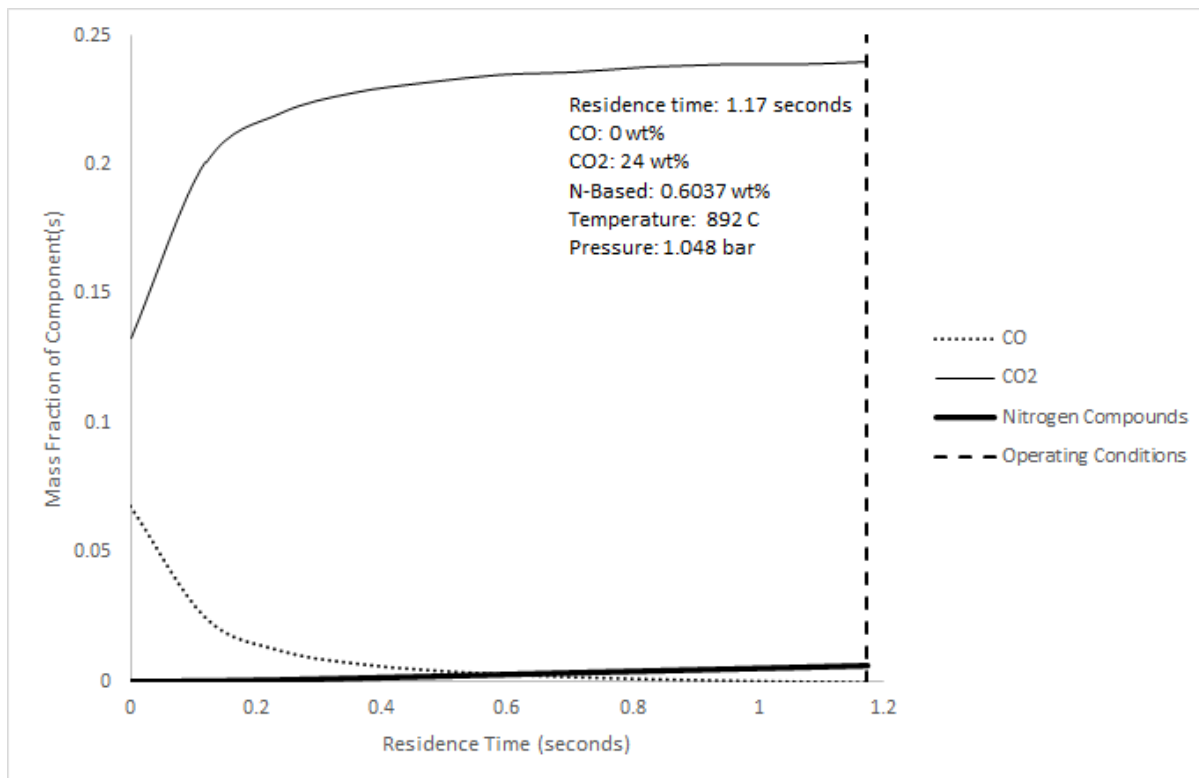


Figure 7. Effect of residence time on the formation of nitrogen products.

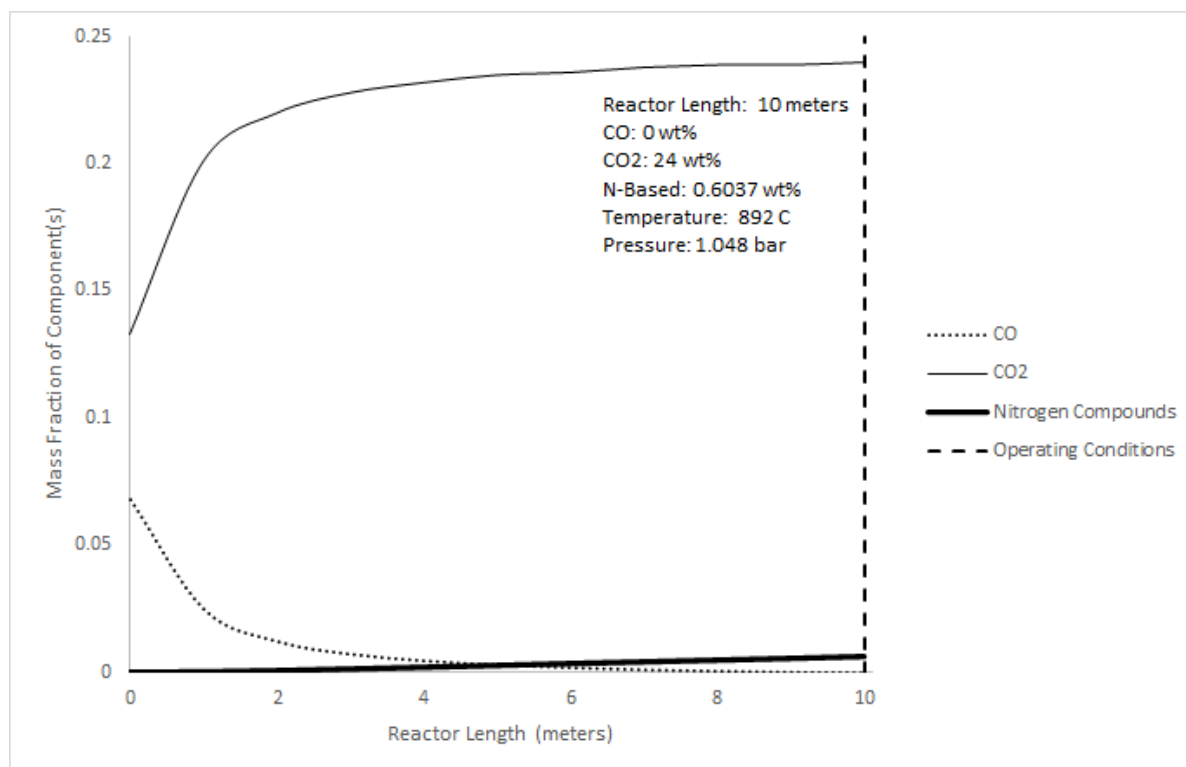


Figure 8. Effect of reactor length on the formation of nitrogen products.

Table 7. Full set of reaction kinetics data for the Regenerator and CO Boiler

Reaction	Pre-Exponential Factor ($\frac{\text{m}^3}{\text{kmol}\cdot\text{s}}$)	Activation Energy ($\frac{\text{J}}{\text{mol}}$)	Reactor the Reaction Takes Place In	Ref.
$\text{C} + \text{O}_2 \rightarrow \text{CO}_2$	$4.12 * 10^7$	97,000	Regenerator (R-2)	(15)
$2\text{C} + \text{O}_2 \rightarrow 2\text{CO}$	$1.65 * 10^7$	97,000	Regenerator (R-2)	
$\text{CO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{O}$	$2.5 * 10^9$	199,576.8	CO Boiler (COB*)	(16)
$\text{CO} + \text{O} \rightarrow \text{CO}_2$	$1.8 * 10^7$	995,792	CO Boiler (COB*)	
$\text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O}$	$5.9 * 10^6$	26,275.52	CO Boiler (COB*)	(17)
$\text{NO} + \text{O}_2 \rightarrow \text{NO}_2 + \text{O}$	$1.7 * 10^9$	194,538.42	CO Boiler (COB*)	(18)
$\text{CO} + \text{NO}_2 \rightarrow \text{CO}_2 + \text{NO}$	$1.9 * 10^9$	122,426.19	CO Boiler (COB*)	(15)
$\text{N}_2 + \text{O} \rightarrow \text{N} + \text{NO}$	$7.6 * 10^{10}$	315,917.10	CO Boiler (COB*)	(18)
$\text{N}_2 + \text{O}_2 \rightarrow \text{N}_2\text{O} + \text{O}$	$6.3 * 10^{10}$	458,911.16	CO Boiler (COB*)	

*= Model seen in the separate Aspen file titled CO Boiler May_7

Separations Processes

Main Fractionator

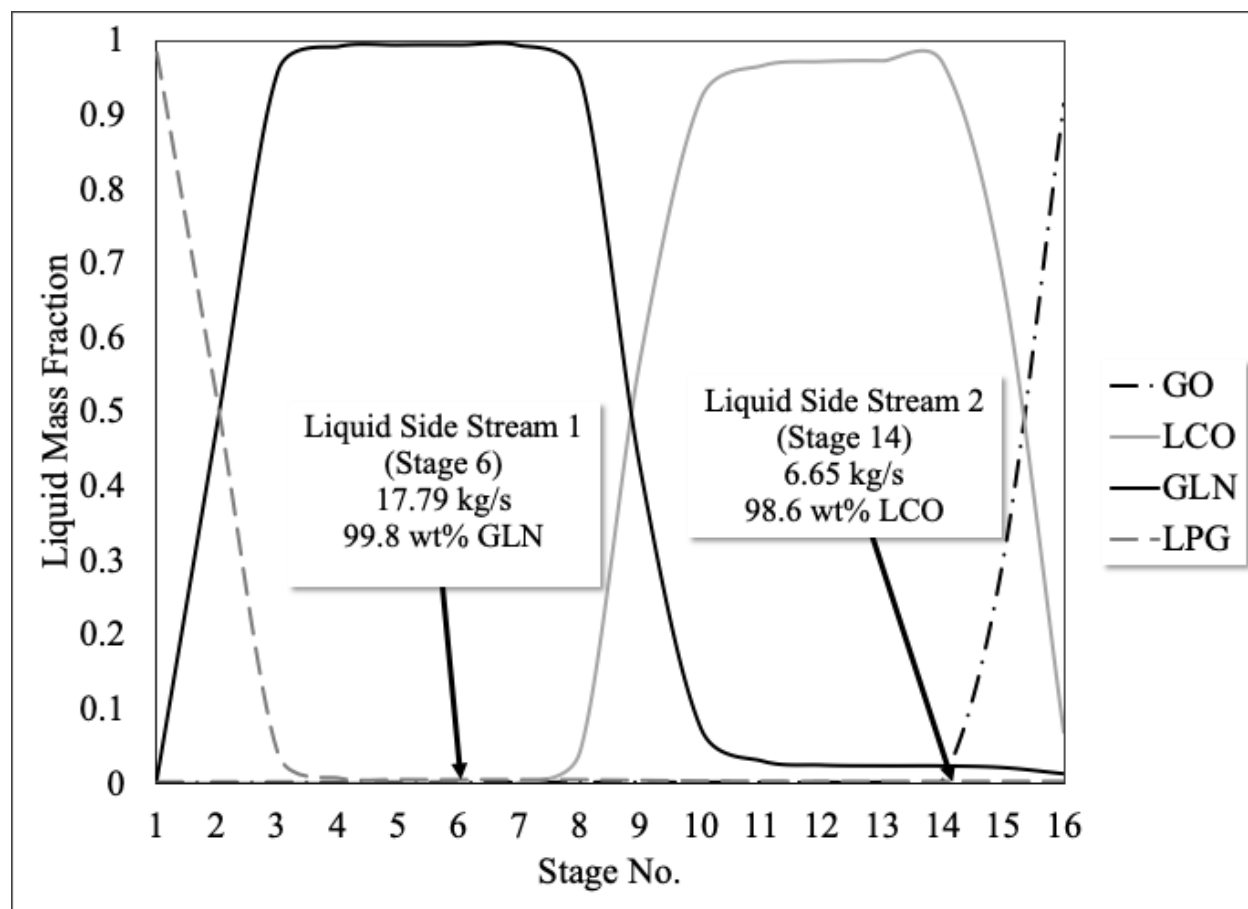


Figure 9. Liquid mass fraction of hydrocarbon components with respect to stage number.

The liquid mass fraction of DG (between stages 1-16) is negligible compared to the mass fractions of other components; hence its composition profile was omitted. Liquid side streams were integrated on stages that were rich in a particular component. Stages 6 and 14 correspond to liquid mass fractions of 99.8 wt. % gasoline and 98.6 wt. % light cycle oil, respectively. Liquid was drawn from these stages. There is a relatively large temperature gradient across the main fractionator (i.e., stage 1 is $\sim -35^\circ\text{C}$ and stage 16 is $\sim 314^\circ\text{C}$). This gradient can be minimized by increasing the column operating pressure. Increasing the column operating pressure increases both the bubble- and dew-point temperature of the overhead mixture leaving the top stage and entering the condenser. Currently, the column (stage 1) pressure is 1.01 bar and the stage-by-stage pressure drop is 0.0069 bar. Further investigation is needed to confidently determine what column operating pressure would: (1) minimize the temperature gradient across the column, (2) not drastically increase the capital cost associated with the column (i.e., higher pressure implies a bigger vessel thickness which increases equipment cost), and (3) does not conflict with specified product purity targets (i.e., adjusting operating pressure causes the liquid and vapor component

mass fraction profiles to also change). Adjusting the number of stages and adjusting the feed stage location could also affect the column's temperature profile. In summary, further investigation is needed to minimize the temperature gradient across the main fractionator.

Table 8. Mass purity, fractional recovery, and total mass flow rate of side streams

Compound	Mass Purity (wt. %)	Fractional Recovery (wt. %)	Side Stream Stage No.	Flow Rate (kg/s)
Gasoline	99.8	99.5	6	17.79
Light Cycle Oil	98.6	99.0	14	6.65

High-Pressure Distillation Column

The overhead vapor distillate (-35.1 °C, 1.01 bar) leaving the main fractionator (T-1) is compressed to an outlet pressure of 28.64 bar and its components are further separated by the high-pressure distillation column (T-2). The column consists of 30 stages and compressed vapor enters through stage 7. The column contains a partial condenser and kettle reboiler. A high-pressure column is necessary so that a chilled refrigerant can be employed as the heat-extracting medium. The column's operating pressure is 28.6 bar with a pressure drop of 0.0068 bar per stage (i.e., based on literature heuristics).^{19, 20} The reflux ratio is 5.59 (mass basis) and the boilup ratio is 1.15 (mass basis). The temperature of the distillate is -67 °C and the bottom product temperature is 127.1 °C. The vapor distillate emerges from the column at a composition of 99.9 wt. % dry gas. The liquid bottoms product composition is 99.9 wt. % liquified petroleum gas.

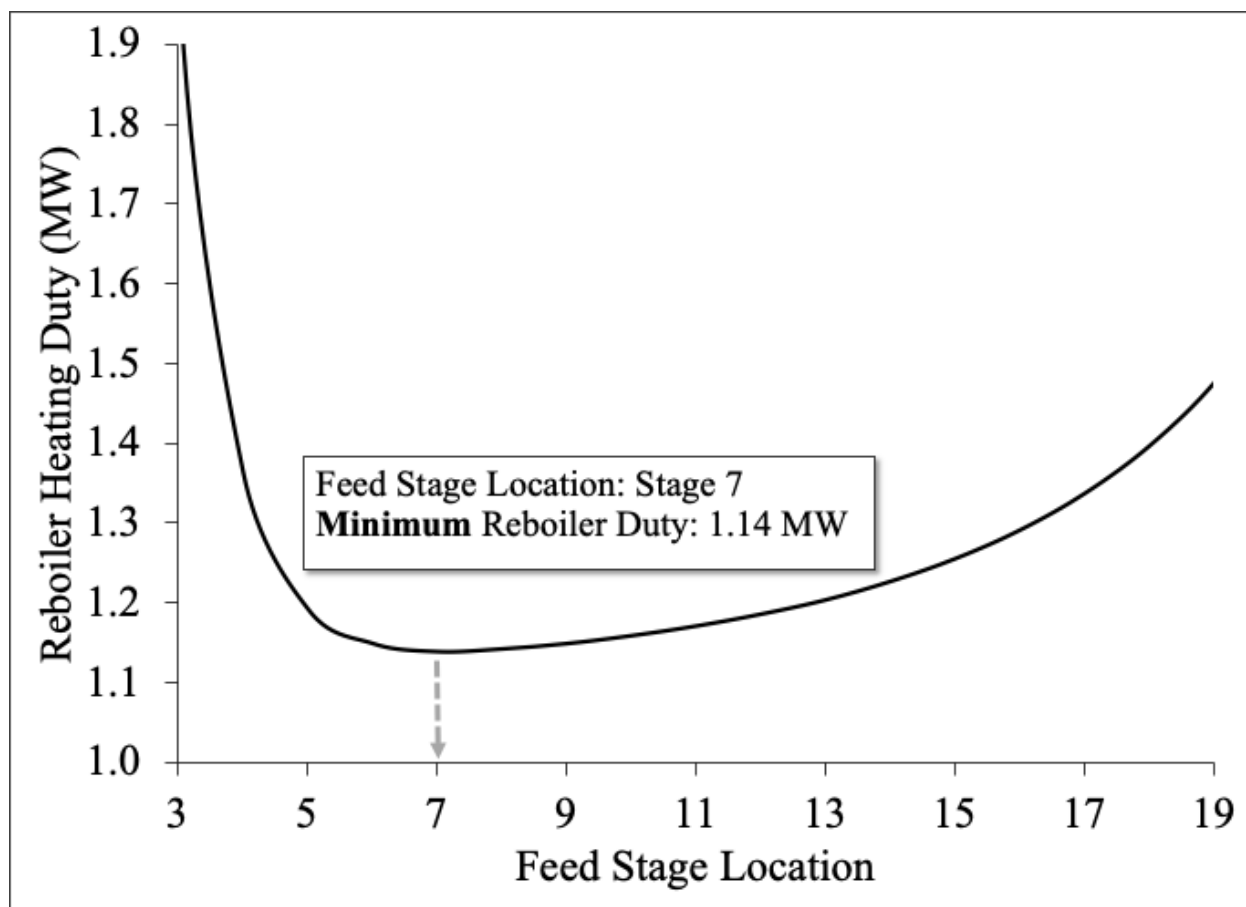


Figure 10. Effect of feed stage location on the reboiler heating duty. Additional variables kept constant were the: number of stages, operating pressure, and pressure drop per stage.

Figure 10 illustrates that a feed stage location of stage 7 corresponds to a minimum reboiler heating duty of approximately 1.14 MW (i.e., 1.14 MW of energy input required to achieve product purities of 99.9 wt. % dry gas in the distillate and 99.9 wt. % liquified petroleum gas in the bottoms product). A design specification was implemented that varied the reflux ratio in order to obtain desired product purities of 99.9 wt. % dry gas (in the distillate) and 99.9 wt. % liquified petroleum gas (in the bottoms product). Table 9 provides a summary of product purities, fractional recoveries, and material flow rates leaving the high-pressure column.

Table 9. Mass purity, mass recovery, and total mass flow rate of distillate and bottoms product streams

Compound	Mass Purity (wt. %)	Mass Recovery (wt. %)	Stage No.	Flow Rate (kg/s)
Dry Gas	99.9	99.8	1	2.16
Liquified Petroleum Gas	99.9	99.2	30	5.76

Economic Analysis

Equipment costs make up most of the capital costs associated with this plant. These cost estimates are shown below in Table 10 and were determined using price history, vendor information, and chemical engineering handbooks.

Table 10. Equipment cost summary

Equipment	Purchased Cost (USD)
Reactor Vessel (R-1 & R-2)	10,057,647.05
Reactor Cyclone (CS-1)	306,433.58
Regenerator Cyclone (CS-2)	1,254,721.29
Main Fractionator (T-1)	3,750,000
Distillation Column (T-2)	70,000
CO Boiler (R-3 and E-1)	1,065,408.73
Heat Exchanger (E-2)	5,360
Water Pump	40,000
Compressor	26,000
Total Purchased Equipment Cost	16,530,210.65

The cost of the riser-reactor and regenerator was estimated using price history of similar equipment and adjusting for inflation. The National Renewable Energy Laboratory (NREL) performed a cost analysis on a large-scale FCC unit and received a quote of \$9,958,080 for the riser-reactor and regenerator bundled together.²¹ Using our design specifications and adjusting for inflation, we estimated the cost of the riser-reactor and regenerator bundled together to be \$10,057,647.05.

The same report from the NREL stated they received a quote of \$910,200 for a set of three reactor cyclones and \$2,484,600 for a set of two regenerator cyclones.²¹ Using our design specifications, adjusting for inflation, and accounting for the number of cyclones needed; we estimated the cost of the reactor cyclones and regenerator cyclones to be \$306,433.58 and \$1,254,721.29, respectively.

The cost of the main fractionator and distillation column was estimated by hand calculations using our design specifications, heuristics used throughout industry, and CAPCOST. We estimated the cost of the main fractionator and distillation column to be \$3,750,000 and \$70,000, respectively. CAPCOST was used in this case because it was much easier to estimate a price, since we were able to specify and consider important factors such as number of trays, column height and diameter, and material of construction.

The CO Boiler consists of the boiler itself and the heat exchanger and was estimated using a report written by the Department of Energy (DOE). The DOE included a chart that estimates the cost of a packaged boiler, which includes fans, instruments, controls, burners, soot-blowers, etc.; based on a pound-per-hour capacity. The mass flow rate entering the heat exchanger (E-1) is 205,266 lb/hr which would correlate to a \$650,000 cost.²² However, when adjusted for inflation the final cost of the CO boiler will be \$1,065,408.73. The cost of the other heat exchanger (E-2), the water pump, and compressor was estimated using CAPCOST for the sake of simplicity. Scaling of equipment and adjustments for inflation were made using a CEPCI index value of 596.2.²³

Table 11. Capital investment summary

Cost	Plant Cost (USD)
Total Direct Cost	59,508,758.34
Total Indirect Plant Cost	23,803,503.34
Fixed Capital Investment	83,312,261.68
Working Capital	14,711,887.48
Total Capital Investment	98,024,149.15

Shown above in Table 11 is a summary of the capital investment associated with this plant. These costs were estimated using values provided by Peters and accounts for many factors such as purchased equipment, installation, buildings, construction, legal expenses, etc.²⁴ A more detailed breakdown is shown in Table 20 (in the Appendix).

Table 12. Flow Rate, Market Price, and Cost of Non-Solid Materials

Component	Flow Rate (gal/s)	Market Price (USD/gal)	Cost (USD/Year)
Gas Oil	18.57	1.2 ^a	702,748,224
Air	6,732	3.2110 ⁻⁵ ^b	6,816,964.303
Water	1.32	0.0037 ^c	154,021.824

^areference (25), ^breference (26), ^creference (27)

Table 13. Flow rate, market price, and cost of solid materials

Component	Flow Rate (ton/s)	Market Price (USD/ton)	Cost (USD/Year)
Catalyst	0.001	3,000 ^d	94,608,000

^dreference (28)

Table 14. Flow rate, market price, and sale of products

Component	Flow Rate (gal/s)	Market Price (USD/gal)	Sales (USD/Year)
Gasoline	7.5	2.54 ^a	600,953,043.5
Dry Gas	43.03	0.000945 ^b	1,282,359.406
LCO	2.91	1.6155 ^c	149,425,814.7
LPG	3.76	1.04 ^d	123,318,374.4
Slurry	0.78	1.18 ^e	28,281,484.80

Note: The cost of each product is based on the previous 5-year average of their monthly prices (2016 - 2021); ^areference (29), ^breference (30), ^creference (31), ^dreference (32), ^ereference (33)

Shown above in Table 12, Table 13, and Table 14 are the cost of raw materials (gas oil feedstock, water, processing of air, and fresh catalyst feed) and sales of products (gasoline, LPG, LCO, and dry gas).

Table 15. Calculated revenue, cost of materials, profit, ROI, and payback period

Revenue (USD/Year)	903,261,076.7
Costs of Materials (USD/Year)	804,327,210.1
Annualized Capital Cost (USD/Year)	9,802,414.915
O&M Costs (USD/Year)	57,053,144.11
Profit Before Taxes (USD/Year)	32,078,307.57
Profit After Taxes (USD/Year)	21,492,466.07
ROI	3.68 %
Payback Period	4.60 Years

Revenue and total cost of materials in Table 15 were calculated based on parameters in the overall mass balance (Figure 1). The annualized capital cost was calculated to be \$9,802,414.915 per year. This was determined by multiplying the total capital investment by the capital recovery factor (CRF). The CRF was calculated to be 0.10 with a discount factor of 10% and a project lifetime of 30 years (see equation Eq. 2 in the Appendix).

The annual operating and maintenance costs accounts for labor, utility, maintenance, rent, depreciation, insurance, overhead, etc.; and were estimated primarily by using values provided by Peters (24). However, the cost of utilities also depends on the amount of electricity the plant requires.

A report by the Internal Energy Agency (IEA) determined that the utility cost associated with running with a refinery to be \$3.30 per barrel when not accounting for the cost of electricity.³⁴ Since we are processing almost 24,000 barrels of oil every day, the daily cost would be \$78,543. The average cost of electricity for industrial use across New York State is \$0.0582 from 2015 to 2020.³⁵ Our FCC unit uses 2981.67 kW per day, which means the cost of electricity is \$4164.80 per day.

In addition, if we consider that our plant has zero salvageable equipment at the end of its 30-year life span and there is a trend of straight-line depreciation; our equipment would depreciate at the amount of \$550,140.36 annually for 30 years.

The annual operating and maintenance cost comes out to \$57,053,144.11. A more detailed breakdown of the operating and maintenance costs is shown in Table 21 (in the Appendix).

The calculated ROI in Table 15 is strictly a function of materials cost, product sales, annualized capital cost, and operation and maintenance costs (see equation Eq. 1 in the appendix). The payback period was calculated assuming we have a discount rate of 0% and that the FCC unit will be operating for 365 days a year for the next 30 years. Before taxes, we will generate an annual profit of \$32,078,307.57 before taxes. After accounting for a yearly flat tax rate of 33%, we will have a total profit of \$21,492,466.07. Accounting for a yearly inflation rate of 3%, over the lifespan of the plant we will generate \$1,022,513,007.83 in profit.

Environmental, Health, and Safety

Petroleum refineries are held accountable for water, air, and soil pollution all around the world. Thus, they are required by state, local, and federal environmental agencies to meet certain air quality emission limits, including discharge criteria for products produced during various chemical processes. The FCCU is a core component in petroleum refineries, yet it is considered the biggest source of atmospheric pollution, primarily from SO_x (sulfur oxides) and NO_x (nitrogen oxides).³⁶

According to the United States Energy Information Administration (EIA), there are 700 petroleum refineries worldwide and 500 of them employ FCC units.³⁷ The average feedstock flow rates range from 56,000 barrels to 227,000 barrels per calendar day.³⁸ The EPA implemented regulations stating that NO_x emissions should be ≤ 20 ppm.³⁹ In order to remain active and functional, petroleum refineries (in the United States) are complying with EPA regulations. The flue gas exiting the riser has the largest amount of NO_x, mainly in the form of nitric oxide (NO) ranging from 100 to 500 ppm.³⁹ From Figures 7 and 8, it can be seen that the results of the simulation produce very low amounts of NO_x alongside the other nitrogen compounds.

During the regeneration process, between 70-90 % of the NO_x that is formed is converted to unarmful nitrogen gas (N₂), which can be released into the atmosphere.³⁸ The NO_x that is not converted is known as fuel NO_x (originates from condensed organic nitrogen compounds in the coke). These compounds include aromatics containing nitrogen atoms, amines, pyridine compounds, pyrrole derivatives and amines.³⁹

Table 16. General health and environmental hazards of FCC products and reactants

Gas Oil	<ul style="list-style-type: none">● Oil spills contaminate land and water; deadly to animals⁴⁰● Air and water pollution hurts local communities⁴⁰
LCO	<ul style="list-style-type: none">● Toxic to aquatic life, with a long-term effect on its environment^{41, 42}● May be fatal if swallowed or enters airways^{41, 42}● Can cause skin and eye irritation^{41, 42}
Gasoline	
LPG	<ul style="list-style-type: none">● Skin and eye irritant⁴³● May cause explosive mixture with air⁴³● At high concentration, may displace oxygen and cause suffocation⁴³
Dry Gas	<ul style="list-style-type: none">● At high concentration, dry gas can displace oxygen and cause suffocation⁴⁴● Extremely flammable gas⁴⁴
Catalyst (Zeolite Y)	<ul style="list-style-type: none">● May cause respiratory irritation if inhaled⁴⁵

References

- (1) Patil, K.D.: Modeling and Simulation for FCC Unit using Aspen Hysys. *Chemcom* 2013, 1-5.
- (2) Natural Gas Explained: Use of Natural Gas. U.S. Energy Information Administration, 2020, <https://www.eia.gov/energyexplained/natural-gas/use-of-natural-gas.php>, last accessed April 9, 2021.
- (3) Uses of LPG - Propane Uses: What is LPG Used For? Uses of Liquefied Petroleum Gas. ELGAS, 2019, <https://www.elgas.com.au/blog/1681-what-is-lpg-used-for-liquefied-petroleum-gas-propane-applications>, last accessed April 9, 2021.
- (4) Gasoline Explained: Use of Gasoline, 2020, <https://www.eia.gov/energyexplained/gasoline/use-of-gasoline.php>, last accessed April 9, 2021.
- (5) Kalaiselvi, T.; Selvasundar, K.; Kumaresan, M. K.: Maximizing Light Cycle Oil (LCO) Production in Fluid Catalytic Cracker. *IEEE* 2017.
- (6) Sadeghbeigi, R.: Process Description. In *Fluid Catalytic Cracking Handbook: An Expert Guide to the Practical Operation, Design, and Optimization of FCC Units*;
- (7) Sadeghbeigi, R.: Products and Economics. In *Fluid Catalytic Cracking Handbook: An Expert Guide to the Practical Operation, Design, and Optimization of FCC Units*; Butterworth-Heinemann: Oxford, UK, 2012; pp 169-189.
- (8) Elliot, J. R.; Lira, C. T.: Phase Equilibria in Mixtures by an Equation of State. *Introductory Chemical Engineering Thermodynamics*; Pearson Education Inc.: London, UK, 2012; pp 571-596.
- (9) Du, Y.; Sun, L.; Berrouk, A. S.; Zhang, C.; Chen, X.; Fang, D.; Ren, W.: Novel Integrated Reactor-Regenerator Model for the Fluidized Catalytic Cracking Unit Bases on an Equivalent Reactor Network. *Energy Fuels* 2019, 33, 7265-7275.
- (10) John, M. Y.; Mustafa, A. M.; Patel, Raj.; Mujtaba M. I.: Parameter estimation of a six-lump kinetic model of an industrial fluid catalytic cracking unit. *Fuel* 2019, 235, 1436-1454.
- (11) Sadeghbeigi, R.: FCC Catalysts. In *Fluid Catalytic Cracking Handbook: An Expert Guide to the Practical Operation, Design, and Optimization of FCC Units*; Butterworth-Heinemann: Oxford, UK, 2012; pp 69-88.
- (12) Wu, D.; Wu, Fanghua.: Particle Size Effect on the Catalyst Attrition in a Lab-Scale Fluidized Bed. *AIChE Journal*, 2017, 63, 914-920.

- (13) Maya-Yescas, R.: Modeling And Simulation Of Fluidized-Bed Catalytic Cracking Converters. In *Modeling and Simulation of Catalytic Reactors for Petroleum Refining*; Anchetya, J., Ed.; John Wiley & Sons, Inc.: Hoboken, NJ, 2011; pp 368-473.
- (14) Thermal Oxidizers. United States Environmental Protection Agency, https://www3.epa.gov/ttnchie1/mkb/documents/TO_B.pdf, last accessed April 16, 2021.
- (15) Sorensen M. D. P.: The establishment of a coke-burn kinetic model for zeolite catalysts. *Chemical Engineering Science*, 2017, 168, 465-479.
- (16) Allen, M. T.; Yetter, R. A.; Dryer, F. L.: High pressure studies of moist carbon monoxide/nitrous oxide kinetics. *Combustion and Flame*, 1997, 3, 449-470.
- (17) Glarborg, P.; Miller, A. M.; Ruscic, B.; Klippenstein S.J.: Modeling Nitrogen Chemistry in Combustion. *Argonne*, 1-157.
- (18) Westley, F.: Table of Recommended Rate Constants for Chemical Reactions Occurring in Combustion. United States Department of Commerce: Washington, D.C, 1980.
- (19) Seider, W. D.; Seader, J. D.; Lewin, D. R.; Widago, S.: Separation Tower Design. In *Product and Process Design Principles: Synthesis, Analysis, and Evaluation*; John Wiley & Sons, Inc.: Hoboken, NJ, 2009; pp 498-509.
- (20) Wankat, P. C.: Introduction to Column Distillation. In *Separation Process Engineering*; Pearson Education, Inc.: Westford, MA, 2012; pp 122-141.
- (21) Equipment Design and Cost Estimation for Small Modular Biomass Systems, Synthesis Gas Cleanup, and Oxygen Separation Equipment. National Renewable Energy Laboratory, 2006, <https://www.nrel.gov/docs/fy06osti/39943.pdf>, last accessed May 5, 2021.
- (22) Loh, H. P.; Lyons, J.; Charles, W. W.: Process Equipment Cost Estimation Final Report. United States Department of Energy 2002, pp 1-78, <https://www.osti.gov/biblio/797810->
- (23) 2020 Annual CEPCI Average Value. Chemical Engineering: Essentials For The CPI Professional, 2020, <https://www.chemengonline.com/2020-annual-cepci-average-value/>, last accessed May 5, 2021.
- (24) Peters, M. S.; Timmerhaus, K. D.; West, R. E.: In *Plant Design and Economics for Chemical Engineers*. McGraw Hill: Fairfield, PA, 2003.
- (25) Petroleum & Other Liquids: Cushing OK WTI Spot Price FOB. U.S. Energy Information Administration, 2021, <https://www.eia.gov/dnav/pet/hist/rwtcM.htm>, last accessed February 25, 2021.
- (26) Energy Tips - Compressed Air: Determine the Cost of Compressed Air for Your Plant. U.S. Department of Energy, 2004, https://www.energy.gov/sites/prod/files/2014/05/f16/compressed_air1.pdf, last accessed February 18, 2021

- (27) Commercial and Industrial Water Rates. West Sound Utility District, <https://www.wsud.us/water/page/commercial-and-industrial-water-rates>, last accessed February 18, 2021.
- (28) Fluidized Catalytic Cracking. Colorado School of Mines, 2018, https://inside.mines.edu/~jjechura/Refining/07_Catalytic_Cracking.pdf, last accessed April 16, 2021.
- (29) Weekly U.S. All Grades All Formulations Retail Gasoline Prices. U.S. Energy Information Administration, 2021, https://www.eia.gov/dnav/pet/hist/LeafHandler.ashx?n=PET&s=EMM_EPM0_PTE_NUS_DPG&f=W, last accessed April 16, 2021.
- (30) Natural Gas: New York Natural Gas Industrial Price. United States Energy Information Administration, 2021, <https://www.eia.gov/dnav/ng/hist/n3035ny3m.htm>, last accessed May 5, 2021.
- (31) Light Cycle Oil. United Refining Company, 2017, http://www.urc.com/pdfs/sds/Light_Cycle_Oil_SDS_NA2015+MEX_090117_FINAL.PDF, last accessed February 25, 2021.
- (32) Petroleum & Other Liquids: Weekly New York Propane Wholesale/Resale Price. United States Energy Information Administration, 2021, https://www.eia.gov/dnav/pet/hist/LeafHandler.ashx?n=PET&s=W_EPLLPA_PWR_SNY_DPG&f=W, last accessed May 5, 2021.
- (33) U.S. Residual Fuel Oil Wholesale/Resale Price by Refiners. U.S. Energy Information Administration, 2021, https://www.eia.gov/dnav/pet/hist/LeafHandler.ashx?n=PET&s=EMA_EPPR_PWG_NUS_DPG&f=M, last accessed April 16, 2021.
- (34) IEA Refinery Margins: Methodology Notes. International Energy Agency, 2012, https://iea.blob.core.windows.net/assets/cbf37dfc-5fe1-4854-b248-95e6a2e5240a/Refining_Margin_Supplement_OMRAUG_12SEP2012.pdf, last accessed April 9, 2021.
- (35) Monthly Average Retail Price of Electricity - Industrial. New York State Energy Research and Development Authority, 2021, <https://www.nyserda.ny.gov/Researchers-and-Policymakers/Energy-Prices/Electricity/Monthly-Avg-Electricity-Industrial>, last accessed April 9, 2021.
- (36) Evaluating FCC flue gas emission-control technologies. Digital Refining, 2008, <https://www.digitalrefining.com/article/1000300/evaluating-fcc-flue-gas-emission-control-technologies#.YIwXkGZKjUp>, last accessed April 30, 2021.
- (37) Number and Capacity of Petroleum Refineries. United States Energy Information Administration, 2020, https://www.eia.gov/dnav/pet/PET_PNP_CAP1_DCU_NUS_A.htm, last accessed April 30, 2021.
- (38) Kunz, R. G.: Air Pollution Aspects of the Fluid Catalytic Cracking Process. In *Environmental Calculations: A Multimedia Approach*; John Wiley & Sons, Inc., Hoboken, NJ, 2009; pp 661-680.

- (39) Evaluating FCC flue gas emission-control technologies. Digital Refining, 2008, <https://www.digitalrefining.com/article/1000300/evaluating-fcc-flue-gas-emission-control-technologies#.YIwxkGZKjUp>, last accessed April 30, 2021.
- (40) Safety Data Sheet: Gasoil. Mercuria, 2015, https://mercuria.com/sites/default/files/EN_SDS_Gasoil%20VGO_SDS%20SGS%20GHS%20%28Reach%20ANNEXII%29_2015130_MERCURIA-01_NR_1.pdf, last accessed May 7, 2021.
- (41) Safety Data Sheet: Light Cycle Oil. Hess, 2012, https://www.hess.com/docs/eu-safety-data-sheets/lightcycleoil_eu.pdf?sfvrsn=2, last accessed May 7, 2021.
- (42) Safety Data Sheet: Gasoline. Hess, 2012, <https://www.hess.com/docs/us-safety-data-sheets/gasoline-all-grades.pdf?sfvrsn=2>, last accessed May 7, 2021.
- (43) Safety Data Sheet: Propane. Hess, 2012, https://www.hess.com/docs/eu-safety-data-sheets/propane_eu.pdf?sfvrsn=2, last accessed May 7, 2021.
- (44) Safety Data Sheet: Methane. Airgas, 2019, <https://www.airgas.com/msds/001033.pdf>, last accessed May 7, 2021.
- (45) Material Safety Data Sheet: Zeolite. Sigma-Aldrich, 2014, <https://www.nwmissouri.edu/naturalsciences/sds/z/Zeolite.pdf>, last accessed May 7, 2021.

Appendix

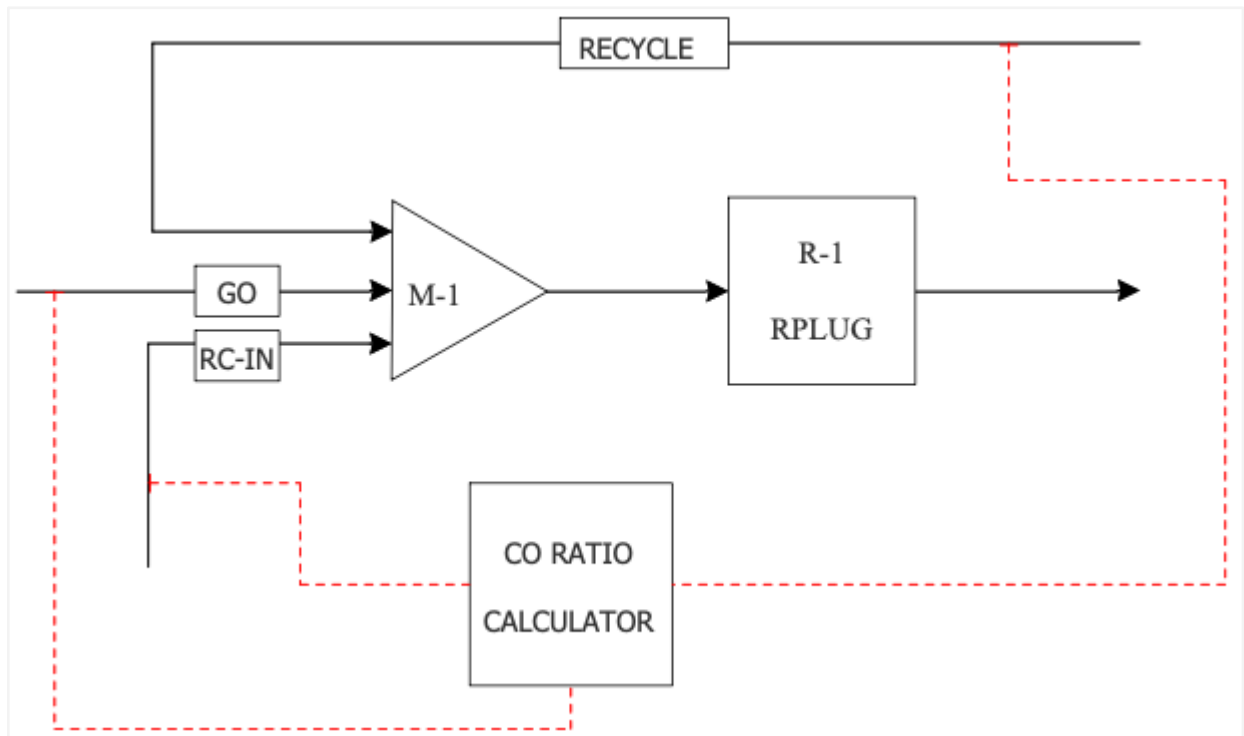


Figure 11. Calculator block employed to automatically adjust catalyst mass flowrate

Variable Definitions:

- MREGCAT = mass flow rate (kg/s) of regenerate catalyst in RC-IN stream
- MGOFEED = mass flow rate (kg/s) of gas oil in the GO stream
- MGORECYC = mass flow rate (kg/s) of gas oil in the RECYCLE stream

Import Variables:

- MGOFEED
- MGORECYC (Stream Variables/Substream Mixed)

Export Variable:

- MREGCAT (Stream Variable/Substream CIPSD)

Fortran Statement:

CORATIO = 5.4

MREGCAT = CORATIO * (MGOFEED + MGORECYC)

This calculator block is to automatically adjust the component mass flow rate of zeolite catalyst in the RC-IN stream. Typically, the catalyst-to-oil ratio varies from 4 - 10 (weight basis). The mass flow rate of catalyst entering the mixer will be 5.4 times the combined mass flow rate of gas oil and recycled gas oil entering the mixer.

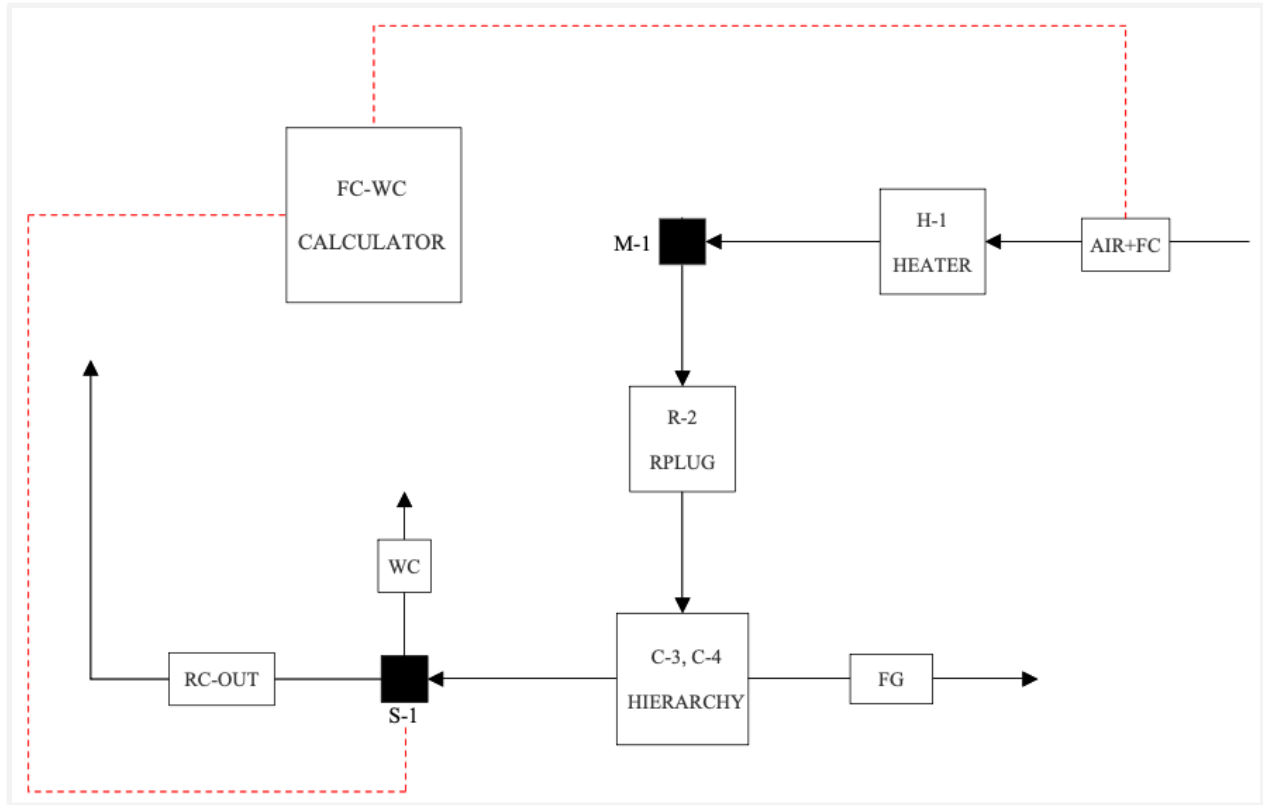


Figure 12. Calculator block employed to set the mass flow rate of catalyst leaving exiting the splitter equal to the mass flow rate of catalyst in the AIR+FC stream

Variable Definitions:

- MFC = mass flow rate (kg/s) of fresh catalyst in the AIR+FC stream
- MWC = mass flow rate (kg/s) of withdrawn catalyst in the WC stream

Import Variable:

- MFC

Export Variable:

- MWC (Block Variable; Splitter S-1)

Fortran Statement:

MWC = MFC

The mass flow rate of the withdrawn catalyst is set equal to the mass flow rate of the fresh catalyst entering the system. The splitter's (S-1) flow rate was accessed.

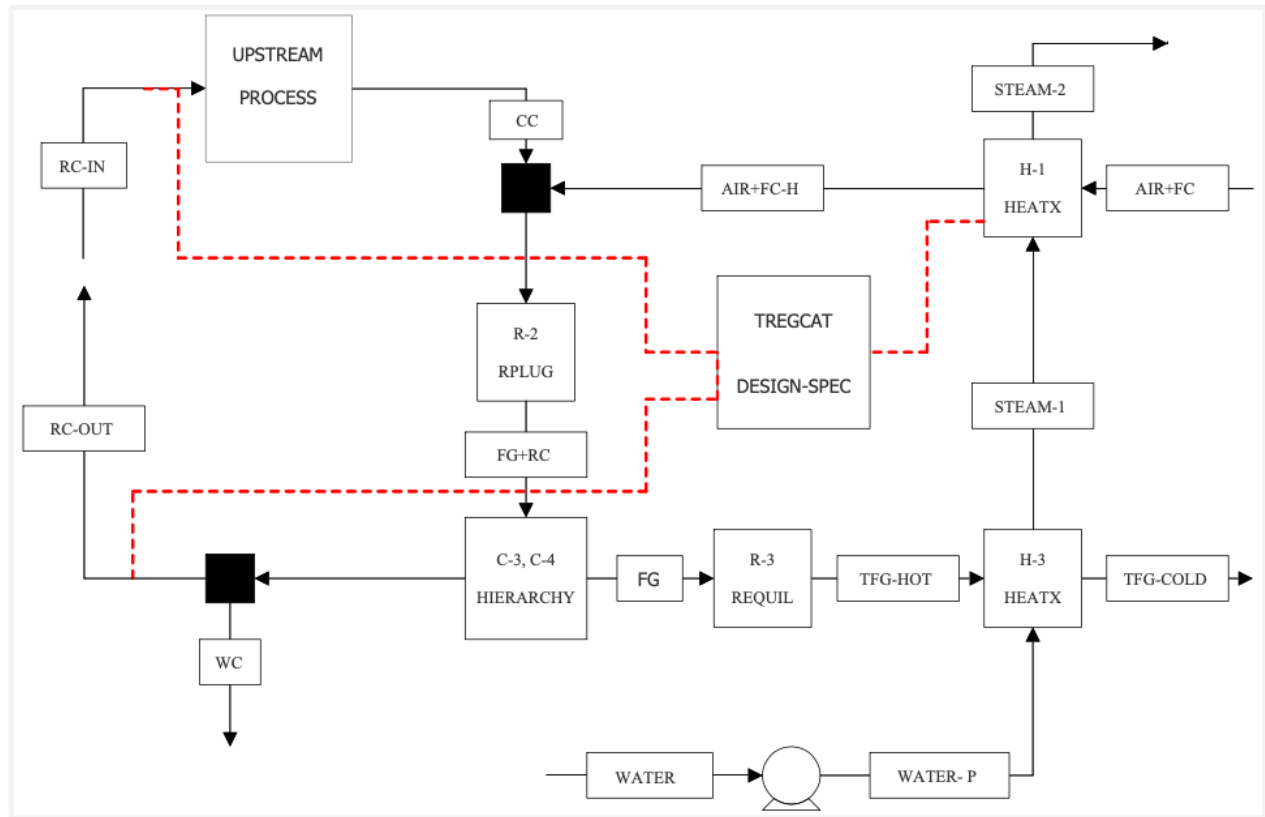


Figure 13. Design specification block used to match the temperatures of the RC-IN and RC-OUT stream. Varied the cold outlet stream temperature of H-1.

Variable Definitions:

- TRCIN = temperature (°C) of regenerated catalyst in the RC-IN stream
- TRCOUT = temperature (°C) of regenerated catalyst in the RC-OUT stream

Design Specification Expressions:

- Spec = TRCOUT
- Target = TRCIN
- Tolerance = 0.1

The cold outlet stream temperature variable of the H-1 (HEATX) block was allowed to vary between 100 and 200 °C. Results show that an AIR+FC-H temperature of 165 °C is required to ensure that RC-OUT is equal to RC-IN (both streams are at 660 °C and are identical). In real-life, streams RC-IN and RC-OUT are combined into a single recirculating catalyst stream.

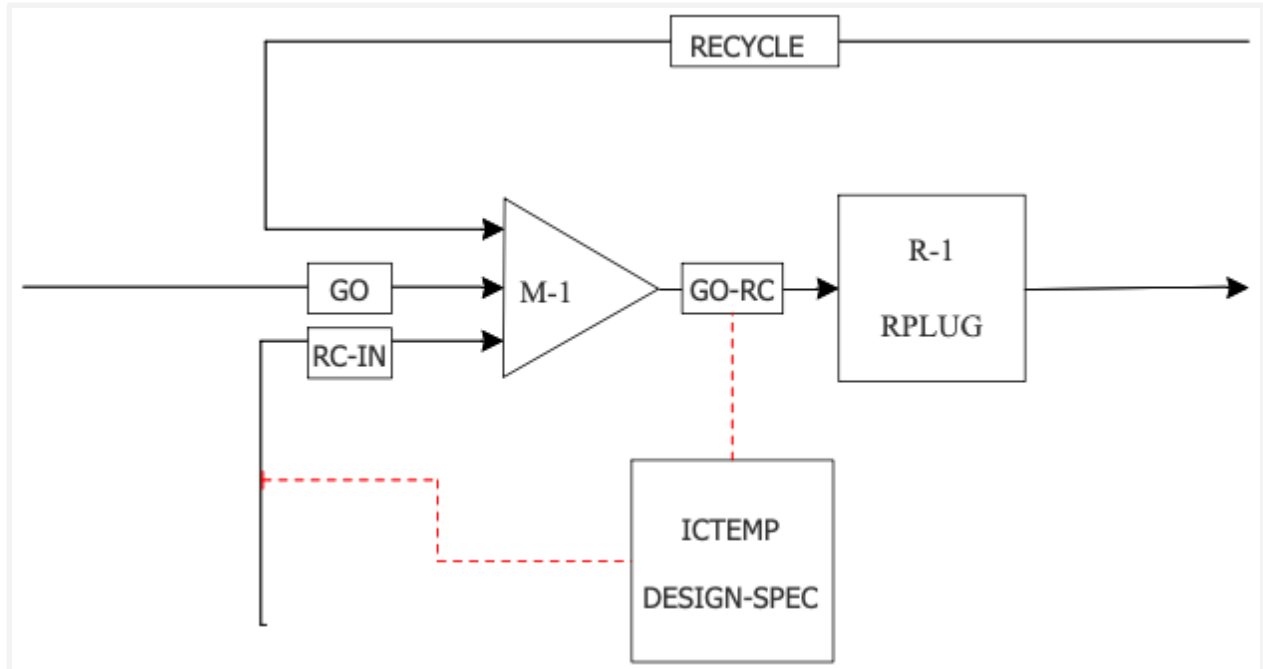


Figure 14. Design specification block used to obtain a target outlet stream temperature by varying the regenerated catalyst temperature

Variable Definitions:

- TRCGOIN = temperature (°C) of the gas oil - regenerated catalyst mixture in the GO-RC stream (i.e., riser inlet stream)

Design Specification Expressions:

- Spec = TRCGOIN
- Target = 565
- Tolerance = 0.1

Vary:

- Temperature (°C) of the regenerated catalyst in the RC-IN stream

The temperature was allowed to vary between 430 and 815 °C. Based on our survey of the literature, the ideal cracking temperature range is between 496 °C and 565 °C. The research group we referred to for kinetic parameters also achieved gas oil-catalyst mixture temperatures that near 560 °C.

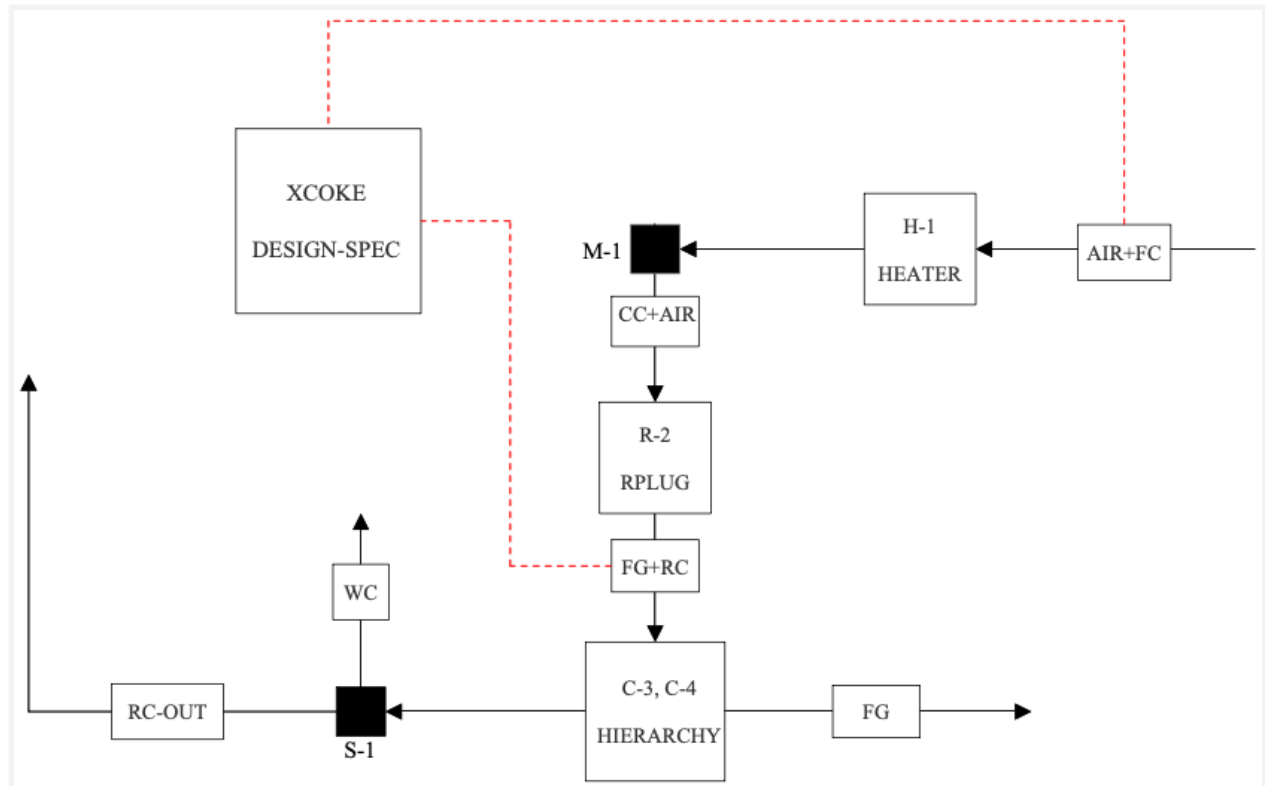


Figure 15. Maximize the fractional conversion of coke (solid carbon) by varying the mass flow rate of atmospheric air

Variable Definitions:

- NCOKEIN = molar flow rate (kmol/hr) of carbon in the CC+AIR stream
- NCOKEOUT = molar flow rate (kmol/hr) of carbon in the FG+RC stream

Fortran Statements:

$$XCOKE = (NCOKEIN - NCOKEOUT) / NCOKEOUT$$

Design Specification Expressions:

- Spec = XCOKE
- Target = 1.0
- Tolerance = 0.1

Vary:

- Mass flow rate (kg/s) of air in the AIR+FC stream

The mass flow rate of air was allowed to vary between 1 and 300 kg/sec. In order to achieve a fractional conversion of 1.0, of carbon, an air flow rate of 20 kg/s is required. All the carbon converts.

Table 17. Gas oil catalytic cracking reactions, kinetic, and activity parameters

Reaction No.	Reaction (Explicit Form)	Pre-exponential Factor (1/s)	Activation Energy (kJ/kmol)	Activity Parameter
1	$C_{28}H_{58} \rightarrow C_{14}H_{30} + C_{14}H_{28}$	7957.29	53927.70	1
2	$C_{28}H_{58} \rightarrow C_8H_{18} + 2.5C_8H_{16}$	14,433.40	57186.60	0.3
3	$C_{28}H_{58} \rightarrow C_4H_{10} + 6C_4H_8$	2337.1	51308.60	1
4	$C_{28}H_{58} \rightarrow C_2H_6 + 13C_2H_4$	449.917	48620.40	1
5	$C_{28}H_{56} \rightarrow 28C + 28H_2$	40.253	61159.40	1
6	$C_{14}H_{30} \rightarrow C_8H_{18} + 0.75C_8H_{16}$	197.933	48114.50	0.15
7	$C_{14}H_{30} \rightarrow C_4H_{10} + 2.5C_4H_8$	3.506	67792.90	0.15
8	$C_{14}H_{30} \rightarrow C_2H_6 + 6C_2H_4$	3.395	64266.60	0.25
9	$C_8H_{18} \rightarrow C_4H_{10} + C_4H_8$	2.189	56194.40	1
10	$C_8H_{18} \rightarrow C_2H_6 + 3C_2H_4$	1.658	63319.10	1
11	$C_4H_{10} \rightarrow C_2H_6 + C_2H_4$	3.411	55513.00	0.6
12	$C_{14}H_{28} \rightarrow 14C + 14H_2$	75.282	61159.40	0.15
13	$C_8H_{16} \rightarrow 8C + 8H_2$	2.031	61785.10	1
14	$C_4H_8 \rightarrow 4C + 4H_2$	0.601	52548.20	25
15	$C_2H_4 \rightarrow 2C + 2H_2$	2.196	53046.00	12

$$\text{ROI (\%)} = \frac{\text{R}-\text{M}-\text{C}-\text{O}}{\text{M}+\text{C}+\text{O}} \times 100 \quad (\text{Eq. 1})$$

R = Total revenue (daily)

M = Total cost of materials (daily)

C = Capital cost (daily)

O = Operation and Maintenance Costs (daily)

$$\text{CRF} = \frac{d \times (1+d)^n}{(1+d)^n - 1} \quad (\text{Eq. 2})$$

Table 18. Overall mass balance calculations

Overall Mass Balance		
Mass Flow In	kg/hr	kg/sec
GO	132480.00	37
AIR+FC	87321.71	24
AIR-2	28599.87	8
WATER	18000.00	5
Total	266402	74
Mass Flow Out	kg/hr	kg/sec
TFG-COLD	121707.14	34
STEAM-O	18000.00	5
WC	3600.00	1
Gas Oil	6320	2
Light Cycle Oil	23826	7
Gasoline	64242	18
Liquified Petroleum Gas	20917	6
Dry Gas	7795	2
Total	266408	74

Table 18. Overall energy balance calculations

Overall Energy Balance		
Enthalpy In	Gcal/hr	MW
GO	-24.65	-29
AIR+FC	-13.73	-16
AIR-2	-0.002	0
WATER	-68.67	-80
Total	-107.06	-124
Enthalpy Out		
TFG-COLD	-46.16	-54
STEAM-O	-57.11	-66
WC	-13.19	-15
Petroleum Products	-28.95	-34
Total	-145.41	-169
Heat Addition Rate		
Reboiler (T-2)	0.978	1
Heat Removal Rate		
Condenser (T-1)	-37.201	-43
Condenser (T-2)	-5.249	-6
Work Input Rate		
Pump (P-1)	0.00087	0
Compressor (C-1)	4.06	5
RHS	-102	-119
LHS	-103	-120
Ein - Eout	0.948	1.102

Table 20. Operation and maintenance cost calculations

Direct Cost	Percent of Delivered Equipment Cost	Plant Cost
<i>Purchased Equipment Delivered</i>	1	16,530,210.65
<i>Purchased Equipment Installation</i>	0.47	7,769,199.006
<i>Instrumentation and Controls</i>	0.36	5,950,875.834
<i>Piping (Installed)</i>	0.68	11,240,543.24
<i>Electrical Systems (Installed)</i>	0.11	1,818,323.172
<i>Buildings</i>	0.18	2,975,437.917
<i>Yard Improvement</i>	0.1	1,653,021.065
<i>Service Facilities (Installed)</i>	0.7	11,571,147.46
Total Direct Cost	3.6	59,508,758.34
Indirect Costs		
<i>Engineering and Supervision</i>	0.33	5,454,969.515
<i>Construction Expenses</i>	0.41	6,777,386.367
<i>Legal Expenses</i>	0.04	661,208.426
<i>Contractor's Fee</i>	0.22	3,636,646.343
<i>Contingency</i>	0.44	7,273,292.686
Total Indirect Plant Cost	1.44	23,803,503.34
Fixed Capital Investment	5.04	83,312,261.68
<i>Working Capital</i>	0.89	14,711,887.48
Total Capital Investment	5.93	98,024,149.15

Table 21. Direct cost, indirect cost, fixed and capital investment calculations

Operations & Maintenance	Cost (USD)
Materials	804,172,164.65
Labor	600,000
Direct Supervisory	120,000
Utilities	30,188,347
Maintenance and Repairs	8,331,226.17
Operating Supplies	1,666,245.23
Laboratory Charges	120,000
Depreciation	3,267,471.64
Local Taxes	3,332,490.47
Insurance	833,122.62
Rent	297,543.79
Plant Overhead	6,335,858.32
Administrative Cost	1,810,245.23
Research and Development	150,593.64
Cost (Excluding Materials)	57,053,144.11
Cost (Including Materials)	861,225,308.76

