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CHE 625

Final

May 3rd, 2023

Upscaling of Ammonia Decomposition to Hydrogen

CHE 625 Final (Spring 2023)

You are asked to design a packed bed reactor that utilizes ammonia to produce 75 mol/h of hydrogen, which is sufficient to produce over 5 kW of power and is suitable for powering a 3-bedroom house. The reaction kinetics as well as reactor operating conditions are available in the following reference: Alagharu, V., Palanki. S., and West, K.N., "Analysis of ammonia decomposition reactor to generate hydrogen for fuel cell applications," *Journal of Power Sources*, 195, 829–833, 2010 (see "Journal Articles" section in eCampus to download this paper).

In the above paper, the reactor is designed for a much lower flowrate of hydrogen (only 0.75 mol/h of hydrogen) since the power application under consideration was only 100 W. Your task is the following:

1. Utilize the kinetics and reactor conditions given in the above reference and develop a simulation in ASPENPlus to simulate a reactor that produces 75 mol/h of hydrogen. Choose an appropriate inlet flow rate of ammonia, reactor diameter and length.
2. The paper assumed that the reaction happened in the kinetic regime and there were no mass transfer limitations (i.e. effectiveness factor = 1). What happens if the effectiveness factor is 0.5? Show calculations of how the hydrogen flowrate is affected.

<u>*Instructions*</u>

- *This is an individual assignment and is due on Wednesday, May 3 at 9:00 a.m. on eCampus. You are not allowed to collaborate with anybody and must turn in your own work.*
- *Since the problem is open-ended, there are multiple solutions. I am expecting each student solution to be different in terms of parameters chosen.*
- *The report should have sufficient details of your calculations (both by hand as well as in ASPENPlus) for me to be able to reproduce the results.*

Question 1

The parameters given in *Alagharu et. al* (referred to as the source going forward) were used to create an initial model for the reaction in ASPEN. Some differences were noticed between the paper's results and the results obtained in ASPEN, most likely due to the fact that the source assumed ideal gas conditions and the modeling in ASPEN used the Peng-Robinson Equation of State; however, the trends followed the same patterns. The modeling parameters have been re-written and are available in Appendix A. In ASPEN, a Packed Bed Reactor was created, modeling with the single reaction given (decomposition of ammonia to hydrogen and nitrogen or $NH_3 \rightarrow 1.5H_2 + 0.5N_2$). A constant heat was added to the reactor (70 kW/m^3 or 0.875 kW/m^2 given the geometry of the reactor), and the Ergun Equation was used for calculating pressure drop. The inlet was considered to be pure ammonia.

For the upscaling of the process, context was first expanded upon for the use case. Since this set up was made to produce hydrogen on demand to power a 3-bedroom house, it was assumed that this sort of installation would need to be available on the property itself. The set up imagined consists of an ammonia storage tank, similar to large propane tanks currently used to heat remote homes without a natural gas connection. The ammonia would then be fed into a building that contains both the reactor to produce the hydrogen and the fuel cell to produce electricity. This auxiliary dwelling was taken to be the size of a conservatively small shed of 7ft-by-7ft, half of the shed being used for the reactor and the other half for the fuel cell. For proper maintenance and clearance, a foot of space was given on each side of the reactor. An additional foot is added onto each side as well to allow for piping arrangement to auxiliary equipment (such as a heater or compressor to get the gas up to operating conditions), giving a maximum length for the reactor of three feet.

The diameter of the reactor given in the source was roughly two inches. The primary concern of the original arrangement was the need for heat to be added to the reactor via electric heat generation due to the endothermic decomposition reaction. With the high operating temperature (roughly 520°C inlet) and the 70 kW/m^3 heat flux requirement (roughly 46 W/ft given the geometry which was converted to give more of an apples-to-apples comparison to products on the market), I was unable to find anything that met this heat duty demand, but it is assumed that there is a product on the market that can at least achieve the base case scenario mentioned in the source. Since increasing the diameter would increase the volume and therefore increase the amount of heat duty per foot (assuming the same heat duty per volume is needed), it was chosen to go no larger than the two-inch diameter to make sure the reactor's heat duty need could be met since products for this sort of setup could not be found during research. The two-inch diameter itself was chosen over smaller sizes to maximize the volume of the reactor. To scale to the needed outlet flowrate, multiple tubes are used in a bundle. This gives the added benefit of having redundant reactor tubes in an economic fashion to ensure reliability, gives the option for variable flowrates to meet variable electric demands by actuating reactor tubes on and off, being able to perform modular maintenance, and increases the surface area of the reactor per volume to help meet heat flux demand.

With these assumptions in mind, inlet flow rate and reactor length were the primary variables to consider when designing a single reactor tube of the bank. A search was performed with limiting criteria being the pressure drop needed to stay at or below the paper's 8% of inlet pressure, the outlet needs to have over 99.5% conversion of ammonia to avoid performance loss in the fuel cell (it is noted that there are sorbents in the paper that would allow for less conversion; however, with the limited space in the setup, we can hopefully avoid additional equipment), and the number of tubes cannot be over 10 to allow for proper spacing and access for maintenance (assuming a minimum of two inches of insulation around the reactor to prevent excessive heat loss and for safety concerns).

Upon completion of the search, the following setup provided a reasonable set of results:

Table 1: Initial Scenario from Parameter Sweep for Single Reactor Tube

Parameter	**Value**
Length of Reactor	2.1 ft
Diameter of Reactor	1.97 inches (0.05 m)
Inlet Flow Rate of Ammonia	6.48 mol/hr
Conversion	99.6%
Inlet Pressure	2.00 bar
Outlet Pressure	1.84 bar
Outlet Flowrate of Hydrogen	9.646 mol/hr
Number of Reactors in Bank Required	7.77 tubes (8 tubes rounded up)
Inlet Temperature	793.15 K

The results met all the criteria set forth. However, there was a slight difference from a realistic setup (using a whole number of tubes) as shown in the partial number of tubes. Therefore, a slight modification was made to achieve results closer to 8 tubes exactly in a more economical way. The inlet flowrate was slightly reduced to not waste reactant and the concern of high temperatures in residential areas led to a decrease in inlet temperature. The final results are shown in Table 2.

Table 2: Final Scenario for Single Reactor Tube

Parameter	**Value**
Length of Reactor	2.1 ft
Diameter of Reactor	1.97 inches (0.05 m)
Inlet Flow Rate of Ammonia	6.3 mol/hr
Conversion	99.8%
Inlet Pressure	2.00 bar
Outlet Pressure	1.85 bar
Outlet Flowrate of Hydrogen	9.418 mol/hr
Number of Reactors in Bank Required	7.96 tubes (8 tubes rounded up)
Inlet Temperature	780 K

The final results for a single reactor tube were modeled in ASPEN and the results can be seen in the figures in Appendix B.

Question 2

Since the effectiveness factor is defined as the actual overall rate of reaction divided by the ideal rate of reaction, the rate of ammonia decomposition can be shown by the following equations from the source:

$$\eta = \frac{\text{Actual Reaction Rate}}{\text{Ideal Rate}}$$

$$r_{NH_3} = \eta k_o \exp\left(\frac{-E}{RT}\right) P_{NH_3}$$

Figure 1: Rate of Ammonia Decomposition with Constant Effectiveness Factor

While initially, it looks like the reaction rate will be cut in half if the effectiveness factor is equal to 0.5, this does not happen due to the endothermic nature of the reaction. While initially the rate of reaction is reduced, less decomposition happening keeps the temperature and partial pressure of ammonia elevated, giving a balancing force to the reaction rate. This means while the rate of hydrogen formation will be smaller at the beginning of the reactor, compared to the case in question 1, later on down the reactor bed, the reaction rate will be higher compared to the initial case in question 1 for the same length down the reactor. This balnace can be shown in the figure below.

$$r_{NH_3} = \underbrace{\eta}_{\text{Decreases due to } \eta} k_o \underbrace{\exp\left(\frac{-E}{RT}\right) P_{NH_3}}_{\text{Increases due to } \eta \text{ (Higher T and } P_{NH_3})}$$

where

$$\frac{dF_{H_2}}{dV} = 1.5\, r_{NH_3}$$

Figure 2: Explaination of Balancing Force for Hydrogen Production

Further expanding on the temperature, because the heat supplied to the reactor is not changing when the effectiveness factor is reduced, the initial decline in temperature will not be as severe with less reaction happening. This means the temperature throughout the reactor will be higher when the effectiveness factor is 0.5, increasing the reaction rate.

$$\frac{dT}{dV} = \frac{\overset{\text{constant}}{Q} + \overbrace{C_{NH_3}\Delta H}^{\text{smaller negative number}}}{\sum F_i C_{pi}}$$

Figure 3: Differential Energy Balance for Temperature Increase Explaination

While the temperature change does effect the viscosity of the fluid, overall, the change in pressure drop is minimal and does not play a major role in this analysis.

This can be implemented in ASPEN by multiplying k_0 by the effectiveness factor. When modeling in this way, the overall results of the reactor presented in question 1 are similar; however the profiles are different. There is a small change in overall conversion and outlet temperature, but largely the outlets are very similar. The profiles can be seen in Appendix C while the overall resutls comparing the cases can be seen in Table 3.

Table 3: Results Comparison Between Effectiveness Factors

Variable	**Effectiveness Factor = 1**	**Effectiveness Factor = 0.5**
Conversion	99.8%	99.6%
Outlet Pressure	1.85 bar	1.85 bar
Outlet Temperature	456 °C	462°C

Appendix A: Table of Parameters from Alagharu et. al

Parameter	**Value**
k_0 (Frequency Factor)	$1.33x10^{11}$ mol/ m^3 s Pa
E (Activation Energy)	$1.9x10^5$ J/mol
D_p (Catalyst Particle Diameter)	0.00035 m
ρ (Catalyst Density)	2000 kg/m^3
φ (Void Fraction)	0.3
L (Initial Reactor Length)	0.31 m
D_i (Initial Reactor Diameter)	0.05 m
F_{NH3} (Initial Inlet Flow Rate of Ammonia)	0.0009 mol/s
P (Inlet Pressure)	2.0 bar
T (Inlet Temperature)	793 K
Q (Volumetric Heat Added)	70 kW/m^3

Appendix B: Single Reactor Tube Results for Question 1

Main Flowsheet | Results Summary - Streams (All)

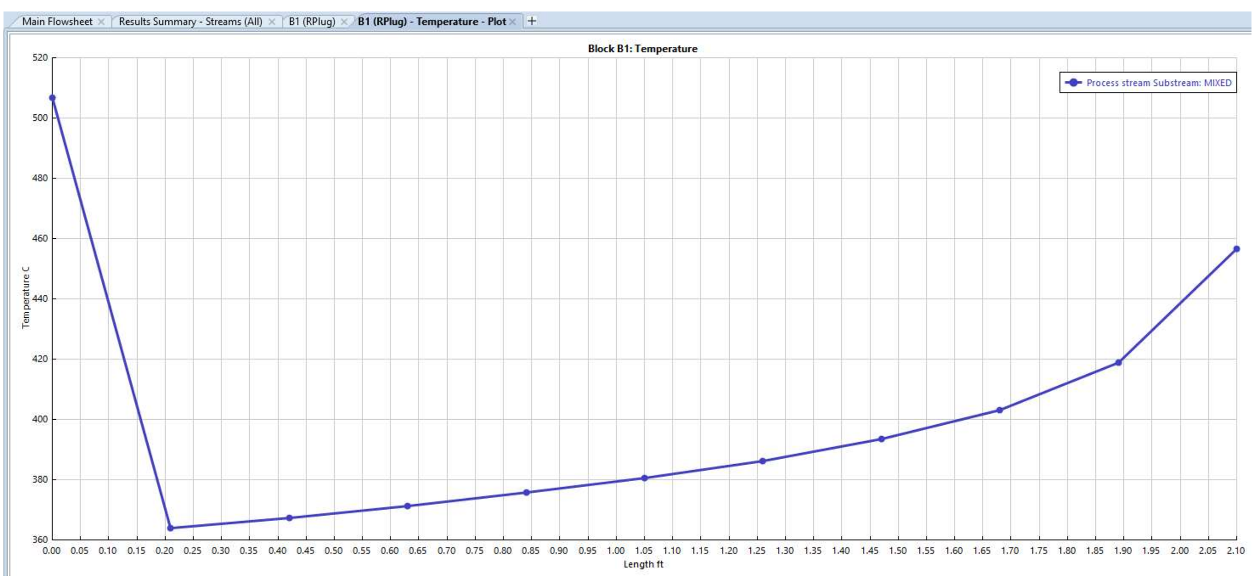
Material | Heat | Load | Work | Vol.% Curves | Wt. % Curves | Petroleum | Polymers | Solids

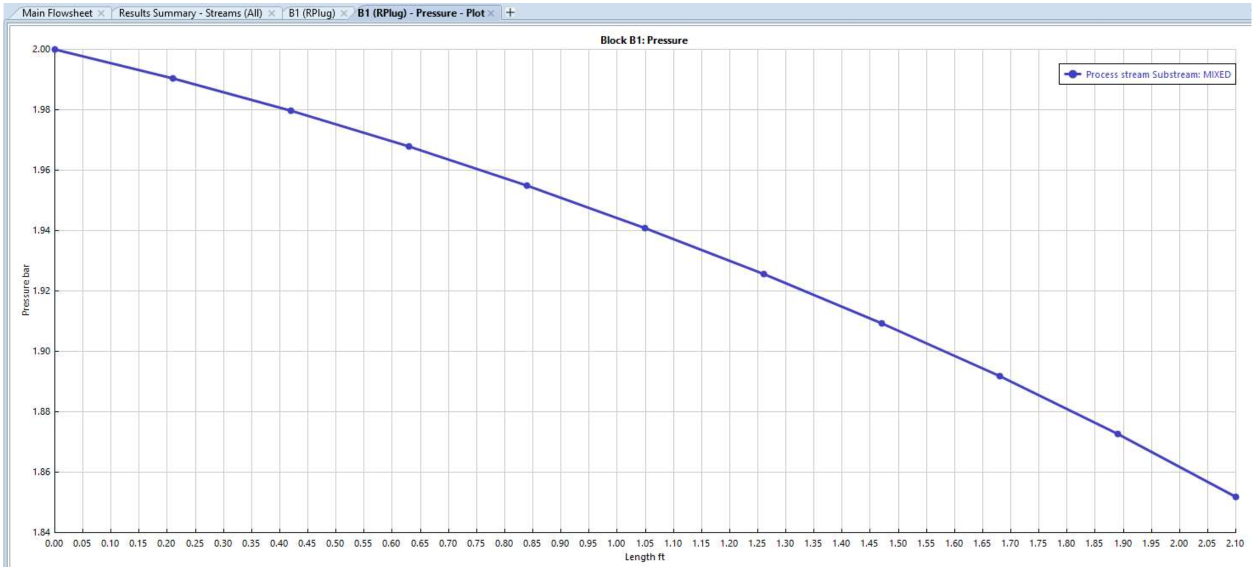
	Units	INLET	OUTLET	
− MIXED Substream				
Phase		Vapor Phase	Vapor Phase	
Temperature	C	506.85	456.581	
Pressure	bar	2	1.85191	
Molar Vapor Fraction		1	1	
Molar Liquid Fraction		0	0	
Molar Solid Fraction		0	0	
Mass Vapor Fraction		1	1	
Mass Liquid Fraction		0	0	
Mass Solid Fraction		0	0	
Molar Enthalpy	cal/mol	-5990.18	3013.58	
Mass Enthalpy	cal/gm	-351.731	353.307	
Molar Entropy	cal/mol-K	-15.3295	6.17587	
Mass Entropy	cal/gm-K	-0.900117	0.72405	
Molar Density	mol/cc	3.08514e-05	3.0508e-05	
Mass Density	gm/cc	0.000525417	0.000260222	
Enthalpy Flow	cal/sec	-10.4828	10.5298	
Average MW		17.0306	8.52962	
− Mole Flows	**mol/hr**	**6.3**	**12.5788**	
NITROGEN	mol/hr	0	3.13941	
H2	mol/hr	0	9.41822	
NH3	mol/hr	6.3	0.021186	
+ Mole Fractions				

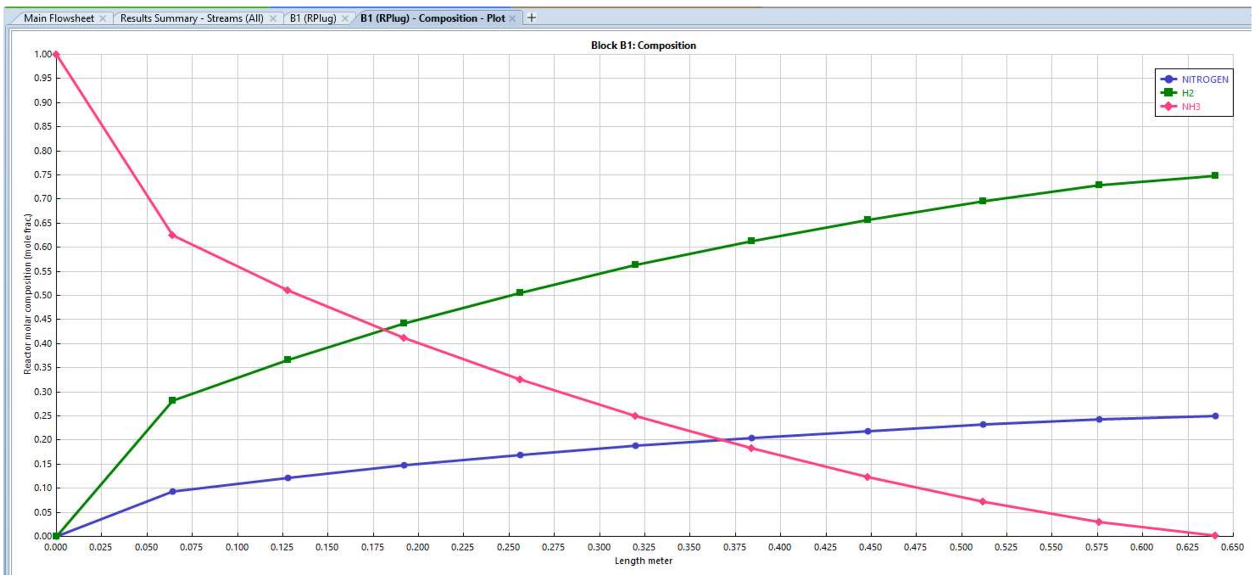
Main Flowsheet | Results Summary - Streams (All)

Material | Heat | Load | Work | Vol.% Curves | Wt. % Curves | Petroleum | Polymers | Solids

	Units	INLET	OUTLET
Molar Solid Fraction		0	0
Mass Vapor Fraction		1	1
Mass Liquid Fraction		0	0
Mass Solid Fraction		0	0
Molar Enthalpy	cal/mol	-5990.18	3013.58
Mass Enthalpy	cal/gm	-351.731	353.307
Molar Entropy	cal/mol-K	-15.3295	6.17587
Mass Entropy	cal/gm-K	-0.900117	0.72405
Molar Density	mol/cc	3.08514e-05	3.0508e-05
Mass Density	gm/cc	0.000525417	0.000260222
Enthalpy Flow	cal/sec	-10.4828	10.5298
Average MW		17.0306	8.52962
− Mole Flows	**mol/hr**	**6.3**	**12.5788**
NITROGEN	mol/hr	0	3.13941
H2	mol/hr	0	9.41822
NH3	mol/hr	6.3	0.021186
− Mole Fractions			
NITROGEN		0	0.249579
H2		0	0.748737
NH3		1	0.00168426
+ Mass Flows	**kg/hr**	**0.107293**	**0.107293**




Main Flowsheet
Results Summary - Streams (All)
B1 (RPlug)
B1 (RPlug) - Pressure - Plot
Block B1: Pressure
Process stream Substream: MIXED
Pressure bar
Length ft

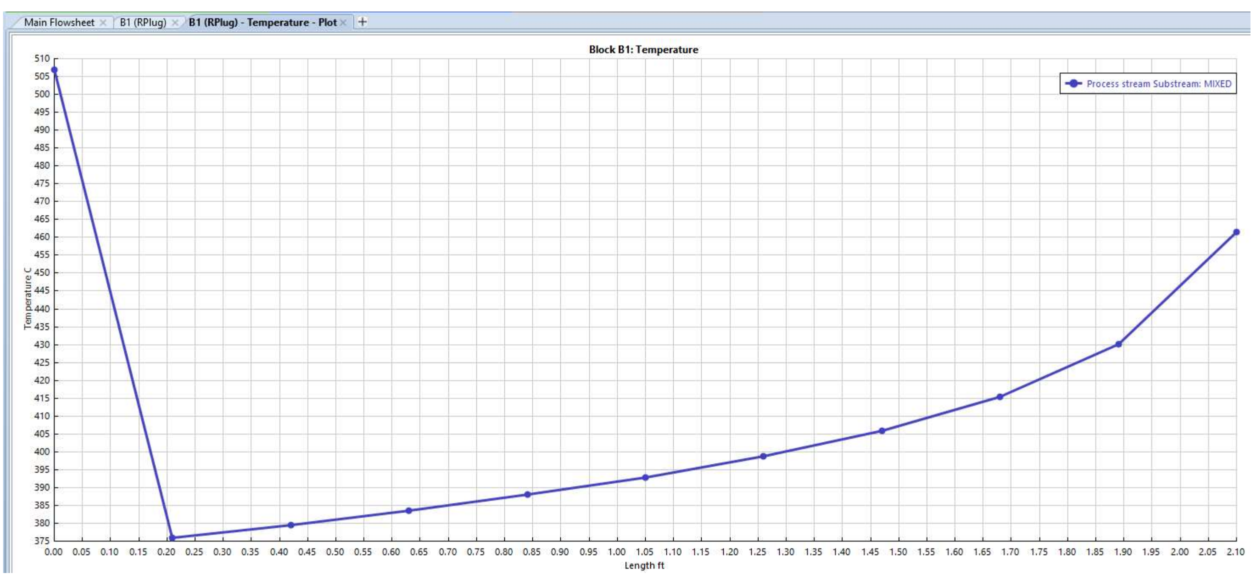

Main Flowsheet
Results Summary - Streams (All)
B1 (RPlug)
B1 (RPlug) - Composition - Plot
Block B1: Composition
NITROGEN
H2
NH3
Reactor molar composition (mole frac)
Length meter

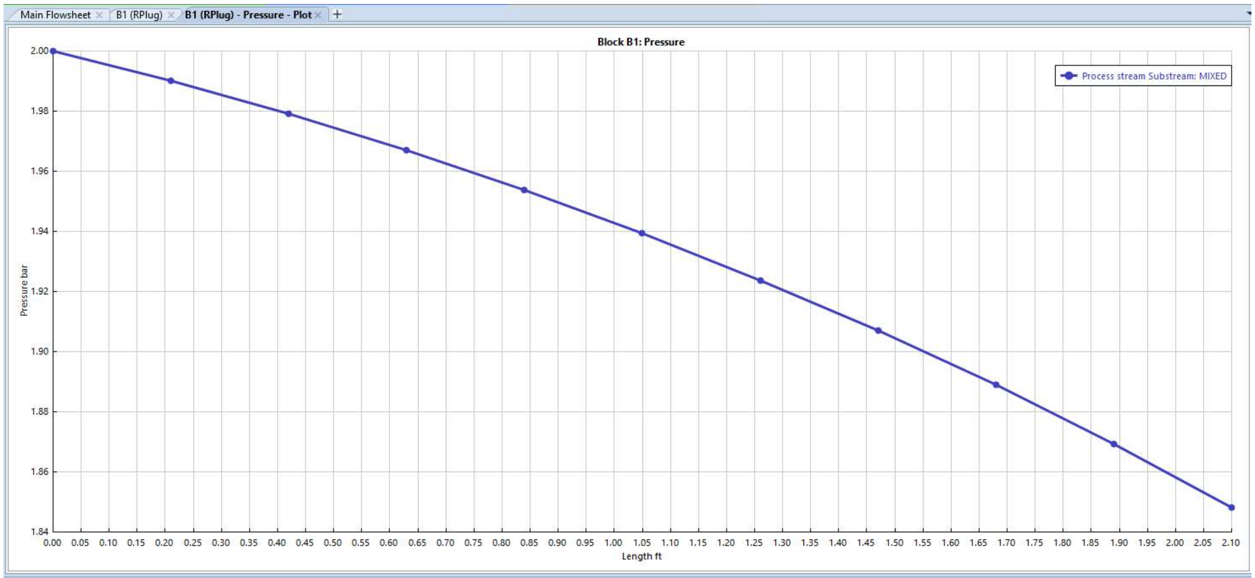
Appendix C: Single Reactor Tube Results for Question 2

Material	Units	INLET	OUTLET	
− MIXED Substream				
Phase		Vapor Phase	Vapor Phase	
Temperature	C	506.85	461.561	
Pressure	bar	2	1.84819	
Molar Vapor Fraction		1	1	
Molar Liquid Fraction		0	0	
Molar Solid Fraction		0	0	
Mass Vapor Fraction		1	1	
Mass Liquid Fraction		0	0	
Mass Solid Fraction		0	0	
Molar Enthalpy	cal/mol	-5990.18	3022.06	
Mass Enthalpy	cal/gm	-351.731	353.307	
Molar Entropy	cal/mol-K	-15.3295	6.19854	
Mass Entropy	cal/gm-K	-0.900117	0.724669	
Molar Density	mol/cc	3.08514e-05	3.02405e-05	
Mass Density	gm/cc	0.000525417	0.000258666	
Enthalpy Flow	cal/sec	-10.4828	10.5298	
Average MW		17.0306	8.55362	
− Mole Flows	**kmol/hr**	**0.0063**	**0.0125435**	
NITROGEN	kmol/hr	0	0.00312176	
H2	kmol/hr	0	0.00936528	
NH3	kmol/hr	0.0063	5.64832e-05	

Material | Heat | Load | Vol.% Curves | Wt. % Curves | Petroleum | Polymers | Solids

	Units	INLET	OUTLET	
Molar Liquid Fraction		0	0	
Molar Solid Fraction		0	0	
Mass Vapor Fraction		1	1	
Mass Liquid Fraction		0	0	
Mass Solid Fraction		0	0	
Molar Enthalpy	cal/mol	-5990.18	3022.06	
Mass Enthalpy	cal/gm	-351.731	353.307	
Molar Entropy	cal/mol-K	-15.3295	6.19854	
Mass Entropy	cal/gm-K	-0.900117	0.724669	
Molar Density	mol/cc	3.08514e-05	3.02405e-05	
Mass Density	gm/cc	0.000525417	0.000258666	
Enthalpy Flow	cal/sec	-10.4828	10.5298	
Average MW		17.0306	8.55362	
− Mole Flows	**kmol/hr**	**0.0063**	**0.0125435**	
NITROGEN	kmol/hr	0	0.00312176	
H2	kmol/hr	0	0.00936528	
NH3	kmol/hr	0.0063	5.64832e-05	
− Mole Fractions				
NITROGEN		0	0.248874	
H2		0	0.746623	
NH3		1	0.00450298	
+ Mass Flows	**kg/hr**	**0.107293**	**0.107293**	
+ Mass Fractions				

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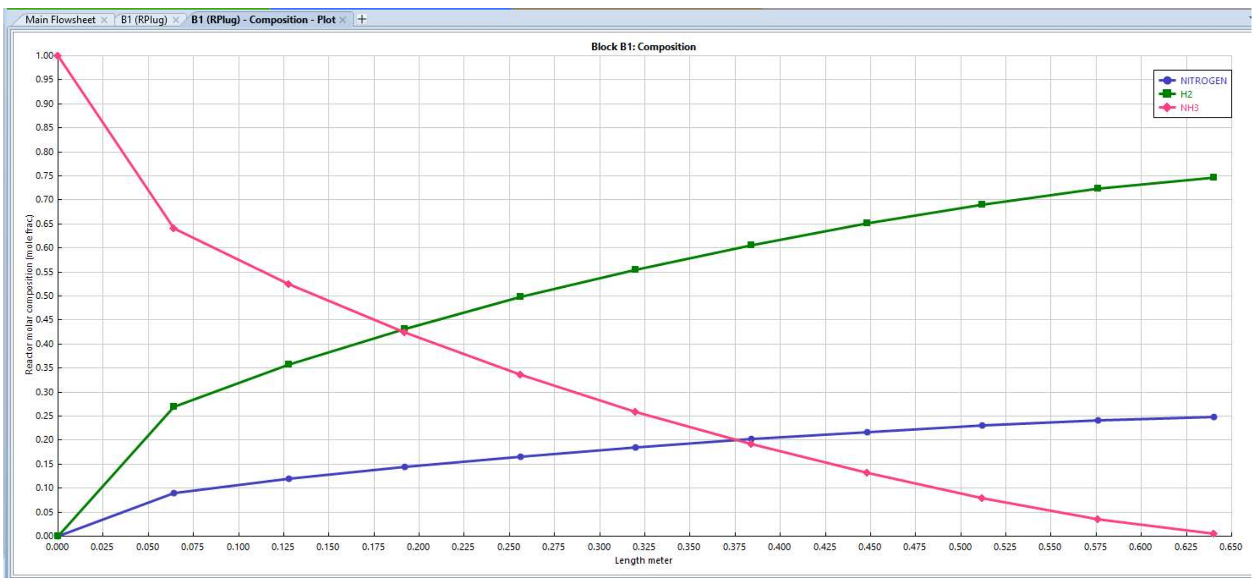
B1 (RPlug)
B1 (RPlug) - Pressure - Plot
Block B1: Pressure
Process stream Substream: MIXED
Pressure bar
Length ft


Main Flowsheet
B1 (RPlug)
B1 (RPlug) - Composition - Plot
Block B1: Composition
NITROGEN
H2
NH3
Reactor molar composition (mole frac)
Length meter