2. Chemical Processes and Process Description

In the process, methanol at a rate of 100,000 ton/y and a purity of > 99.9 mol % is to be produced by the steam reforming of natural gas followed by the reaction of carbon monoxide

and dioxide with hydrogen to produce methanol. T

Referring to Figure 1, natural gas at 25°C and 2.5 bar (Stream 1) is compressed in compressor C-401 to 30 bar. High pressure saturated steam at 41 bar (Stream 2) is throttled to 30 bar and mixed with the natural gas to form Stream 5. The ratio of steam to natural gas in Stream 5 is maintained at 3:1 (by mole), which is higher than the required stoichiometric ratio but is used to suppress the coking of the catalyst in the reforming reactor. This stream is heated in Exchanger E-401 to 850°C and fed to the steam reforming reactor, R-401. The steam reforming reactions are highly endothermic and require a significant energy transfer to the reactor to maintain the reaction. The processes for this heat transfer and the reactor configuration are explained later. The reactor effluent, Stream 7, is quenched in E-402 to a temperature of 130°C and sent to the high-pressure separator, V-401. Stream 9 leaving the bottom of V-401 is a liquid at 130°C and contains mostly water and a small amount of dissolved gases and is cooled to 40°C in E-410 prior to being sent to wastewater treatment. The gas stream leaving the top of V-401 (Stream 10) is reheated to 250°C in E-403 using high pressure steam and sent to the methanol reactor, R-402. The methanol reactions are exothermic, and heat must be removed from the reacting process stream, this heat transfer process is explained later. The reactor effluent stream, Stream 12, is cooled to a temperature of 100°C in E-404 using cooling water. Stream 13, leaving E-404, is fed to the methanol flash/separator, V-402. The vapor leaving V-402, Stream 15, contains a significant amount of hydrogen that can be combusted and used to provide heat for the process. The liquid leaving V-402 contains mostly methanol and water with small amounts of dissolved gases. This stream is throttled to 3.5 bar, Stream 14, prior to being fed to the methanol column, T-401. The bottom product, Stream 16, leaving T-401 contains virtually all the water fed to the column (water recovery > 0.999) and should contain no more than 1 mol% methanol. It is cooled in E-409 to 40°C prior to being sent to wastewater treatment. The top product, Stream 17, is liquid methanol with a purity > 99.9 mol% and a rate equivalent to 100,000 tons per year (10499.5 kg/h - using an operating basis of 360 day per year). A gas vent, Stream 18, leaves the top of the reflux drum, and contains most of the dissolved gases in the column feed along with some non-condensed methanol. This off-gas stream is sent to an incinerator/flare.

The configuration to provide heat to Reactor, R-1, is shown in Figure 2. In reality, the steam reforming reactor comprises catalyst filled tubes that are placed within a furnace. Natural gas and steam are fed through the tubes and a combustible gas and air are fed to the furnace (on the outside of the tubes). The combustion process provides the heat to drive the endothermic reactions that occur inside the tubes. For this project, the reforming reactor is simulated by the 3 pieces of equipment contained in the dotted box in Figure 2, i.e. B-401, E-401 and R-401. Combustion air, Stream 19, is pressurized to 1.51 bar in C-402 and preheated to 300°C in E-407 prior to being fed (Stream 20) to the burner B-401 along with the throttled hydrogen-rich gas in Stream 15. All the combustible species in Stream 15 are completely oxidized in the burner and the heat (Q_{in}) needed to drive the steam reforming reactions in R-401 is provided by the combustion process. The high temperature stream (flue gas) leaving B-401 (Stream 21) is then used to provide the heat needed to preheat the reactor feed, Stream 5, to 850°C in E-401. Additional energy from the flue gas is used to preheat the combustion air in E-407 and to make medium pressure steam in E-408.

In Figure 3, the configuration to remove heat from the methanol synthesis reactor, R-402, is shown. The heat to be removed, Q_{out}, is exchanged from the reactor to heat exchanger E-411 where boiler feed water is converted to medium pressure steam. In reality, the reactor and steam boiler are one process unit rather than the two units (R-402 and E-411) shown in the figure.

A stream table, showing flowrates, conditions, and compositions for Streams 1 -24 in Figures 1-3, is shown in Table 1.

C-401	**NG Feed Compressor**
E-401	**Reactor Feed Heater**
R-401	**NG Steam Reforming Reactor**
E-402	**Reformer Reactor Effluent Cooler**
V-401	**HP Flash**
E-403	**Methanol Reactor Feed Heater**
R-401	**Methanol Reactor**
E-404	**Methanol Reactor Effluent Cooler**
V-402	**Methanol Flash**
T-401	**Methanol Tower**
P-402a/b	**Methanol Reflux Pumps**
V-403	**Methanol Reflux Drum**
E-405	**Methanol Tower Reboiler**
E-406	**Methanol Tower Condenser**
E-409	**Methanol Wastewater Cooler**
E-410	**HP Flash Wastewater Cooler**

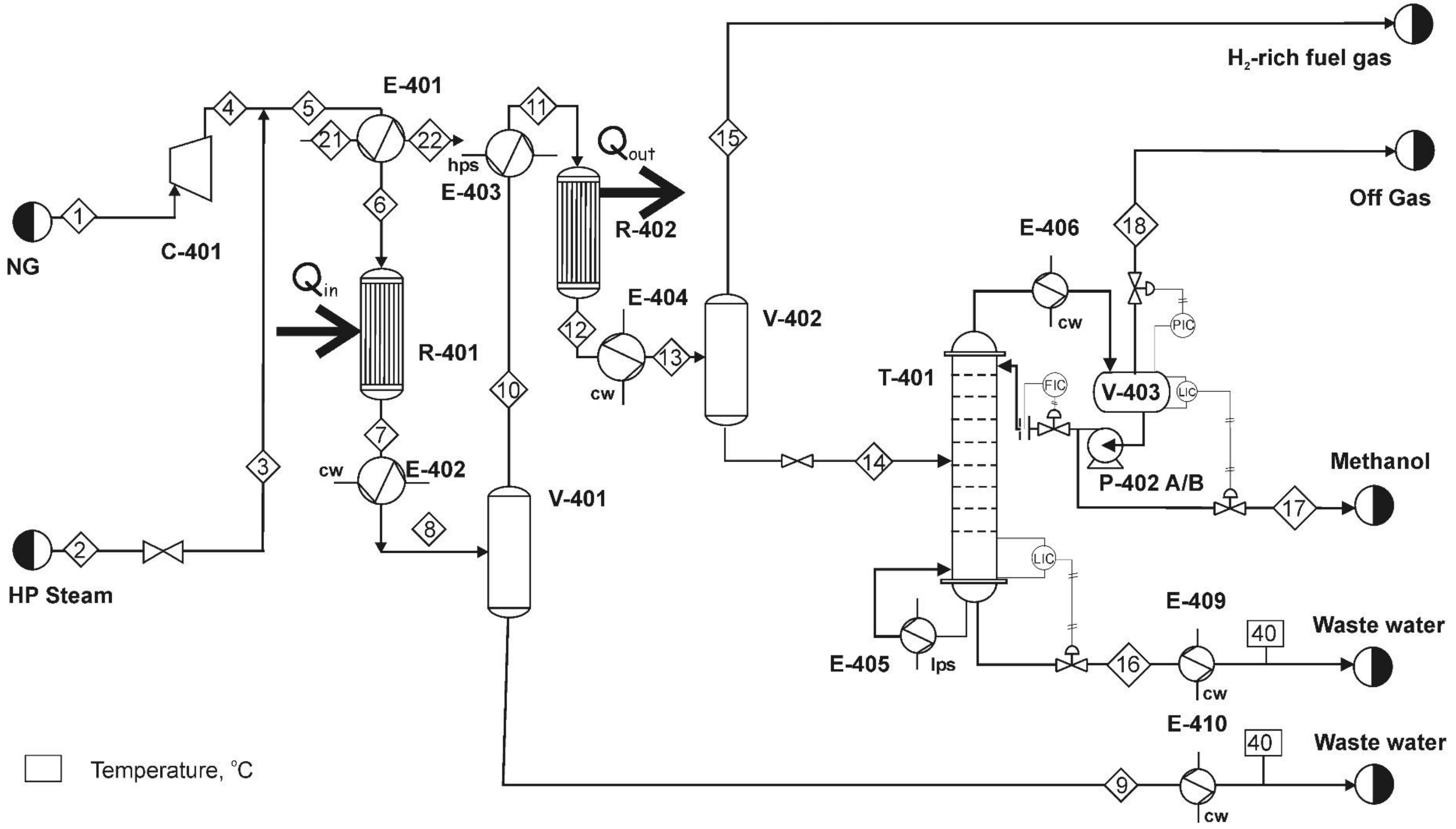

Figure 1: Preliminary PFD for Methanol Synthesis Process

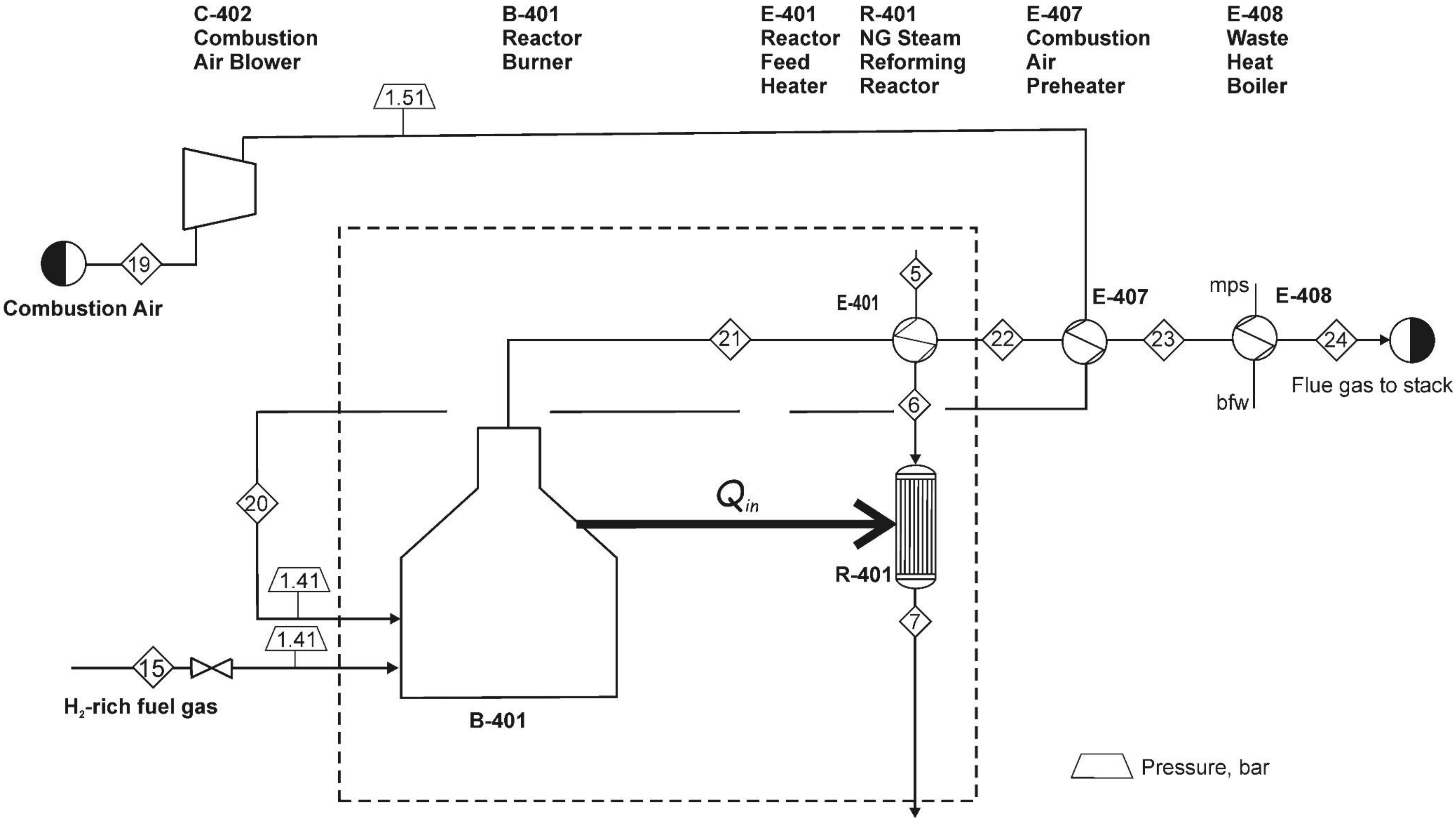

Figure 2: Preliminary PFD for Methanol Synthesis Process - Steam Reforming Reactor

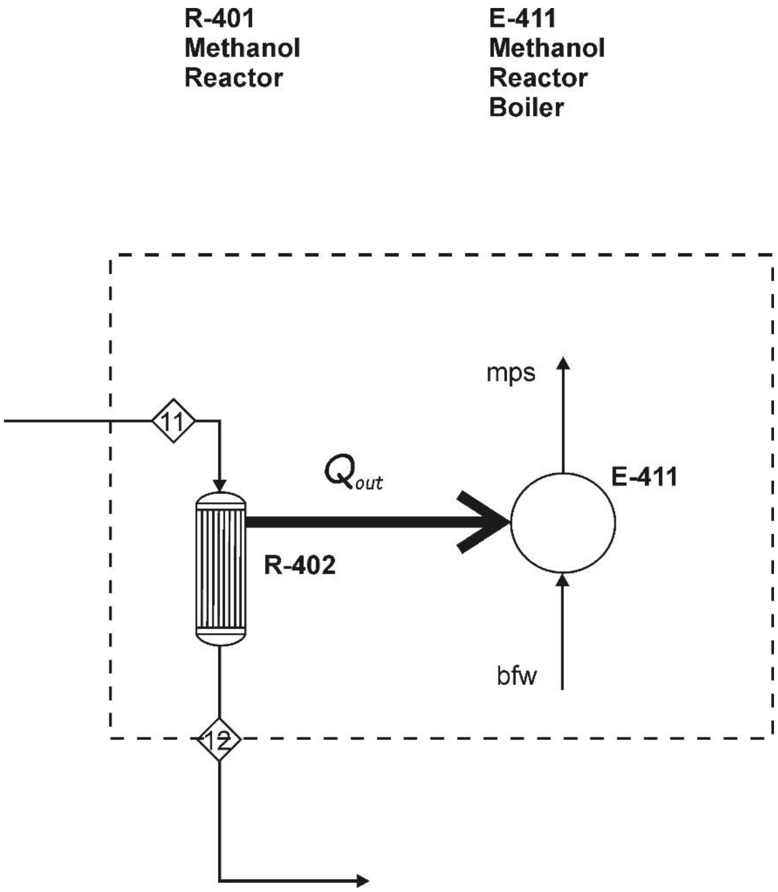

Figure 3: Preliminary PFD for Methanol Synthesis Process - Methanol Reactor

Table 1: Flows for design case corresponding to the PFD in Figure 3

Stream	1	2	3	4	5	6	7
Temp, °C	25	252	238	264	239	850	850
Pres, kPa	250	4100	3000	3000	3000	2950	2900
vf	1	1	1	1	1	1	1
Mass flow, kg/h	12979	39837	39837	12979	52816	52816	52816
Mole flow, kmol/h	776	2211	2211	776	2987	2987	4179
Comp mole fraction							
hydrogen	-	-	-	-	-	-	0.4743
nitrogen	0.0080	-	-	0.0080	0.0021	0.0021	0.0015
oxygen	-	-	-	-	-	-	-
CO	-	-	-	-	-	-	0.0883
CO_2	-	-	-	-	-	-	0.0543
methane	0.9500	-	-	0.9500	0.2468	0.2468	0.0494
ethane	0.0420	-	-	0.0420	0.0109	0.0109	-
methanol	-	-	-	-	-	-	-
water	-	1.0000	1.0000	-	0.7403	0.7403	0.3322

Stream	8	9	10	11	12	13	14
Temp, °C	130	130	130	250	261	100	77
Pres, kPa	2890	2890	2890	2880	2830	2820	350
vf	0.7397	0	1	1	1	0.6618	0.0626
Mass flow, kg/h	52816	19598	33218	33218	33218	33218	18168
Mole flow, kmol/h	4179	1088	3091	3091	2204	2204	745
Comp mole fraction							
hydrogen	0.4743	-	0.6412	0.6412	0.4318	0.4318	0.0006
nitrogen	0.0015	-	0.0020	0.0020	0.0028	0.0028	-
oxygen	.0000	-	-	-	-	-	-
CO	0.0883	-	0.1193	0.1193	0.0309	0.0309	-
CO_2	0.0543	-	0.0734	0.0734	0.0381	0.0381	0.0008
methane	0.0494	-	0.0668	0.0668	0.0937	0.0937	0.0002
ethane	-	-	-	-	-	-	-
methanol	-	-	-	-	0.2014	0.2014	0.4529
water	0.3322	0.9999	0.0973	0.0973	0.2014	0.2014	0.5455

Stream	15	16	17	18	19	20	21
Temp, °C	100	142	84	84	25	300	1432
Pres, kPa	2820	405	245	245	101.3	141	141
vf	1	0	0	1	1	1	1
Mass flow, kg/h	15050	7452	10500	216	219575	219575	234625
Mole flow, kmol/h	1458	410	328	7	7611	7611	8613
Comp mole fraction							
hydrogen	0.6521	-	-	0.0631	-	-	-
nitrogen	0.0043	-	-	0.0004	0.7900	0.7900	0.6988
oxygen	-	-	-	-	0.2100	0.2100	0.0600
CO	0.0467	-	-	0.0044	-	-	-
CO_2	0.0572	-	0.0006	0.0598	-	-	0.0539
methane	0.1414	-	-	0.0154	-	-	-
ethane	-	-	-	-	-	-	-
methanol	0.0729	0.0100	0.9990	0.8567	-	-	-
water	0.0255	0.9900	0.0004	0.0001	-	-	0.1873

Stream	22	23	24
Temp, °C	1175	1017	240
Pres, kPa	131	121	111
vf	1	1	1
Mass flow, kg/h	234625	234625	234625
Mole flow, kmol/h	8613	8613	8613
Comp mole fraction			
hydrogen	-	-	-
nitrogen	0.6988	0.6988	0.6988
oxygen	0.0600	0.0600	0.0600
CO	-	-	-
CO_2	0.0539	0.0539	0.0539
methane	-	-	-
ethane	-	-	-
methanol	-	-	-
water	0.1873	0.1873	0.1873

Perform a preliminary design of the steam reforming and methanol synthesis processes. You should simulate the process to give the same (or as close as possible) stream conditions (*T*, *P*, phase, and composition) as given in Table 1.

3.1 Process Hints

1. Both reactors should be simulated using the "isothermal" option. The kinetics and relevant reaction stoichiometry are given in detail in the appendix. Since the kinetics are complex, and involve many parameters, the kinetic models have been provided.
2. The design for the column for this part of the project should make use of the internal condenser and reboiler options.
3. The conversion of methane in R-401 is 72% and the conversion of hydrogen in R-402 is 52% (these can be confirmed from Table 1).
4. Pressure drops for heat exchangers should be set for 0.1 bar on the shell side and 0.35 bar on the tube side.
5. The Burner or furnace shown in Figure 3 should use the "Burner" unit operation in APS. The duty should be set equal to the duty of R-401 and the excess oxygen should be set to 6%. All combustible species in Stream 15 (the hydrogen-rich fuel gas) should be completely combusted in the burner. You will need to input the model for this combustion in a separate burner file.

3

6. **Specifications**

5.1 Feed Specification for Natural gas :

CH_4 (Methane) - 95.0 mol%
C_2H_6 (Ethane) - 4.2 mol%
N_2 (Nitrogen) - 0.8 mol%
Supply Condition: 25°C, 2.5 bar

5.2 Available utilities
Cooling water (cw) supply: 30°C , 4.0 bar
Cooling water (cw) return: 40°C , 3.5 bar
High pressure steam (hps): 41 barg (saturated)
Medium pressure steam (mps): 21 bar (saturated),
Low pressure steam (lps): 5 bar (saturated)
Burner Air supply: 25°C, 1.013 bar
Fuel gas (Natural gas): 25°C, 2.5 bar
Boiler feed water (bfw): 120°C, 21.0 bar

5.3 Methanol product - 99.9mol%, liquid.

Appendix - Synthesis Reactions

A.1 Hydrogen Synthesis Kinetics (Steam-Methane reforming reactions)

The production of hydrogen from the steam reforming of natural gas follows the follows the synthesis reactions:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \tag{A.1}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{A.2}$$

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \tag{A.3}$$

$$C_2H_6 + 2H_2O \leftrightarrow 2CO + 5H_2 \tag{A.4}$$

$$C_2H_6 + 4H_2O \leftrightarrow 2CO_2 + 7H_2 \tag{A.5}$$

The kinetic data for the methane reactions are due to Xu and Froment (1) with the addition of kinetics for the ethane reactions.

$$r_1 = \frac{K_1}{(p_{H2})^{2.5}}\left[p_{CH4}p_{H2O} - \frac{(p_{H2})^3 p_{CO}}{Keq_1}\right]\frac{1}{K_4^2}$$

$$r_2 = \frac{K_2}{p_{H2}}\left[p_{CO}p_{H2O} - \frac{p_{H2}p_{CO2}}{Keq_2}\right]\frac{1}{K_4^2}$$

$$r_3 = \frac{K_3}{(p_{H2})^{3.5}}\left[p_{CH4}p_{H2O}^2 \quad - \frac{(p_{H2})^4 p_{CO2}}{Keq_3}\right]\frac{1}{K_4^2}$$

$$r_4 = K_{1ET}p_{c2H6}$$

$$r_5 = K_{2ET}p_{c2H6}$$

$Keq_1 = \exp(-26{,}830/T + 30.144)$

$Keq_2 = \exp(4400/T - 4.036)$

$Keq_3 = Keq_1 \times Keq_2$

$K_1 = \exp(-28{,}879/T + 35.98)$

$K_2 = \exp(-8{,}074/T + 14.49)$

$K_3 = \exp(-29{,}336/T + 34.56)$

$K_a[CO] = \exp(8498/T - 9.41)$

$K_a[H2] = \exp(8498/T - 9.41)$

$K_a[CH4] = \exp(8498/T - 9.41)$

$K_a[H2O] = \exp(8498/T - 9.41)$

$$K_4 = 1 + K_a[CO]p_{CO} + K_a[H2]p_{H2} + K_a[CH4]p_{CH4} + \frac{K_a[H2O]p_{H2O}}{p_{H2}}$$

$K_{1ET} = 4.0\times10^6\exp(-3608.4/T)$

$K_{2ET} = 1.0\times10^6\exp(-3608.4/T)$

p_i is the partial pressure of species i in bar

r is the rate of reaction in kmol/vol of reactor/h

T is the temperature in Kelvin

A.2 Methanol Synthesis Kinetic Expressions

The production of methanol using the starting materials of hydrogen and carbon monoxide and dioxide utilizes the following synthesis reactions:

$$CO + 2H_2 \leftrightarrow CH_3OH \tag{A.6}$$

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \tag{A.7}$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O \tag{A.8}$$

The three reactions shown as Equations A.6-8 are not independent and the kinetics and equilibrium relationships can be expressed by any two of the reactions. For this problem, the kinetics of the CO and CO_2 synthesis reactions (Equations A.6 and A.7) will be given and the parameters are taken from the work of Song et al. [2]. Note that in the original reference, the kinetics are expressed in terms of partial fugacities, but here the kinetics are given in terms of partial pressures.

Designating the forward and reverse reactions for CO as r_{1f} and r_{1r} and the corresponding reactions for CO_2 as r_{2f} and r_{2r}, we may write:

$$r_{6f} = \frac{k_{1f}p_{CO}(p_{H2})^2}{(1+K_{CO}p_{CO}+K_{CO2}p_{CO2}+K_{H2}p_{H2})^3}$$

$$r_{6r} = \frac{k_{1r}p_{MeOH}}{(1+K_{CO}p_{CO}+K_{CO2}p_{CO2}+K_{H2}p_{H2})^3}$$

$$r_{7f} = \frac{k_{2f}p_{CO2}(p_{H2})^3}{(1+K_{CO}p_{CO}+K_{CO2}p_{CO2}+K_{H2}p_{H2})^4}$$

$$r_{7r} = \frac{k_{2r}p_{MeOH}p_{H2O}}{(1+K_{CO}p_{CO}+K_{CO2}p_{CO2}+K_{H2}p_{H2})^4}$$

Where

k_{1f} = 19.12exp(-41,770/RT)

k_{1r} = k_{1f}/K_{1eq}

k_{2f} = 639.0exp(-60,920/RT)

k_{2r} = k_{2f}/K_{2eq}

K_{CO} = 5.4913×10^{-2}exp(-246,427[1/T-1/508.9]/R)

K_{CO2} = 5.5446×10^{-4}exp(29,590/RT)

K_{H2} = 9.39343exp(-16,636/RT)

K_{1eq} = 2.2344×10^{12}exp(-118,000/RT)

K_{2eq} = 7.77×10^{8}exp(-63,500/RT)

p_i is the partial pressure of species i in MPa

r is the rate of reaction in kmol/vol of reactor/h

T is the temperature in Kelvin

R is 8.314 kJ/kmol/K

A

Another important issue with using hydrogen is how to transport and store it. Hydrogen is not easily liquified and is either stored as a liquid at very low temperatures (-250°C) and moderate pressure or as a pressurized gas at very high pressure (350-700 bar). Hydrogen leakage and boil-off are significant in these systems and lead to unwanted losses. Another way to store and transport hydrogen is to react it to an intermediate chemical (NH_3 or Methanol) that is easily stored and transported and then to decompose the chemical back to hydrogen at the point of use. In this problem, we will consider the steam-reforming of natural gas to produce hydrogen and the subsequent reaction to form methanol.

2. Chemical Processes and Process Description

In the process considered for this project, methanol at a rate of 100,000 ton/y and a purity of > 99.9 mol % is to be produced by the steam reforming of natural gas followed by the reaction of carbon monoxide and dioxide with hydrogen to produce methanol. The simulation of the hydrogen and subsequent methanol production processes, shown in Figures 1-3, will form the basis for this project. Aveva Process Simulation (APS) version 2024.1, should be used for all simulations.

Referring to Figure 1, natural gas at 25°C and 2.5 bar (Stream 1) is compressed in compressor C-401 to 30 bar. High pressure saturated steam at 41 bar (Stream 2) is throttled to 30 bar and mixed with the natural gas to form Stream 5. The ratio of steam to natural gas in Stream 5 is maintained at 3:1 (by mole), which is higher than the required stoichiometric ratio but is used to suppress the coking of the catalyst in the reforming reactor. This stream is heated in Exchanger E-401 to 850°C and fed to the steam reforming reactor, R-401. The steam reforming reactions are highly endothermic and require a significant energy transfer to the reactor to maintain the reaction. The processes for this heat transfer and the reactor configuration are explained later. The reactor effluent, Stream 7, is quenched in E-402 to a temperature of 130°C and sent to the high-pressure separator, V-401. Stream 9 leaving the bottom of V-401 is a liquid at 130°C and contains mostly water and a small amount of dissolved gases and is cooled to 40°C in E-410 prior to being sent to wastewater treatment. The gas stream leaving the top of V-401 (Stream 10) is reheated to 250°C in E-403 using high pressure steam and sent to the methanol reactor, R-402. The methanol reactions are exothermic, and heat must be removed from the reacting process stream, this heat transfer process is explained later. The reactor effluent stream, Stream 12, is cooled to a temperature of 100°C in E-404 using cooling water. Stream 13, leaving E-404, is fed to the methanol flash/separator, V-402. The vapor leaving V-402, Stream 15, contains a significant amount of hydrogen that can be combusted and used to provide heat for the process. The liquid leaving V-402 contains mostly methanol and water with small amounts of dissolved gases. This stream is throttled to 3.5 bar, Stream 14, prior to being fed to the methanol

Perform an economic analysis of the base case. Normally, the capital investment cost for equipment would be calculated and combined with the operating costs to yield and equivalent operating cost. However, due to the complexity of the reactors used in this process and the difficulty in estimating their capital costs, only the operating costs will be used.

Once the operating costs for the preliminary design of the steam reforming and methanol synthesis process have been determined, a subsequent optimization of the process should be carried out. The variable used for the optimization (objective function or **OF**) will be the total annual operating cost [\$/y] divided by the annual production rate of methanol, which is fixed at 100×10^6 [kg/y]. Thus, the **OF** is the net cost (without initial capital investment) of methanol [\$/kg]. You should minimize the OF, maintaining the constraints and product specifications given in the following sections.

3.1 Process Hints

1. For this project, all reactors should be simulated using the "isothermal" option. The kinetics and relevant reaction stoichiometry are given in detail in the appendix
2. The design for the column for this part of the project should make use of the internal condenser and reboiler options. Note that utility costs for the reboiler and condenser should be included in evaluating the OF.
3. The maximum temperature at which R-401 can operate is 870°C - the reactor volume should not exceed that of the base case (~100 m^3).
4. Pressure drops for heat exchangers should be set for 0.1 bar on the shell side and 0.35 bar on the tube side. For the air preheater (E-407 - use 0.1 bar for the pressure drops on both sides of the heat exchanger).
5. The burner/furnace unit shown in Figure 3 should use the "Burner" unit operation in APS. The duty should be set equal to the duty of R-401 and the excess oxygen should be set to 6%. All combustible species in Stream 15 (the hydrogen-rich fuel gas) should be completely combusted in the burner.
6. For heat exchangers using cooling water or streams that do not undergo a phase change, a minimum temperature approach of 10°C should be used.
7. Multiple methanol reactors may be considered but the volume of any additional reactor should not exceed the base case value (~630 m^3).

8. Any steam produced in the process that is not consumed within the process may be exported for a credit of $0.006/kg.

4. Specifications

4.1 Feed Specification for Natural gas

CH_4 (Methane) - 95.0 mol%
C_2H_6 (Ethane) - 4.2 mol%
N_2 (Nitrogen) - 0.8 mol%
Supply Condition: 25°C, 2.5 bar

4.2 Available utilities

Cooling water (cw) supply: 30°C , 4.0 bar, cost = default value in APS
Cooling water (cw) return: 40°C , 3.5 bar, no cost
High pressure steam (hps): 41 barg (saturated), cost = \$0.0096/kg
Medium pressure steam (mps): 21 bar (saturated), cost = \$0.0094/kg
Low pressure steam (lps): 5 bar (saturated), cost = \$0.0092/kg
Burner Air supply: 25°C, 1.013 bar, no cost
Fuel gas (Natural gas): 25°C, 2.5 bar, cost = \$0.11619/m^3
Boiler feed water (bfw): 120°C, 21.0 bar, cost = \$4.65989/m^3
Condensate produced (at T and P conditions leaving exchanger), cost = -\$4.65989/m^3 (negative sign indicates a credit) Any steam produced and exported from the unit, -\$0.006/kg (credit) Electricity, cost = \$0.16187/kWh

4.3 Methanol product - 99.9 mol%, liquid - 100,000 ton/y.

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