Indian Institute of Technology Gandhinagar

CL 317 Process Synthesis, Design, and Simulation

Interim project report (mid-semester)

Conversion of CO_2 to Methanol

Group Members

Ishan Agarwal (22110100), Keshav Sobania (22110118), Kaushik (22110113)

Susmita R (22110265), Anushri Sanodia (22110030), Ankit Singh (2211025)

Bukke Ashwini Shankar (22110052)

Under the guidance of

Prof. Hari Ganesh

Introduction :

The increasing levels of carbon dioxide (CO_2) emissions have raised significant concerns about climate change and environmental sustainability. One promising approach to mitigating CO_2 accumulation is its utilization in chemical synthesis, particularly in the production of methanol through CO_2 hydrogenation. Methanol is a valuable chemical feedstock widely used in fuel production, energy storage, and the synthesis of formaldehyde, acetic acid, and other industrial chemicals.

This project focuses on modeling and simulating the methanol production process using Aspen Plus. A critical aspect of this study involves selecting an appropriate thermodynamic model to accurately describe phase equilibria and gas solubilities. The RKSMHV2 model was chosen due to its predictive capability and flexibility, and its performance was compared with other models, including NRTL, NRTL-RK, and Peng-Robinson, by generating Txy and Pxy diagrams.

Further, a process flow sheet was developed, incorporating a reactor (RPlug), compressors, and separation units to simulate the methanol synthesis process. The simulation results were analyzed to determine the methanol yield and evaluate the efficiency of different process configurations. This study aims to identify optimal thermodynamic models and process setups that enhance methanol production efficiency while addressing sustainability challenges related to CO_2 utilization.

System description :

Scheme 1 :

- The model includes six components: carbon dioxide (CO_2), hydrogen (H_2), carbon monoxide (CO), methanol (CH_4O), nitrogen (N_2), and water (H_2O).
- To account for mixture properties, the RX MHV2 thermodynamic model is applied.

Reaction :

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$$

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

	Rxn No.	Reaction type	Stoichiometry	Delete
▶	1	Kinetic	CO + 2 H2 --> CH3OH(MIXED)	✕
▶	2	Kinetic	CO2 + H2 --> CO(MIXED) + H2O(MIXED)	✕
▶	3	Kinetic	CO2 + 3 H2 --> CH3OH(MIXED) + H2O(MIXED)	✕

Method used: PENG ROB

CO_2-to-Methanol Production Process:

1. CO_2 Compression and Mixing with Hydrogen

Carbon dioxide (CO_2) is compressed using a three-stage compressor to increase its pressure for efficient reaction. The compressed CO_2 is then mixed with hydrogen (H_2) to form a reactant mixture in the desired stoichiometric ratio for methanol synthesis.

2. Heating and Reactor Stage

The CO_2-H_2 mixture is heated to the required temperature for methanol synthesis. The heated gas is fed into an RPlug reactor, where the reaction occurs.

Rxn No.	Reaction type	Stoichiometry	Delete
1	Kinetic	CO + 2 H2 --> CH3OH(MIXED)	✕
2	Kinetic	CO2 + H2 --> CO(MIXED) + H2O(MIXED)	✕
3	Kinetic	CO2 + 3 H2 --> CH3OH(MIXED) + H2O(MIXED)	✕

Inside the reactor, methanol and water are formed as products, along with some unreacted gases.

3. Cooling and Pressure Reduction

The reactor's product stream is cooled to condense methanol and water while keeping unreacted gases in vapor form. The pressure is reduced using a control valve, preparing the stream for separation.

4. Flash Separation

- The cooled stream undergoes further chilling to reach a lower temperature, enhancing phase separation.
- It enters a flash separator, where the mixture is split:
- 30% of the contents (mainly unreacted gases) are removed.
- 70% of the vapor is recycled to improve process efficiency.

5. Vapor Recompression and Condensation

- The recycled vapor is compressed and converted into liquid form.
- This liquid is then processed to extract methanol.

6. Distillation for Methanol Purification

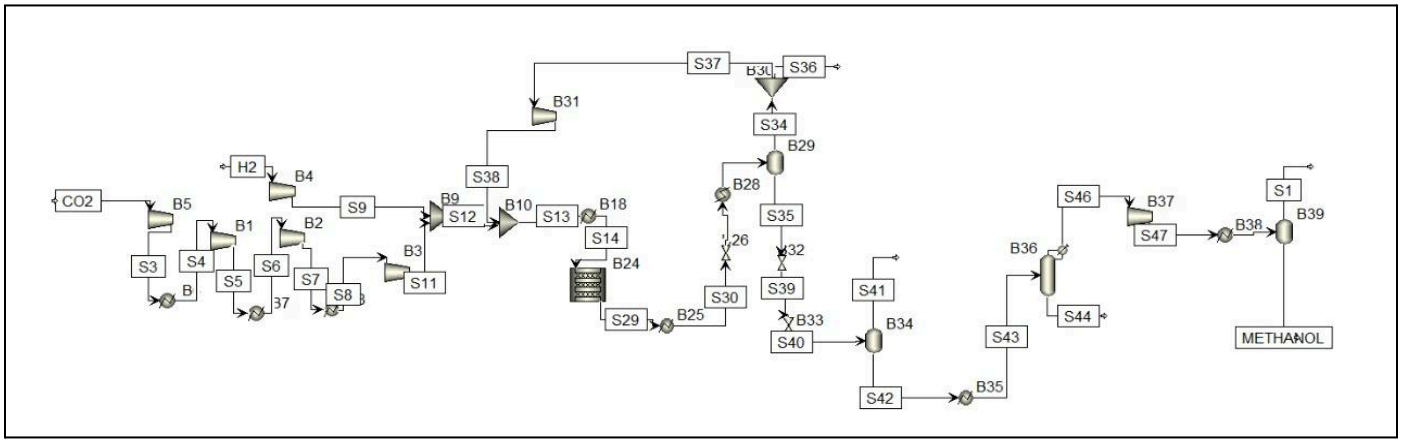
The condensed liquid is sent to a distillation column where Methanol is obtained as the distillate and water and other impurities are removed as bottoms.

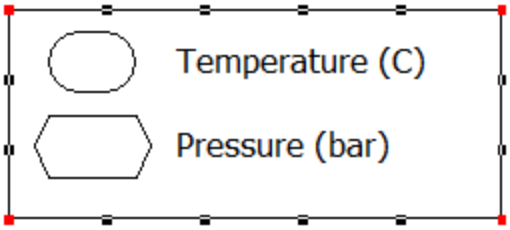
7. Final Methanol Compression

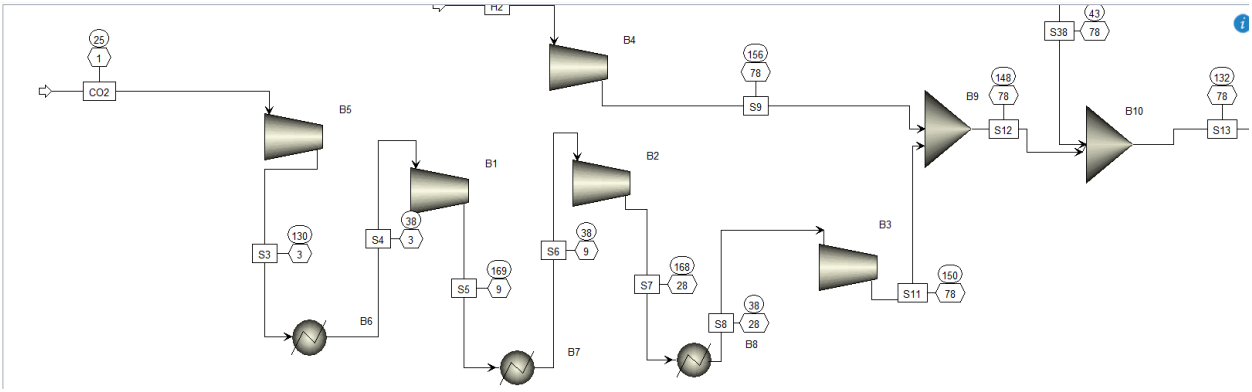
The methanol vapor is compressed to obtain liquid methanol, which is the final product ready for storage or further use.

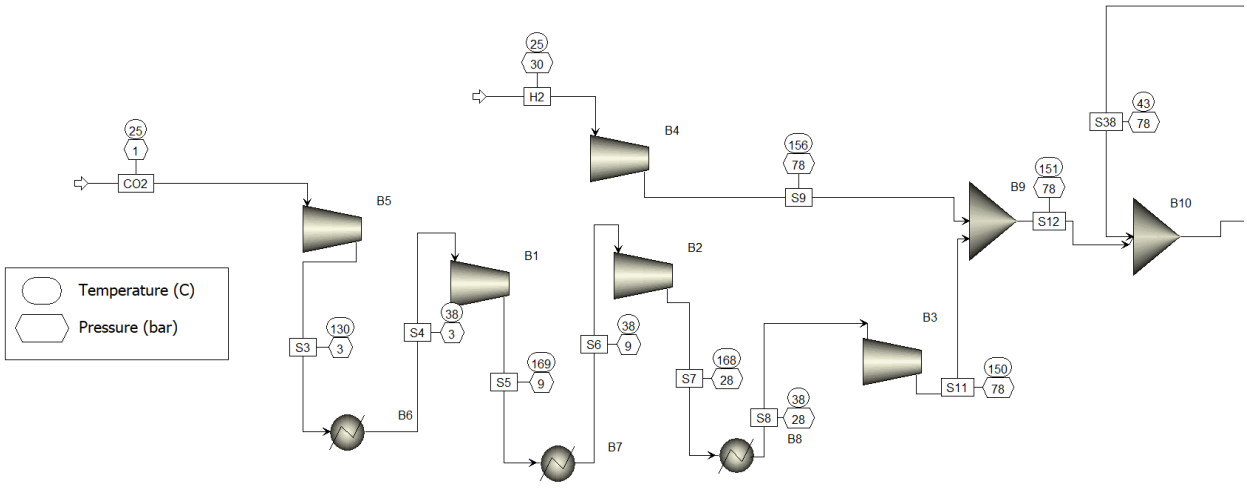
Methodology :

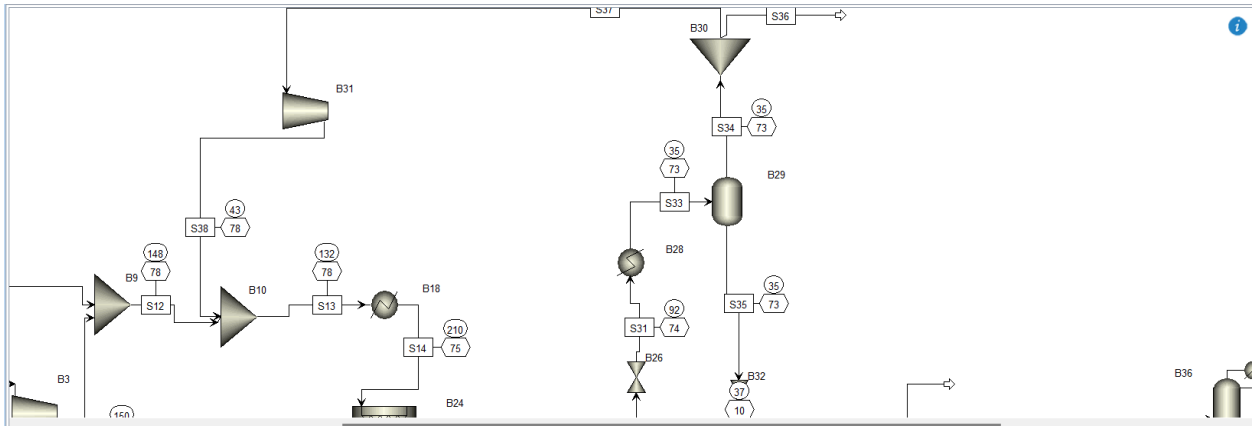
Flowsheet designed :

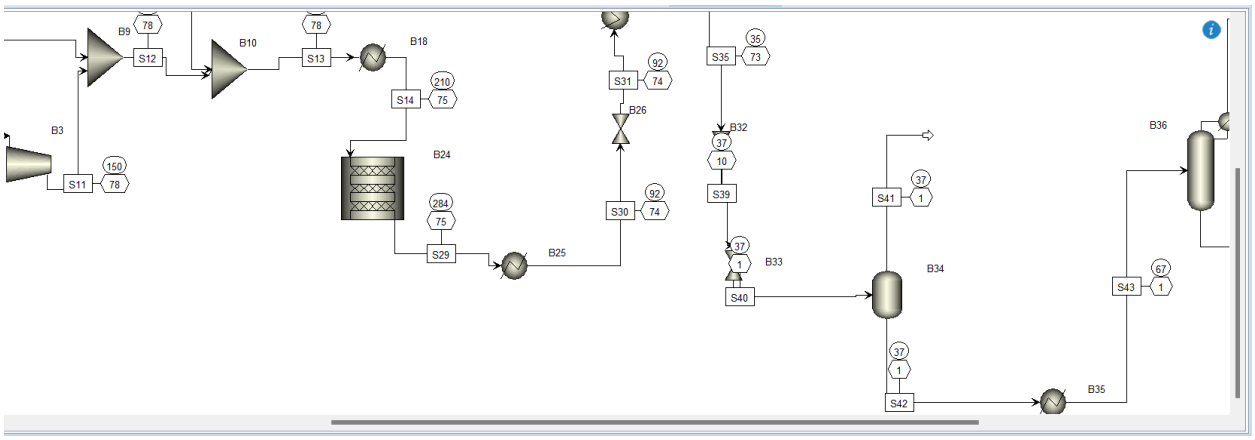


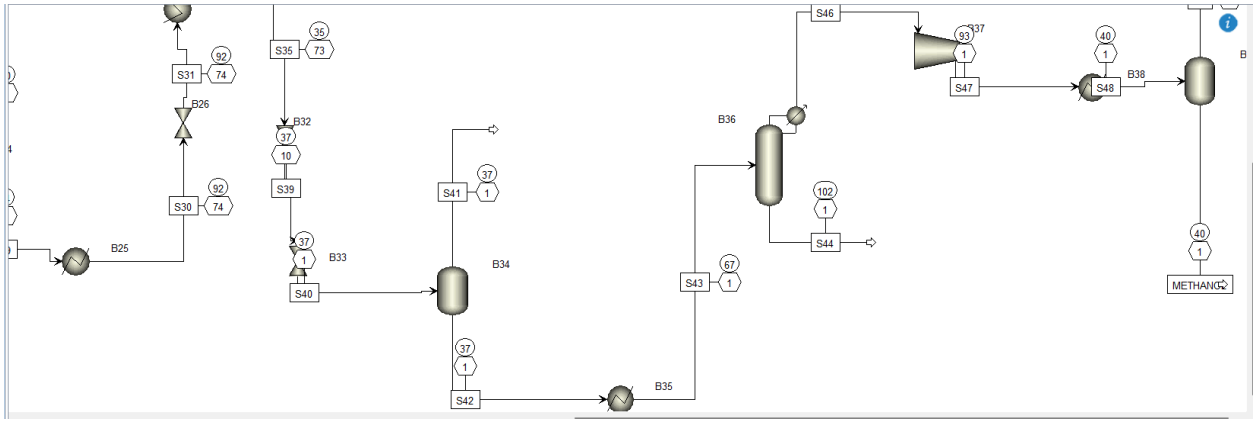

Temperature (C)
Pressure (bar)

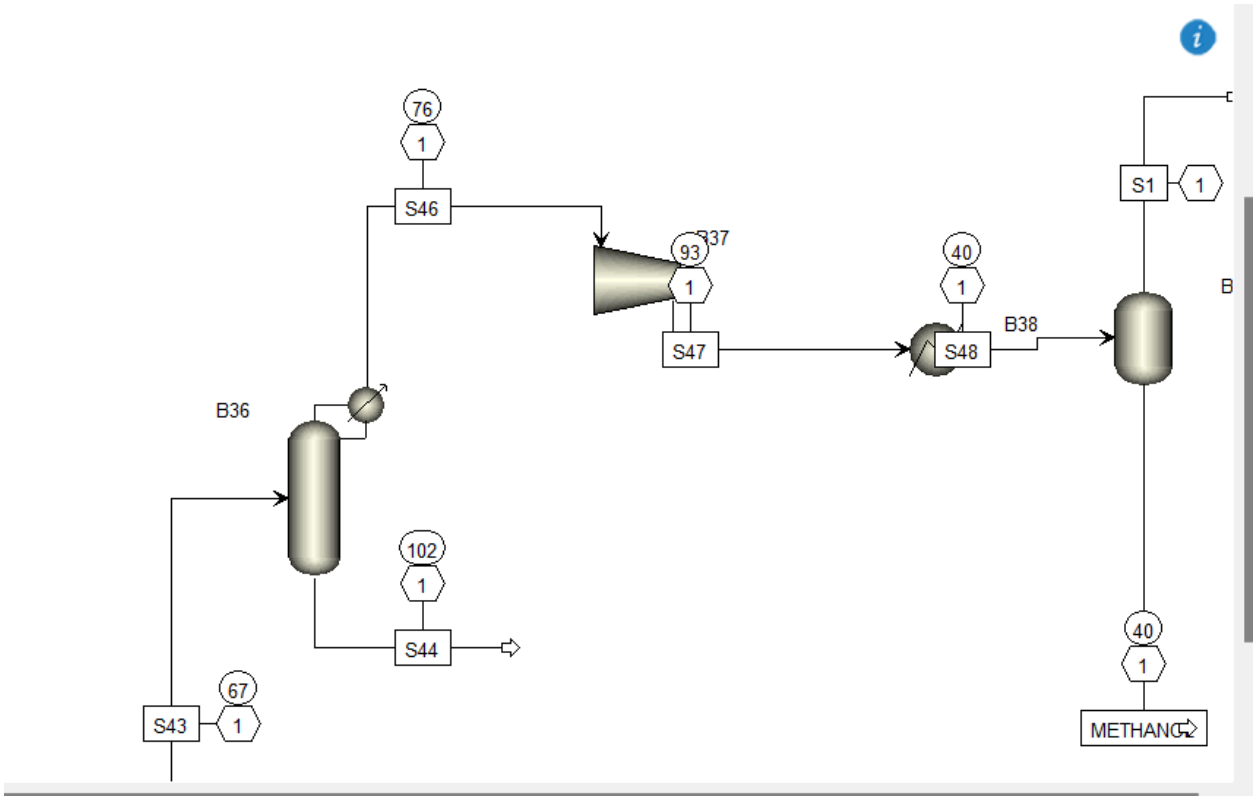

CO2
H2
B1
B2
B3
B4
B5
B6
B7
B8
B9
B10
S3
S4
S5
S6
S7
S8
S9
S11
S12
S13
S38


Temperature (C)
Pressure (bar)
CO2
H2
B1
B2
B3
B4
B5
B6
B7
B8
B9
B10
S3
S4
S5
S6
S7
S8
S9
S11
S12
S38

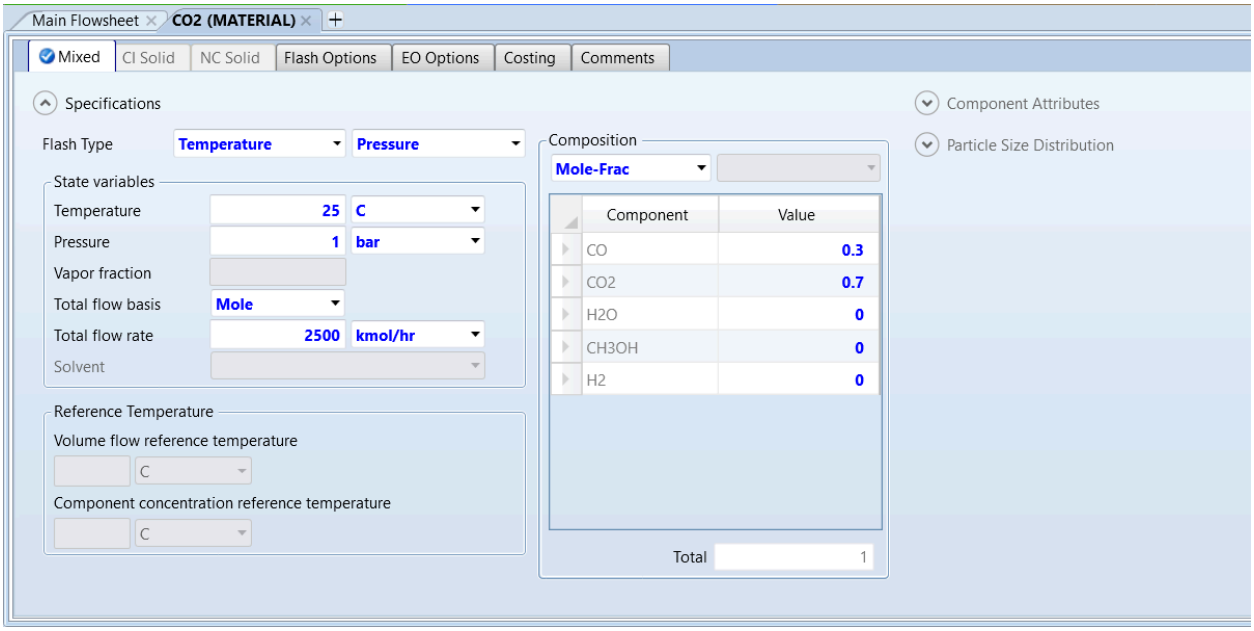

S37
S36
B30
B31
S34
35
73
B29
S33
B28
S38
43
78
148
78
B9
S12
B10
132
78
S13
B18
S14
210
75
B24
B3
S31
92
74
B26
S35
B32
37
10
B36

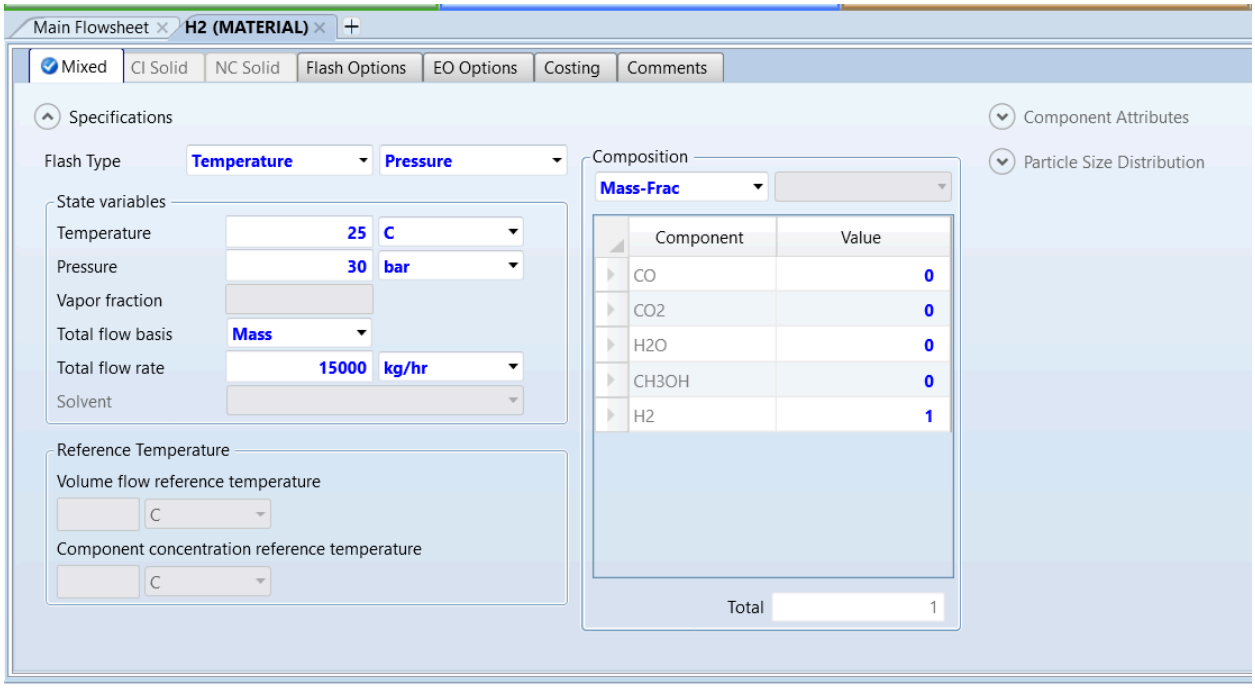

B9
78
S12
B10
78
S13
B18
S14
210
75
B24
B3
S11
150
78
S31
92
74
B26
S35
35
73
B32
37
10
S39
B36
S41
37
1
B34
S30
92
74
284
75
S29
B25
37
1
B33
S40
S43
67
1
S42
B35

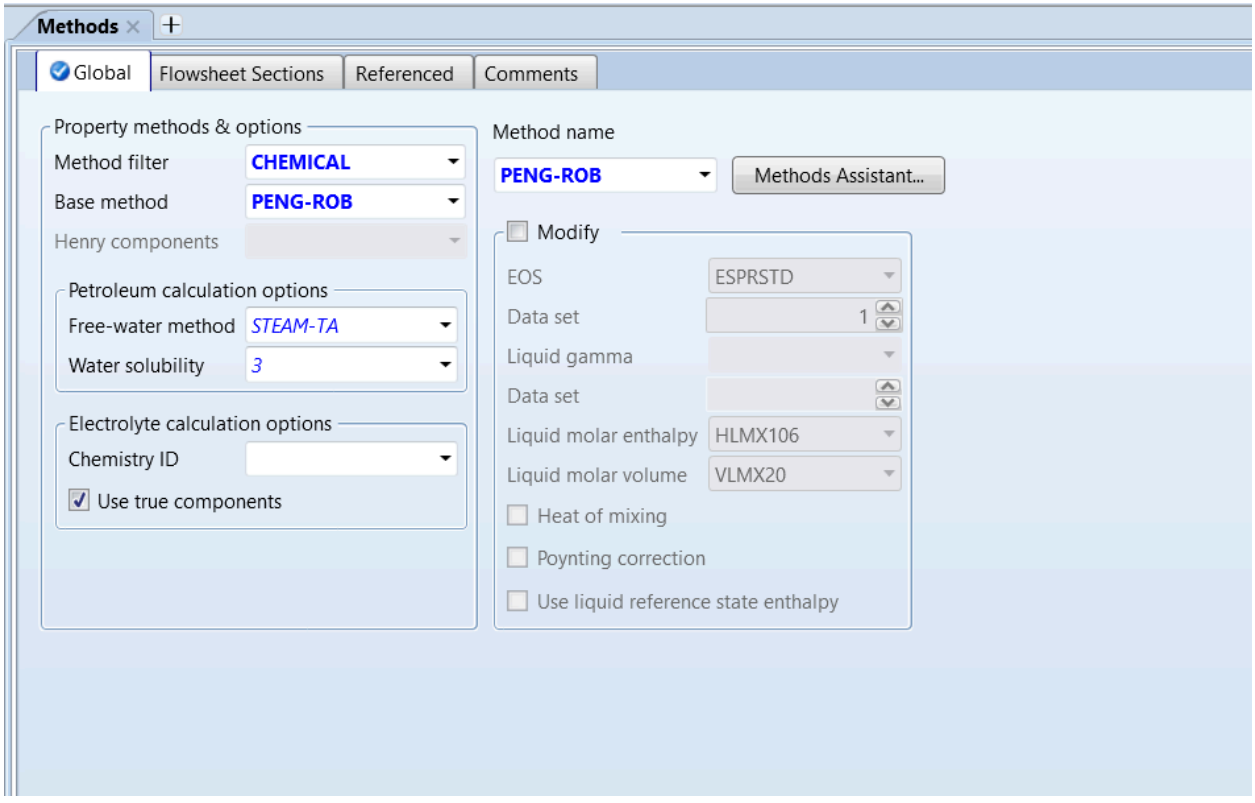

S46
S37
93
1
S47
40
1
S48
B38
B36
S31
92
74
B26
S35
35
73
B32
37
10
S39
S41
37
1
102
1
S44
S30
92
74
B25
37
1
B33
S40
B34
S43
67
1
40
1
METHANO
37
1
S42
B35



PARAMETERS FOR FEED:







Preliminary results :

Results obtained :

We can see the molar flow rates, mole fractions, mass flow rates, temperature, etc in the results obtained below :

Flowsheet | B29 (Flash2) | B39 (Flash2) | B38 (Heater) | B37 (Compr) | **Results Summary - Streams (All)** | Main Flowsheet | B36 (RadFrac) | B35 (Heater) | B34 (Flash2)

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

	Units	CO2	H2	METHANOL	S1	S3	S4	S5	S6	S7
MIXED Substream										
Phase		Vapor Phase	Vapor Phase	Liquid Phase	Vapor Phase	Vapor Phase	Vapor Phase	Vapor Phase	Vapor Phase	Vap
Temperature	C	25	25	40	40	130.481	38	169.236	38	
Pressure	bar	1	30	1	1	2.7	2.7	8.8	8.8	
Molar Vapor Fraction		1	1	0	1	1	1	1	1	
Molar Liquid Fraction		0	0	1	0	0	0	0	0	
Molar Solid Fraction		0	0	0	0	0	0	0	0	
Mass Vapor Fraction		1	1	0	1	1	1	1	1	
Mass Liquid Fraction		0	0	1	0	0	0	0	0	
Mass Solid Fraction		0	0	0	0	0	0	0	0	
Molar Enthalpy	cal/mol	-73718.9	6.24324	-60220	-15824.4	-72802.5	-73621.3	-72464	-73663.9	
Mass Enthalpy	cal/gm	-1880.11	3.09703	-2148.78	-1319.05	-1856.73	-1877.62	-1848.1	-1878.7	
Molar Entropy	cal/mol-K	8.10143	-6.74435	-51.3056	-4.88667	8.76045	6.45993	7.22248	4.01232	
Mass Entropy	cal/gm-K	0.206616	-3.34561	-1.83069	-0.40733	0.223424	0.164752	0.1842	0.102329	
Molar Density	mol/cc	4.04779e-05	0.00118784	0.0218496	3.851e-05	8.06438e-05	0.000105194	0.000240208	0.000349144	

Flowsheet | B29 (Flash2) | B39 (Flash2) | B38 (Heater) | B37 (Compr) | **Results Summary - Streams (All)** | Main Flowsheet | B36 (RadFrac) | B35 (Heater) | B34 (Flash2)

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

	Units	S8	S9	S11	S12	S13	S14	S29	S30	S3
MIXED Substream										
Phase		Vapor Phase	Vapor Phase	Vapor Phase	Vapor Phase	Vapor Phase	Vapor Phase	Vapor Phase		
Temperature	C	38	156.084	150.384	151.425	136.355	210	284	92	
Pressure	bar	28.3	78	78	78	78	75	75	74	
Molar Vapor Fraction		1	1	1	1	1	1	1	0.384195	
Molar Liquid Fraction		0	0	0	0	0	0	0	0.615805	
Molar Solid Fraction		0	0	0	0	0	0	0	0	
Mass Vapor Fraction		1	1	1	1	1	1	1	0.101395	
Mass Liquid Fraction		0	0	0	0	0	0	0	0.898605	
Mass Solid Fraction		0	0	0	0	0	0	0	0	
Molar Enthalpy	cal/mol	-73807.4	936.797	-72891.3	-17629.9	-15226.1	-14655.7	-30699.8	-37684.8	
Mass Enthalpy	cal/gm	-1882.36	464.709	-1859	-1550.61	-1490.29	-1434.47	-1749.44	-2147.48	
Molar Entropy	cal/mol-K	1.34559	-6.10952	1.96854	-2.96662	-3.41561	-2.05485	-14.3075	-29.8396	
Mass Entropy	cal/gm-K	0.0343176	-3.03069	0.050205	-0.260924	-0.334313	-0.201125	-0.815316	-1.70042	
Molar Density	mol/cc	0.00119453	0.00210593	0.00230729	0.00215961	0.00223572	0.00181995	0.00174801	0.0052646	

Flowsheet | B29 (Flash2) | B39 (Flash2) | B38 (Heater) | B37 (Compr) | **Results Summary - Streams (All)** | Main Flowsheet | B36 (RadFrac) | B35 (Heater) | B34 (Flash2)

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

	Units	S31	S33	S34	S35	S36	S37	S38	S39	S
MIXED Substream										
Phase				Vapor Phase	Liquid Phase	Vapor Phase	Vapor Phase	Vapor Phase		
Temperature	C	91.9807	35	35	35	35	35	42.5796	36.2394	
Pressure	bar	73.6	73.4	73.4	73.4	73.4	73.4	78	10	
Molar Vapor Fraction		0.384336	0.369691	1	0	1	1	1	0.0212589	
Molar Liquid Fraction		0.615664	0.630309	0	1	0	0	0	0.978741	
Molar Solid Fraction		0	0	0	0	0	0	0	0	
Mass Vapor Fraction		0.101512	0.0783246	1	0	1	1	0.999996	0.00387181	
Mass Liquid Fraction		0.898488	0.921675	0	1	0	0	4.37395e-06	0.996128	
Mass Solid Fraction		0	0	0	0	0	0	0	0	
Molar Enthalpy	cal/mol	-37684.8	-38697.6	-1729.44	-60380.2	-1729.44	-1729.44	-1675.02	-60380.2	
Mass Enthalpy	cal/gm	-2147.48	-2205.19	-465.168	-2353.06	-465.168	-465.168	-450.528	-2353.06	
Molar Entropy	cal/mol-K	-29.8346	-32.8385	-6.61597	-48.2186	-6.61597	-6.61597	-6.56754	-47.963	
Mass Entropy	cal/gm-K	-1.70013	-1.87131	-1.7795	-1.87911	-1.7795	-1.7795	-1.76646	-1.86915	
Molar Density	mol/cc	0.00523991	0.0062275	0.00274487	0.0243422	0.00274487	0.00274487	0.00284057	0.0104668	

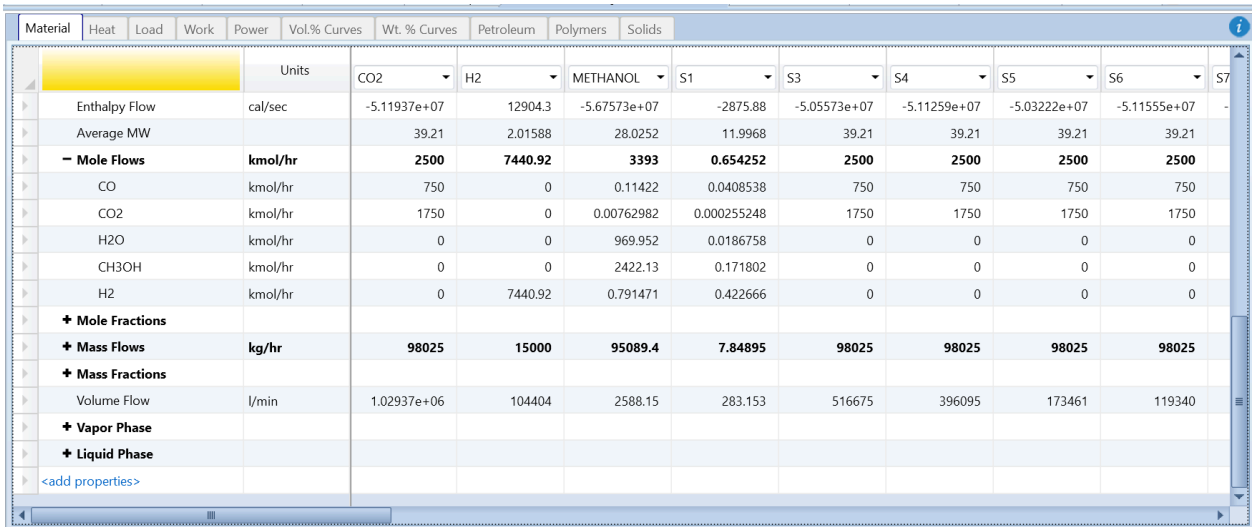
Material | Heat | Load | Work | Power | Vol.% Curves | Wt. % Curves | Petroleum | Polymers | Solids

	Units		S39	S40	S41	S42	S43	S44	S46	S47
MIXED Substream										
Phase					Vapor Phase	Liquid Phase		Liquid Phase	Vapor Phase	Vapor Phase
Temperature	C	6	36.2394	34.5038	37	37	67	99.5776	75.5411	92.5405
Pressure	bar	8	10	1.2	1.2	1.2	1.1	1	1	1.2
Molar Vapor Fraction		1	0.0212589	0.028399	1	0	0.00113507	0	1	1
Molar Liquid Fraction		0	0.978741	0.971601	0	1	0.998865	1	0	0
Molar Solid Fraction		0	0	0	0	0	0	0	0	0
Mass Vapor Fraction		6	0.00387181	0.00939658	1	0	0.00104858	0	1	1
Mass Liquid Fraction		6	0.996128	0.990603	0	1	0.998951	1	0	0
Mass Solid Fraction		0	0	0	0	0	0	0	0	0
Molar Enthalpy	cal/mol	2	-60380.2	-60380.2	-11036.2	-61803.1	-61171.4	-66942.7	-50284.9	-50109.1
Mass Enthalpy	cal/gm	8	-2353.06	-2353.06	-1218.67	-2362.55	-2338.4	-3715.89	-1794.47	-1788.2
Molar Entropy	cal/mol-K	4	-47.963	-47.8319	-2.33282	-49.0035	-47.0595	-35.0263	-22.3681	-22.2327
Mass Entropy	cal/gm-K	6	-1.86915	-1.86404	-0.257601	-1.87326	-1.79895	-1.94425	-0.79823	-0.793397
Molar Density	mol/cc	7	0.0104668	0.00155067	4.66039e-05	0.0240863	0.0139423	0.0393429	3.49964e-05	4.00677e-05

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

	Units	S7	S8	S9	S11	S12	S13	S14	S29	S
Phase		Vapor Phase	Vapor Phase	Vapor Phase	Vapor Phase	Vapor Phase	Vapor Phase	Vapor Phase	Vapor Phase	
Temperature	C	168.312	38	156.084	150.384	151.425	136.355	210	284	
Pressure	bar	28.3	28.3	78	78	78	78	75	75	
Molar Vapor Fraction		1	1	1	1	1	1	1	1	
Molar Liquid Fraction		0	0	0	0	0	0	0	0	
Molar Solid Fraction		0	0	0	0	0	0	0	0	
Mass Vapor Fraction		1	1	1	1	1	1	1	1	
Mass Liquid Fraction		0	0	0	0	0	0	0	0	
Mass Solid Fraction		0	0	0	0	0	0	0	0	
Molar Enthalpy	cal/mol	-72537.3	-73807.4	936.797	-72891.3	-17629.9	-15226.1	-14655.7	-30699.8	
Mass Enthalpy	cal/gm	-1849.97	-1882.36	464.709	-1859	-1550.61	-1490.29	-1434.47	-1749.44	
Molar Entropy	cal/mol-K	4.7542	1.34559	-6.10952	1.96854	-2.96662	-3.41561	-2.05485	-14.3075	
Mass Entropy	cal/gm-K	0.12125	0.0343176	-3.03069	0.050205	-0.260924	-0.334313	-0.201125	-0.815316	
Molar Density	mol/cc	0.000780563	0.00119453	0.00210593	0.00230729	0.00215961	0.00223572	0.00181995	0.00174801	
Mass Density	gm/cc	0.0306059	0.0468374	0.0042453	0.0904689	0.0245541	0.0228419	0.0185941	0.0306747	

Molar flow rate and Mass flow rate :



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

	Units	CO2	H2	METHANOL	S1	S3	S4	S5	S6	S7
Enthalpy Flow	cal/sec	-5.11937e+07	12904.3	-5.67573e+07	-2875.88	-5.05573e+07	-5.11259e+07	-5.03222e+07	-5.11555e+07	
Average MW		39.21	2.01588	28.0252	11.9968	39.21	39.21	39.21	39.21	
− Mole Flows	**kmol/hr**	**2500**	**7440.92**	**3393**	**0.654252**	**2500**	**2500**	**2500**	**2500**	
CO	kmol/hr	750	0	0.11422	0.0408538	750	750	750	750	
CO2	kmol/hr	1750	0	0.00762982	0.000255248	1750	1750	1750	1750	
H2O	kmol/hr	0	0	969.952	0.0186758	0	0	0	0	
CH3OH	kmol/hr	0	0	2422.13	0.171802	0	0	0	0	
H2	kmol/hr	0	7440.92	0.791471	0.422666	0	0	0	0	
+ Mole Fractions										
+ Mass Flows	**kg/hr**	**98025**	**15000**	**95089.4**	**7.84895**	**98025**	**98025**	**98025**	**98025**	
+ Mass Fractions										
Volume Flow	l/min	1.02937e+06	104404	2588.15	283.153	516675	396095	173461	119340	
+ Vapor Phase										
+ Liquid Phase										
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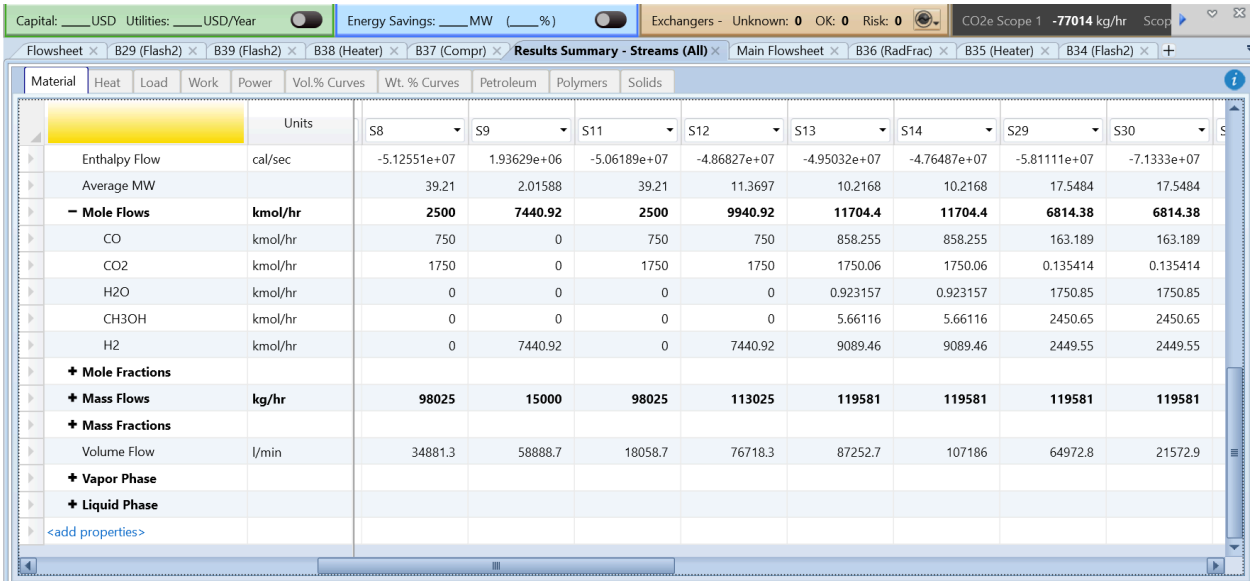
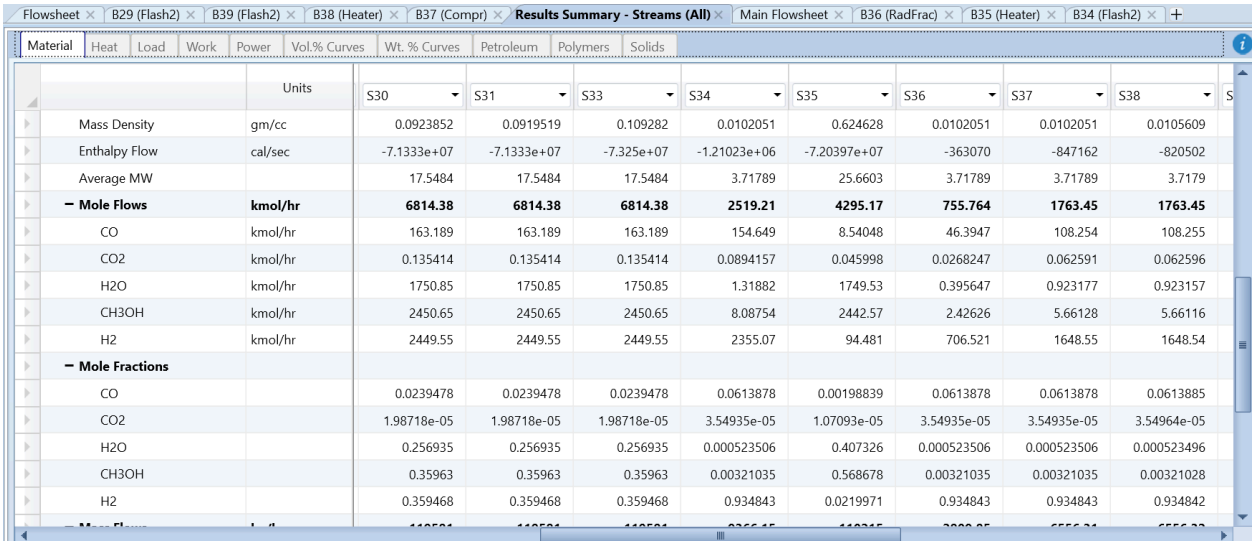


Capital: ____USD Utilities: ____USD/Year | Energy Savings: ____MW (____%) | Exchangers - Unknown: 0 OK: 0 Risk: 0 | CO2e Scope 1 -77014 kg/hr

Flowsheet | B29 (Flash2) | B39 (Flash2) | B38 (Heater) | B37 (Compr) | **Results Summary - Streams (All)** | Main Flowsheet | B36 (RadFrac) | B35 (Heater) | B34 (Flash2)

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

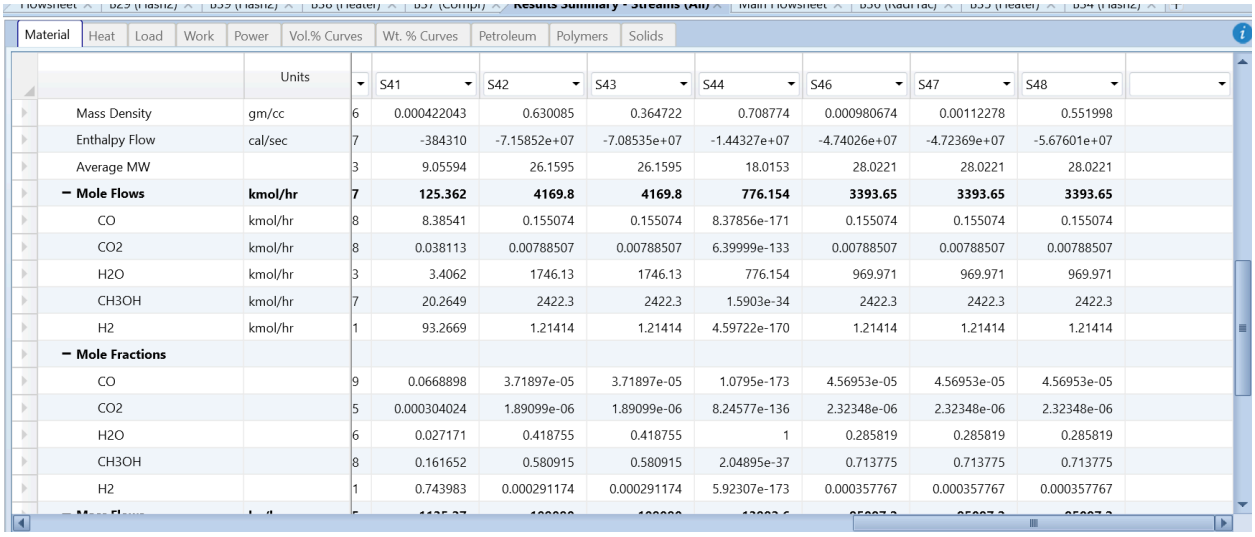
	Units	S8	S9	S11	S12	S13	S14	S29	S30	S
Enthalpy Flow	cal/sec	-5.12551e+07	1.93629e+06	-5.06189e+07	-4.86827e+07	-4.95032e+07	-4.76487e+07	-5.81111e+07	-7.1333e+07	
Average MW		39.21	2.01588	39.21	11.3697	10.2168	10.2168	17.5484	17.5484	
− Mole Flows	**kmol/hr**	**2500**	**7440.92**	**2500**	**9940.92**	**11704.4**	**11704.4**	**6814.38**	**6814.38**	
CO	kmol/hr	750	0	750	750	858.255	858.255	163.189	163.189	
CO2	kmol/hr	1750	0	1750	1750	1750.06	1750.06	0.135414	0.135414	
H2O	kmol/hr	0	0	0	0	0.923157	0.923157	1750.85	1750.85	
CH3OH	kmol/hr	0	0	0	0	5.66116	5.66116	2450.65	2450.65	
H2	kmol/hr	0	7440.92	0	7440.92	9089.46	9089.46	2449.55	2449.55	
+ Mole Fractions										
+ Mass Flows	**kg/hr**	**98025**	**15000**	**98025**	**113025**	**119581**	**119581**	**119581**	**119581**	
+ Mass Fractions										
Volume Flow	l/min	34881.3	58888.7	18058.7	76718.3	87252.7	107186	64972.8	21572.9	
+ Vapor Phase										
+ Liquid Phase										
<add properties>										



Flowsheet | B29 (Flash2) | B39 (Flash2) | B38 (Heater) | B37 (Compr) | **Results Summary - Streams (All)** | Main Flowsheet | B36 (RadFrac) | B35 (Heater) | B34 (Flash2)

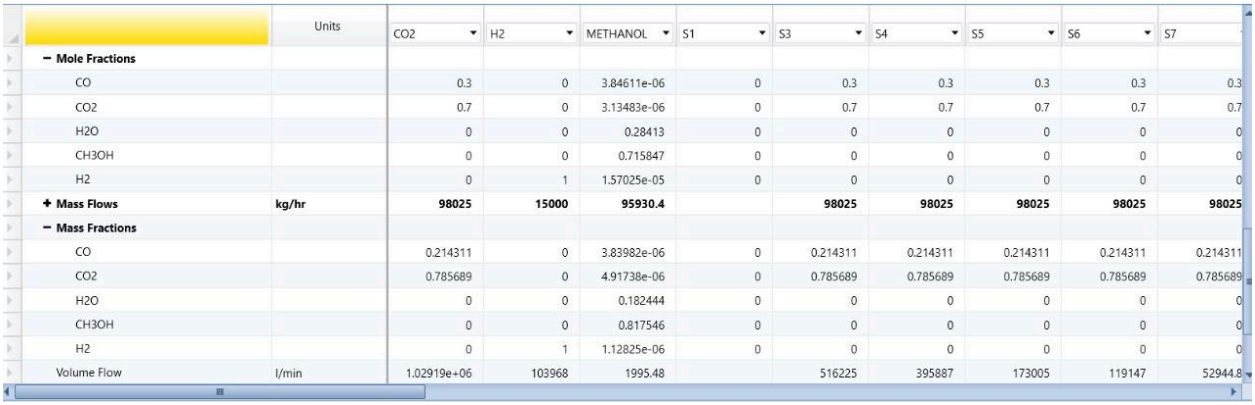
Material | Heat | Load | Work | Power | Vol.% Curves | Wt. % Curves | Petroleum | Polymers | Solids

	Units	S30	S31	S33	S34	S35	S36	S37	S38	S
Mass Density	gm/cc	0.0923852	0.0919519	0.109282	0.0102051	0.624628	0.0102051	0.0102051	0.0105609	
Enthalpy Flow	cal/sec	-7.1333e+07	-7.1333e+07	-7.325e+07	-1.21023e+06	-7.20397e+07	-363070	-847162	-820502	
Average MW		17.5484	17.5484	17.5484	3.71789	25.6603	3.71789	3.71789	3.7179	
− Mole Flows	**kmol/hr**	**6814.38**	**6814.38**	**6814.38**	**2519.21**	**4295.17**	**755.764**	**1763.45**	**1763.45**	
CO	kmol/hr	163.189	163.189	163.189	154.649	8.54048	46.3947	108.254	108.255	
CO2	kmol/hr	0.135414	0.135414	0.135414	0.0894157	0.045998	0.0268247	0.062591	0.062596	
H2O	kmol/hr	1750.85	1750.85	1750.85	1.31882	1749.53	0.395647	0.923177	0.923157	
CH3OH	kmol/hr	2450.65	2450.65	2450.65	8.08754	2442.57	2.42626	5.66128	5.66116	
H2	kmol/hr	2449.55	2449.55	2449.55	2355.07	94.481	706.521	1648.55	1648.54	
− Mole Fractions										
CO		0.0239478	0.0239478	0.0239478	0.0613878	0.00198839	0.0613878	0.0613878	0.0613885	
CO2		1.98718e-05	1.98718e-05	1.98718e-05	3.54935e-05	1.07093e-05	3.54935e-05	3.54935e-05	3.54964e-05	
H2O		0.256935	0.256935	0.256935	0.000523506	0.407326	0.000523506	0.000523506	0.000523496	
CH3OH		0.35963	0.35963	0.35963	0.00321035	0.568678	0.00321035	0.00321035	0.00321028	
H2		0.359468	0.359468	0.359468	0.934843	0.0219971	0.934843	0.934843	0.934842	

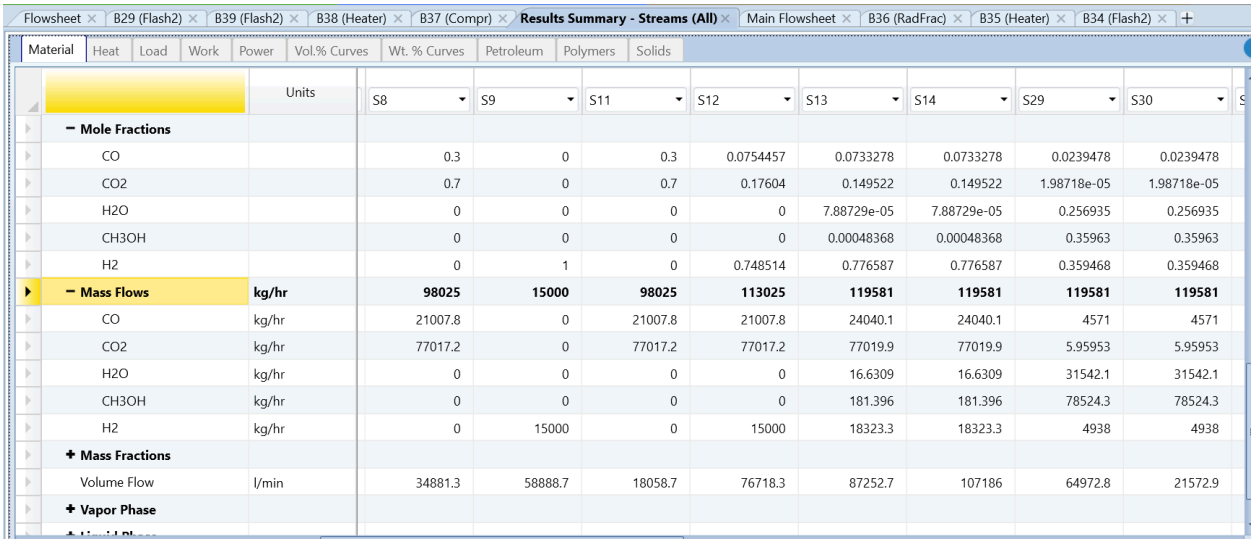


Material | Heat | Load | Work | Power | Vol.% Curves | Wt. % Curves | Petroleum | Polymers | Solids

	Units		S41	S42	S43	S44	S46	S47	S48
Mass Density	gm/cc	6	0.000422043	0.630085	0.364722	0.708774	0.000980674	0.00112278	0.551998
Enthalpy Flow	cal/sec	7	-384310	-7.15852e+07	-7.08535e+07	-1.44327e+07	-4.74026e+07	-4.72369e+07	-5.67601e+07
Average MW		3	9.05594	26.1595	26.1595	18.0153	28.0221	28.0221	28.0221
− Mole Flows	**kmol/hr**	**7**	**125.362**	**4169.8**	**4169.8**	**776.154**	**3393.65**	**3393.65**	**3393.65**
CO	kmol/hr	8	8.38541	0.155074	0.155074	8.37856e-171	0.155074	0.155074	0.155074
CO2	kmol/hr	8	0.038113	0.00788507	0.00788507	6.39999e-133	0.00788507	0.00788507	0.00788507
H2O	kmol/hr	3	3.4062	1746.13	1746.13	776.154	969.971	969.971	969.971
CH3OH	kmol/hr	7	20.2649	2422.3	2422.3	1.5903e-34	2422.3	2422.3	2422.3
H2	kmol/hr	1	93.2669	1.21414	1.21414	4.59722e-170	1.21414	1.21414	1.21414
− Mole Fractions									
CO		9	0.0668898	3.71897e-05	3.71897e-05	1.0795e-173	4.56953e-05	4.56953e-05	4.56953e-05
CO2		5	0.000304024	1.89099e-06	1.89099e-06	8.24577e-136	2.32348e-06	2.32348e-06	2.32348e-06
H2O		6	0.027171	0.418755	0.418755	1	0.285819	0.285819	0.285819
CH3OH		8	0.161652	0.580915	0.580915	2.04895e-37	0.713775	0.713775	0.713775
H2		1	0.743983	0.000291174	0.000291174	5.92307e-173	0.000357767	0.000357767	0.000357767



	Units	CO2	H2	METHANOL	S1	S3	S4	S5	S6	S7
− Mole Fractions										
CO		0.3	0	3.84611e-06	0	0.3	0.3	0.3	0.3	0.3
CO2		0.7	0	3.13483e-06	0	0.7	0.7	0.7	0.7	0.7
H2O		0	0	0.28413	0	0	0	0	0	0
CH3OH		0	0	0.715847	0	0	0	0	0	0
H2		0	1	1.57025e-05	0	0	0	0	0	0
+ Mass Flows	**kg/hr**	**98025**	**15000**	**95930.4**		**98025**	**98025**	**98025**	**98025**	**98025**
− Mass Fractions										
CO		0.214311	0	3.83982e-06	0	0.214311	0.214311	0.214311	0.214311	0.214311
CO2		0.785689	0	4.91738e-06	0	0.785689	0.785689	0.785689	0.785689	0.785689
H2O		0	0	0.182444	0	0	0	0	0	0
CH3OH		0	0	0.817546	0	0	0	0	0	0
H2		0	1	1.12825e-06	0	0	0	0	0	0
Volume Flow	l/min	1.02919e+06	103968	1995.48		516225	395887	173005	119147	52944.8



Flowsheet | B29 (Flash2) | B39 (Flash2) | B38 (Heater) | B37 (Compr) | **Results Summary - Streams (All)** | Main Flowsheet | B36 (RadFrac) | B35 (Heater) | B34 (Flash2)

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

	Units	S8	S9	S11	S12	S13	S14	S29	S30
− Mole Fractions									
CO		0.3	0	0.3	0.0754457	0.0733278	0.0733278	0.0239478	0.0239478
CO2		0.7	0	0.7	0.17604	0.149522	0.149522	1.98718e-05	1.98718e-05
H2O		0	0	0	0	7.88729e-05	7.88729e-05	0.256935	0.256935
CH3OH		0	0	0	0	0.00048368	0.00048368	0.35963	0.35963
H2		0	1	0	0.748514	0.776587	0.776587	0.359468	0.359468
− Mass Flows	**kg/hr**	**98025**	**15000**	**98025**	**113025**	**119581**	**119581**	**119581**	**119581**
CO	kg/hr	21007.8	0	21007.8	21007.8	24040.1	24040.1	4571	4571
CO2	kg/hr	77017.2	0	77017.2	77017.2	77019.9	77019.9	5.95953	5.95953
H2O	kg/hr	0	0	0	0	16.6309	16.6309	31542.1	31542.1
CH3OH	kg/hr	0	0	0	0	181.396	181.396	78524.3	78524.3
H2	kg/hr	0	15000	0	15000	18323.3	18323.3	4938	4938
+ Mass Fractions									
Volume Flow	l/min	34881.3	58888.7	18058.7	76718.3	87252.7	107186	64972.8	21572.9
+ Vapor Phase									

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

	Units	S31	S33	S34	S35	S36	S37	S38	S39
Mole Fractions									
CO		0.0239478	0.0239478	0.0613878	0.00198839	0.0613878	0.0613878	0.0613885	0.00198839
CO2		1.98718e-05	1.98718e-05	3.54935e-05	1.07093e-05	3.54935e-05	3.54935e-05	3.54964e-05	1.07093e-05
H2O		0.256935	0.256935	0.000523506	0.407326	0.000523506	0.000523506	0.000523496	0.407326
CH3OH		0.35963	0.35963	0.00321035	0.568678	0.00321035	0.00321035	0.00321028	0.568678
H2		0.359468	0.359468	0.934843	0.0219971	0.934843	0.934843	0.934842	0.0219971
Mass Flows	**kg/hr**	**119581**	**119581**	**9366.15**	**110215**	**2809.85**	**6556.31**	**6556.32**	**110215**
CO	kg/hr	4571	4571	4331.78	239.222	1299.53	3032.24	3032.27	239.222
CO2	kg/hr	5.95953	5.95953	3.93517	2.02436	1.18055	2.75462	2.75484	2.02436
H2O	kg/hr	31542.1	31542.1	23.759	31518.3	7.12769	16.6313	16.6309	31518.3
CH3OH	kg/hr	78524.3	78524.3	259.142	78265.1	77.7427	181.4	181.396	78265.1
H2	kg/hr	4938	4938	4747.54	190.462	1424.26	3323.28	3323.27	190.462
Mass Fractions									
Volume Flow	l/min	21674.6	18237.3	15296.5	2940.82	4588.95	10707.6	10346.8	6839.38
Vapor Phase									

Flowsheet | B29 (Flash2) | B39 (Flash2) | B38 (Heater) | B37 (Compr) | **Results Summary - Streams (All)** | Main Flowsheet | B36 (RadFrac) | B35 (Heater) | B34 (Flash2)

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

	Units	S40	S41	S42	S43	S44	S46	S47	S48
Mole Fractions									
CO		0.00198839	0.0668898	3.71897e-05	3.71897e-05	1.0795e-173	4.56953e-05	4.56953e-05	4.56953e-05
CO2		1.07093e-05	0.000304024	1.89099e-06	1.89099e-06	8.24577e-136	2.32348e-06	2.32348e-06	2.32348e-06
H2O		0.407326	0.027171	0.418755	0.418755	1	0.285819	0.285819	0.285819
CH3OH		0.568678	0.161652	0.580915	0.580915	2.04895e-37	0.713775	0.713775	0.713775
H2		0.0219971	0.743983	0.000291174	0.000291174	5.92307e-173	0.000357767	0.000357767	0.000357767
Mass Flows	**kg/hr**	**110215**	**1135.27**	**109080**	**109080**	**13982.6**	**95097.2**	**95097.2**	**95097.2**
CO	kg/hr	239.222	234.879	4.34368	4.34368	2.34687e-169	4.34368	4.34368	4.34368
CO2	kg/hr	2.02436	1.67734	0.34702	0.34702	2.81662e-131	0.34702	0.34702	0.34702
H2O	kg/hr	31518.3	61.3636	31456.9	31456.9	13982.6	17474.3	17474.3	17474.3
CH3OH	kg/hr	78265.1	649.332	77615.8	77615.8	5.09568e-33	77615.8	77615.8	77615.8
H2	kg/hr	190.462	188.015	2.44756	2.44756	9.26743e-170	2.44756	2.44756	2.44756
Mass Fractions									
Volume Flow	l/min	46164.7	44832.2	2885.32	4984.61	328.799	1.61619e+06	1.41163e+06	2871.3
Vapor Phase									

CONCLUSION FROM ASPEN SIMULATION:

CH3OH		0	0	0.715847

The final methanol conversion is 0.715847 as shown in the desired methanol stream.

CO		0.3	0	3.84611e-06
CO2		0.7	0	3.13483e-06

The final mole fractions of Carbon monoxide and Carbon dioxide is : $3.84 * 10^{-6}$ and $3.13 * 10^{-6}$. The conversion efficiency of CO is 99.96 % and CO2 is 99.99% from these results obtained from Aspen.

P-x Diagram Analysis for CO_2 Solubility

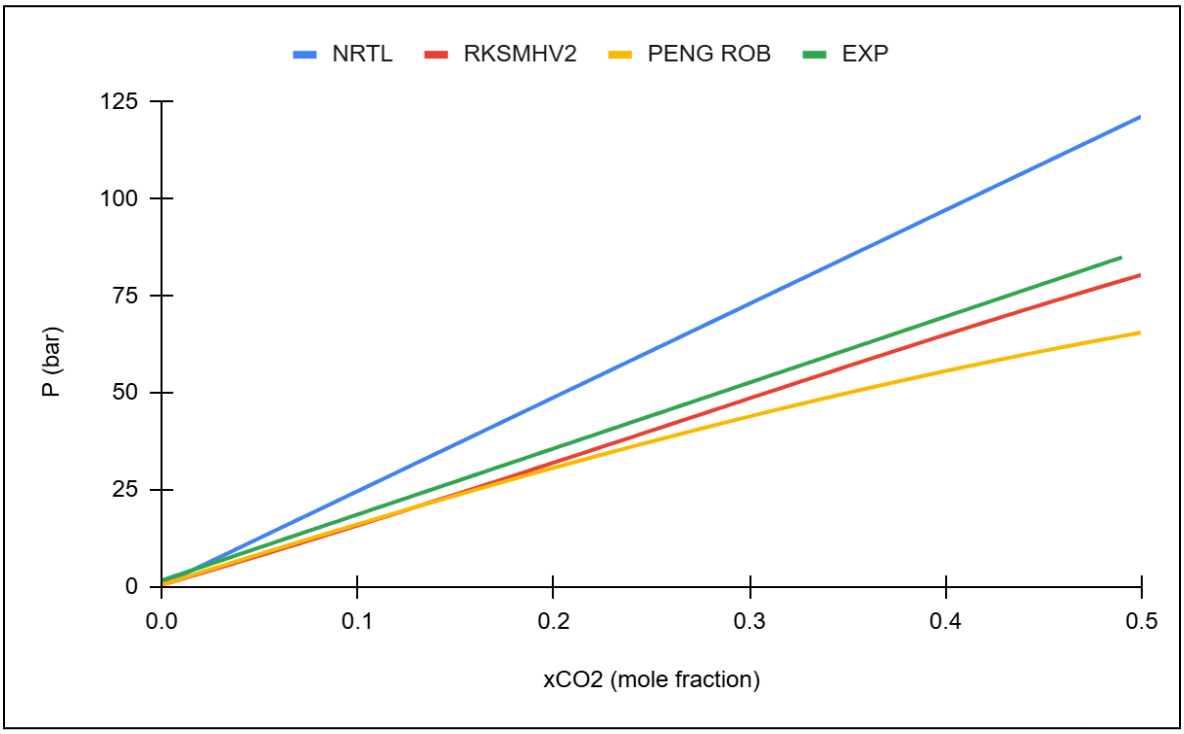


Figure: P-x of CO2 in CH_3OH(Methanol) at 323.15K

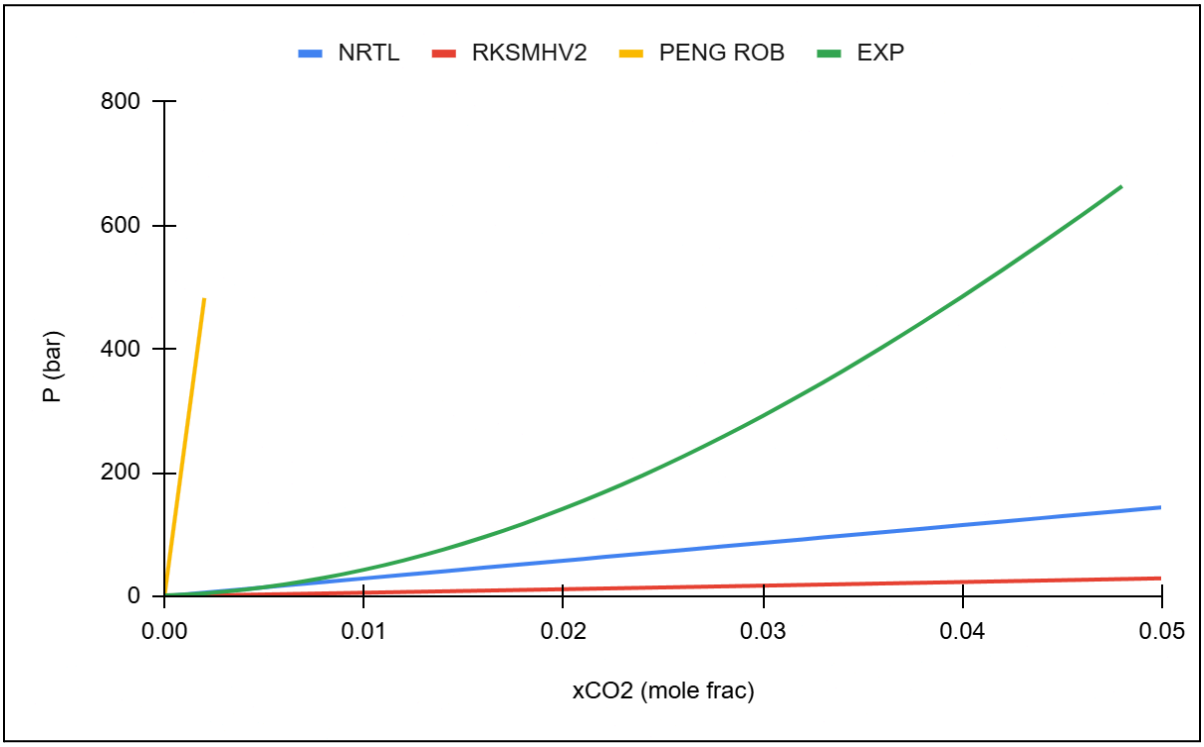


Figure: P-x of CO2 in H20(water) at 323.15K.

In this study, the solubility of CO_2 in methanol and water was analyzed using three thermodynamic models: **RKSM V2, Peng-Robinson (PR), and NRTL**. The predicted solubilities were compared against experimental data at **323.15 K** to assess the accuracy of these models.

Key Observations from P-x Diagrams:

1. **CO_2 Solubility in Methanol:**
    - **RKSMHV2** provided the best solubility predictions, with minimal deviations from experimental values.
    - **Peng-Robinson (PR)** under-predicted solubility, except for the CO_2-methanol system, where the results were more accurate.
    - **NRTL** produced relatively accurate solubility estimates, particularly when Henry's constants were specified.

2. **CO_2 Solubility in Water:**
    - **Both RKSMHV2 and NRTL overestimated solubility**, with RX MHV2 showing greater deviation.
    - The solubility of CO_2 in water was significantly lower than in methanol, meaning these deviations had minimal impact on process simulation results.
    - **PR performed the worst for CO_2-water predictions**, further confirming its limitations in handling polar systems.

Conclusion:

The analysis of P-x diagrams confirmed that RKSMHV2 is a **suitable thermodynamic model for methanol-based systems**, as it **accurately predicts CO_2 solubility in methanol while maintaining computational efficiency**. Despite its minor overestimation in water, the deviations do not significantly impact the overall process design. The results from this study align with previous literature, reinforcing the choice of RKSMHV2 for reactor and separation unit simulations.

T-x-y Diagram Analysis for Methanol-Water System

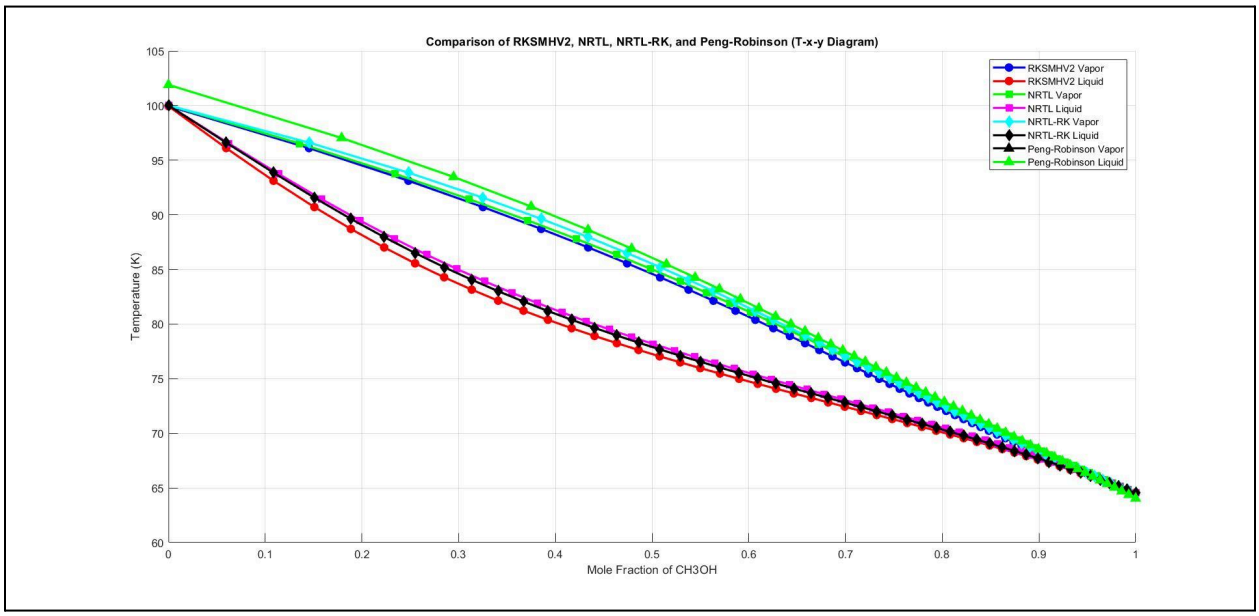


Figure: Comparison of RKSMHV2, NRTL, NRTL-RK, and Peng Robinson(T-xy diagram).

The phase equilibrium behavior of the methanol-water system was analyzed by generating T-x-y diagrams using four thermodynamic models: RKSMV2, NRTL, NRTL-RK, and Peng-Robinson (PR). The objective was to compare their accuracy in predicting vapor-liquid equilibrium (VLE) and determine the most suitable model for process simulation.

Key Observations from T-x-y Diagrams:

1. **Overall Agreement Between Models:**
    - The **bubble point** (liquid-to-vapor transition) and **dew point** (vapor-to-liquid transition) curves were closely aligned for all models, confirming their reliability for VLE calculations.
    - RKSMHV2, NRTL, and NRTL-RK provided **similar temperature predictions**, with minor deviations in composition regions.
    - **Peng-Robinson showed slight deviations** in the vapor phase region, likely due to its cubic equation of state approach.

2. **Model-Specific Differences:**
    - **Bubble Point Temperatures:**
        - RKSMHV2 predicted slightly **lower bubble point temperatures** compared to NRTL models.
        - NRTL and NRTL-RK showed **higher bubble points**, likely due to their explicit treatment of molecular interactions.

- **Dew Point Temperatures:**
  - RKSMHV2 and Peng-Robinson predicted **higher dew point temperatures**, suggesting that equation-of-state models overestimate vapor-phase methanol concentrations.
  - NRTL-based models provided **more accurate liquid-phase equilibrium data** due to their activity coefficient approach.

Conclusion :

The T-x-y diagram analysis confirms that all models provide reasonable phase equilibrium predictions, with RKSMHV2 emerging as the preferred choice due to its balance between predictive accuracy and computational efficiency. While NRTL-based models offer precise liquid-phase data, RKSMV2's ability to model polar and non-polar compounds without requiring binary interaction parameters makes it ideal for methanol-water and methanol-hydrogen systems.

This validation ensures that RKSMHV2 can be confidently used for reactor and separation unit simulations in Aspen Plus, supporting accurate process design and optimization.

Future Work :

For our future work, we plan to implement an optimized dual-stage reactor system that integrates both non-adiabatic and adiabatic reactors to enhance methanol synthesis efficiency. The first-stage non-adiabatic reactor will enable higher conversion at lower temperatures, while the second-stage adiabatic reactor will sustain reaction rates under reduced reactant concentrations.

We also aim to optimize heat recovery by effectively utilizing waste heat to generate steam, minimizing energy deficits, and improving overall process sustainability. This approach will not only enhance conversion efficiency but also reduce operational costs, making the process more economically and environmentally viable.

We also aim to design and develop and develop a flowsheet for the conversion of methanol to formaldehyde.

References:

(1)Chiou, H.-H.; Lee, C.-J.; Wen, B.-S.; Lin, J.-X.; Chen, C.-L.; Yu, B.-Y. Evaluation of Alternative Processes of Methanol Production from CO2: Design, Optimization, Control, Techno-Economic, and Environmental Analysis. *Fuel* 2023, *343*, 127856–127856. https://doi.org/10.1016/j.fuel.2023.127856.