CHE453: Capstone Project

Bi-weekly report number: 2

Team members:

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Operating Conditions

The Molar Ratio (Methanol : MEB : HCl = 16.59 : 2.7 : 0.1215)

High Excess of Methanol: The Primary purpose is to drive the equilibrium toward ester formation. Methanol acts both as a reactant and as a solvent. According to Roberts & Urey (1938)[1], this ratio enabled a large amount of water in the product. In our process, water helped in the energy-efficient separation of methanol to help with efficient methanol recovery.

Low concentration of HCl catalyst: Roberts & Urey (1938)[1], mention that "attempts to make the reaction go to completion in a short time resulted in esterification of the large amount of hydrochloric acid catalyst which must be used". Hence catalyst reaction must be prevented even if the residence time increases.

Moderate Temperature (25°C)

Roberts & Urey (1938)[1] reasoned out that
"This temperature provided a controlled environment that was:
Warm enough to maintain reasonable reaction rates
Cool enough to prevent excessive side reactions."

Our reasons for choosing this temperature: -
At this temperature, methanol, water and HCl remain in the **liquid phase**, thus suitable for our liquid phase reaction. According to the Journal of Chemical Research[2], the **solubility of benzoic acid** in methanol is around 2 mol/L at 25°C, thus well within the initial concentrations we have taken. A higher temperature might lead the HCl to react, forming alkyl chlorides with methanol.

Near Atmospheric Pressure (1 bar)

The primary reason is that this pressure is cost-effective equipment-wise. Another important reason is that no azeotropes are formed at this pressure. Since the mole difference for the reaction is zero, pressure change will not affect the reaction equilibrium conversion.

AZEOTROPE SEARCH REPORT

Physical Property Model: UNIQUAC **Valid Phase:** VAP-LIQ

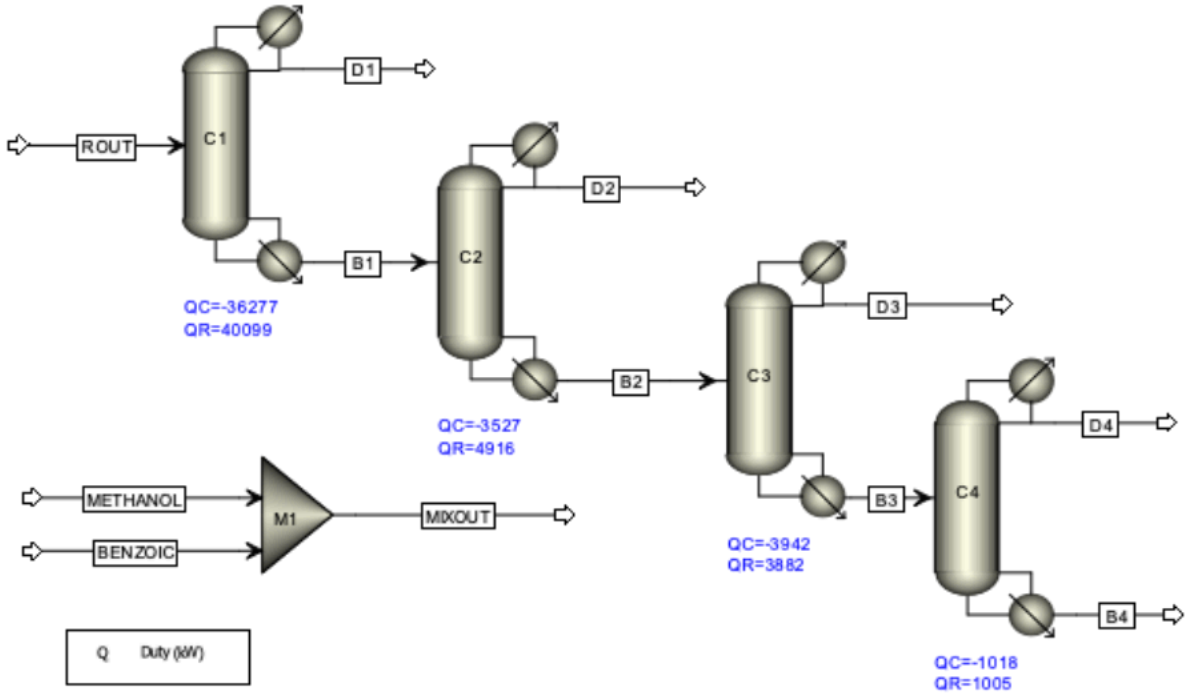
Mixture Investigated For Azeotropes At A Pressure Of 1 BAR

Comp ID	Component Name	Classification	Temperature
METHY-BE	METHYL-BENZOATE	Saddle	198.77 C
METHA-01	METHANOL	Saddle	64.20 C
WATER	WATER	Saddle	99.65 C
HYDRO-01	HYDROGEN-CHLORIDE	Unstable node	-85.32 C
BENZO-01	BENZOIC-ACID	Saddle	248.44 C
PHTHA-01	PHTHALIC-ACID	Stable node	324.61 C

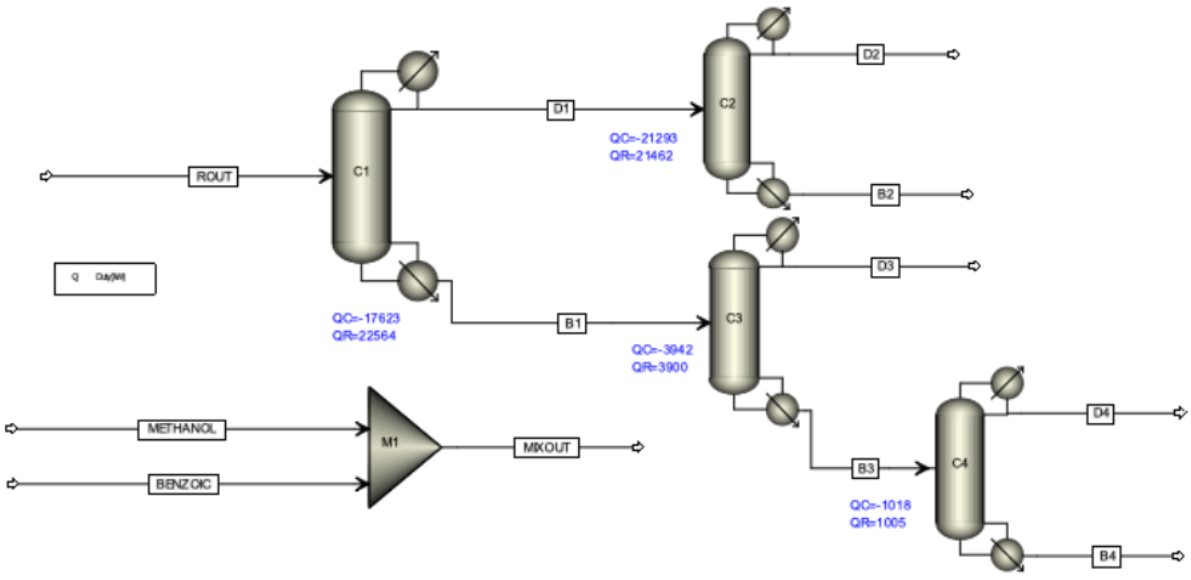
No Azeotropes Were Found

Flowsheet

Method 1:



Method 2:



Key Assumption: Due to the unavailability of kinetics data, we have assumed a conversion of 80% (since recycling will be done in later weeks as instructed in deliverables, which can be expected to take the conversion beyond 90%), and hence the stream ROUT is taken to be the stream that is coming out of the reactor, which will be connected in coming weeks between MIXOUT and ROUT.

Method 1:

Aspen Results:

	Units	METHANOL	BENZOIC	MIXOUT	ROUT	D1	B1	D2	B2	D3	B3	D4	B4
Temperature	C	25	25	31.079447	25	64.222648	113.44837	91.276941	205.76891	190.89376	250.03781	245.75004	286.42371
Pressure	bar	1	1	1	1	1	1.1	1	1.1	1	1.1	1	1.1
Molar Enthalpy	kJ/kmol	-238399.8	-371999.9	-256757.1	-259326.3	-234529.3	-304769.1	-278065.2	-308780.3	-305142.7	-326403.5	-320794.8	-560764.8
Mass Enthalpy	kJ/kg	-7440.191	-3042.037	-5777.334	-5835.144	-7324.084	-3760.472	-13874.19	-2329.822	-2261.379	-2644.361	-2614.976	-3720.213
Enthalpy Flow	kW	-112246.6	-27899.99	-140146.6	-141548.9	-95580.77	-42146.61	-17600.56	-23156.6	-18103.89	-5112.947	-4889.375	-237.2355
Mole Flows	kmol/hr	1695	270	1965	1965	1467.155	497.84501	227.86746	269.97756	213.58537	56.392189	54.869184	1.5230053
MEB	kmol/hr	0	0	0	215.2	0.000785	215.19921	2.1519921	213.04722	210.91675	2.1304722	2.1300777	0.0003946
BENZA	kmol/hr	0	269	269	53.8	0.0001963	53.799804	8.30E-05	53.799721	0.5379972	53.261723	52.729106	0.5326172
WATER	kmol/hr	0	0	0	215.2	2.152	213.048	210.91752	2.13048	2.13048	7.28E-09	7.28E-09	5.97E-15
METH	kmol/hr	1695	0	1695	1479.8	1465.002	14.798	14.79786	0.0001397	0.0001397	1.36E-15	0	0
PTH	kmol/hr	0	1	1	1	3.65E-06	0.9999964	2.92E-06	0.9999934	0	0.9999934	0.0099999	0.9899935
Mole Fractions													
MEB		0	0	0	0.1095165	5.35E-07	0.4322615	0.0094441	0.7891294	0.9875056	0.0377796	0.038821	0.0002591
BENZA		0	0.9962963	0.1368957	0.0273791	1.34E-07	0.1080654	3.64E-07	0.1992748	0.0025189	0.9444876	0.9609967	0.3497146
WATER		0	0	0	0.1095165	0.0014668	0.4279404	0.9256149	0.0078913	0.0099748	1.29E-10	1.33E-10	3.92E-15
METH		1	0	0.8625954	0.7530789	0.9985325	0.0297241	0.0649406	5.17E-07	6.54E-07	2.42E-17	0	0
PTH		0	0.0037037	0.0005089	0.0005089	2.49E-09	0.0020086	1.28E-08	0.003704	0	0.0177328	0.0001823	0.6500263

Enthalpy balance:

Enthalpy Balance			mix out	c1 in		c2 in		c3 in		c4 in		
	-404087652	-100439974.7	-504527626.7	-509576118.8	-344090784.3	-151727789.2	-633620104.05	-833637455.19	-651740100.63	-184066007.87	-176017409.19	-85404.7215
	-504527626.7				-495818573.5		-146725759.2		-835806108.5		-184557966.91	
	mixin				c1 out		c2 out		c3 out		c4 out	

Mole/mass balance:

			mix out	c1 in		c2 in		c3 in		c4 in		
Mole/Mass Balance	1695	270	1965	1964.999999	1467.154985	497.8450143	227.8674582	269.9775562	213.5853672	56.39218901	54.8691837	1.523005308
	1965				1964.999999		497.8450143		269.9775562		56.39218901	
	mixin				c1 out		c2 out		c3 out		c4 out	

Mole recovery:

Mole Recovery	Methanol	Rout	1479.8	D1	1465.002	%recv	99
	Benzoic Ac	Rout	53.79999984	D4	52.72910611	%recv	98.0094912
	MEB	Rout	215.1999997	D3	210.9167503	%recv	98.00964246

Energy Results:

(Kw)	C1	C2	C3	C4		
QR	40099	4916	3882	1005	QR_total	49902
QC	-36277	-3527	-3942	-1018	QC_total	-44764

Method 2:

Aspen Results:

	Units	METHANOL	BENZOIC	MIXOUT	ROUT	D1	B1	D2	B2	D3	B3	D4	B4
Temperature	C	25	25	31.07944699	25	66.16571526	199.6227892	64.22245121	93.89829794	184.2832265	250.0378125	245.7500443	286.4237315
Pressure	bar	1	1	1	1	1	1.1	1	1.1	1	1.1	1	1.1
Molar Enthalpy	kJ/kmol	-238399.7947	-371999.9062	-256757.0619	-259326.2692	-240714.8254	-309886.9344	-234528.6258	-277841.8189	-306254.8299	-326403.5103	-320794.8078	-560764.8819
Mass Enthalpy	kJ/kg	-7440.191133	-3042.037273	-5777.333799	-5835.143963	-7915.711162	-2348.659234	-7324.037071	-13863.6353	-2282.557271	-2644.361118	-2614.976145	-3720.213048
Enthalpy Flow	kW	-112246.57	-27899.99297	-140146.563	-141548.9219	-113231.2519	-23377.09423	-95477.4665	-17585.2084	-18305.74475	-5112.973175	-4889.399893	-237.236969
Mole Flows	kmol/hr	1695	270	1965	1965	1693.425016	271.5749839	1465.573246	227.8517702	215.1825039	56.39248001	54.86946544	1.523014575
MEB	kmol/hr	0	0	0	215.2	2.152	213.048	0	2.152	210.91752	2.13048	2.130085425	0.000394575
BENZA	kmol/hr	0	269	269	53.8	0	53.8	0	0	0.538	53.262	52.72938	0.53262
WATER	kmol/hr	0	0	0	215.2	213.048	2.152	2.13048	210.91752	2.151999987	1.29E-08	1.29E-08	1.06E-14
METH	kmol/hr	1695	0	1695	1479.8	1478.225016	1.574983878	1463.442766	14.78225016	1.574983878	1.74E-11	1.74E-11	5.46E-20
PTH	kmol/hr	0	1	1	1	0	1	0	0	0	1	0.01	0.99
Mole Fractions													
MEB		0	0	0	0.109516539	0.001270797	0.784490519	0	0.009444737	0.980179 69	0.037779505	0.038820962	0.000259075
BENZA		0	0.996296296	0.136895674	0.027379135	0	0.198103666	0	0	0.002500203	0.944487634	0.960996787	0.349714316
WATER		0	0	0	0.109516539	0.125808936	0.007924147	0.001453684	0.925678654	0.010000813	2.29E-10	2.35E-10	6.95E-15
METH		1	0	0.86259542	0.753078 88	0.872920266	0.005799444	0.998546316	0.064876609	0.007319293	3.08E-13	3.17E-13	3.58E-20
PTH		0	0.003703704	0.000508906	0.000508906	0	0.003682224	0	0	0	0.017732861	0.000182251	0.650026609

Enthalpy Balance:

Enthalpy Balance			mix out	c1 in	c2 in	c3 in				c4 in		
	-404087652	-100439974.7	-504527626.7	-50957619	-407632507	-841575309.21	-343718879.4	-633067500.26	-659006811.11	-184067003.43	-176018309.62	-85405300884
	-504527626.7				-491790046.2		-407025629.7		-843073804.54		-184558902.7	
	mixin				c1 out		c2 out		c3 out		c4 out	

Mole/mass Balance:

			mix out	c1 in	c2 in	c3 in				c4 in		
Mole/Mass Balance	1695	270	1965	1965	1693.425016	271.5749839	1465.573246	227.8517702	215.1825039	56.39248001	54.86946544	1.523014575
	1965				1965		1693.425016		271.5749839		56.39248001	
	mixin				c1 out		c2 out		c3 out		c4 out	

Mole recovery:

Mole Recovery	Methanol	Rout	1479.8	D2	1463.442766	%recv	98.89463211
	Benzoic Ac	Rout	53.8	D4	52.72938	%recv	98.01
	MEB	Rout	215.2	D3	210.91752	%recv	98.01

Energy Results:

(Kw)	C1	C2	C3	C4		
QR	22564	21462	3900	1005	QR_total	48931
QC	-17623	-21293	-3942	-1018	QC_total	-43876

Summary—Method 1:

- **Likely routing (from stream names & splits):** C1 first strips **methanol** overhead (D1), keeping **water + MEB + acids** in B1; C2 then removes **water** (mainly to D2); C3 recovers **MEB** (to D3); C4 polishes **benzoic acid / PTH** (to D4/B4).

- **Key recoveries (from "Mole recovery"):**
  • Methanol: D1 = **1465.002 kmol/h** (≈**99.0%** of 1479.8)
  • MEB: D3 = **210.9175 kmol/h** (≈**98.01%** of 215.2)
  • Benzoic acid: D4 = **52.7291 kmol/h** (≈**98.01%** of 53.8)

- **Losses/carryover:** **~2.152 kmol/h** MEB appears in light distillates (mostly **D2**, almost none in D1). The methanol tail in B2 is **~1.4×10^{-4} kmol/h** (negligible). PTH mostly to **B4**.

- **Duty profile:**
  • Duties: **QR_total ≈ 49,902 kW**; C1 bears the peak load (**~40,099 kW**), with much lighter C2. **QC_total ≈ 44,764 kW**.

- **Takeaways:** Very clean **MeOH** recovery early; **water** removal pushed to C2; **high peak reboiler load on C1** but similar overall energy to Method 2—excellent final purities/yields.

Summary - Method 2:

Likely routing: C1 now sends a **MeOH+H_2O-rich** overhead (D1 shows large water), with a **heavier mix** in B1; **C2** then becomes the **main methanol column** (D2 is the methanol product), and water comes out from B2. C3 and C4 again target **MEB** and **benzoic acid/PTH,** respectively.

Key recoveries:
• Methanol: **D2 = 1463.443 kmol/h** (≈**98.895%**) — ~0.1 percentage point lower than Method 1.
• MEB: **D3 = 210.9175 kmol/h** (≈**98.01%**)
• Benzoic acid: **D4 = 52.7294 kmol/h** (≈**98.01%**)

Losses/carryover: Similar **~2.152 kmol/h** MEB in light distillates, but now mostly in **D1** (rather than D2). PTH again concentrated in **B4**.

Duty profile:
• Duties: **QR_total ≈ 48,931 kW** (≈**1.95%** lower than M1); heat is **more evenly split** between C1 (**~22,564 kW**) and C2 (**~21,462 kW**). **QC_total ≈ 43,876 kW**.

Takeaways: Slightly **lower total reboiler duty** and **reduced peak load** on the first column vs. M1, at the cost of a **hair lower MeOH recovery** to the designated methanol product stream. Product yields (MEB/BA) remain essentially identical to Method 1.

Comparison between Method-1 & Method-2:

- **Energy:** Method 2 cuts **QR_total by ~971 kW (~2%)** and spreads the load across C1 & C2; Method 1 concentrates ~80% of QR in C1.
- **Recoveries:** MEB & BA ≈ **98.01%** in both. Methanol is **~99.0%** (M1) vs **~98.895%** (M2). If MeOH recycle purity/specs are tight, M1 has a slight edge; otherwise, M2's tiny shortfall may be operationally negligible.
- **Where losses appear:** The **~1% MEB loss** to lights is inevitable in both, but shows up in **D2** in **M1** and **D1** in **M2.**

Practical recommendation

- For **lower duty / easier utility integration / smaller reboiler**, **Method 2** is preferable.
- To obtain **slightly higher MeOH recovery in the designated methanol product stream** for recycle specifications and for **keeping MEB out of the first distillate**, **Method 1** has a marginal edge.
- **Notable Observation:** The above results are obtained when **light key recoveries at each shortcut distillation** were fixed at **0.99**. When recovery was made **tighter** at each column with light key recovery **at around 0.999**, the **reboiler duty energy requirements in M1** shot

up to twice its value, around **~102,000 kWh;** hence, it does not provide an economical repeatability.

- Percentage change in **methanol recovery** with change in **reboiler duty.**

Recovery 1	Recovery 2		%Recovery/Reboiler Duty
99	98.8946321		
			0.010851483
Reboiler Duty 1	Reboiler Duty 2		
49902	48931		

Objectives that could not be accomplished with reasons:

- The reactor block could not be connected, as no direct reference sheet with kinetics data was available.
- Experimental T-x-y data could not be found for any of the other pairs, even after a thorough search, and hence, we require some more time to find and analyse data of exactly similar but different pairs.

Any other challenges:

- Unavailability of kinetic data and rate law expression as a direct reference; hence, we need some time to find out ways of estimating the value of K and activation energy.

Bibliography:

[1] A Study of the Esterification of Benzoic Acid with Methyl Alcohol Using Isotopic Oxygen, Irving Roberts and Harold C. Urey

[2] Solubility of Benzoic Acid in Seven Solvents

Number of hours spent on Capstone project during this period: 17 hours total

Contributions from individual members:

1. Aaditya Amlan Panda (Configuration Visualisation and Design)
2. Abhijit Dalai (Method Selection and Flowsheeting)
3. Adarsh Pal (Method Selection and Flowsheeting)
4. Akash Kumar Gupta (Operating Condition Identification)
5. Kushagra Tiwari (Configuration Visualisation and Design)
6. Saurabh Yadav (Method Selection and Flowsheeting)
7. Snehil Tripathi (Operating Condition Identification)
8. Tushar Verma (Configuration Visualisation and Design)

Signatures of members:

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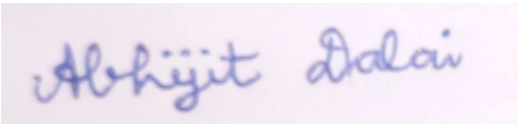
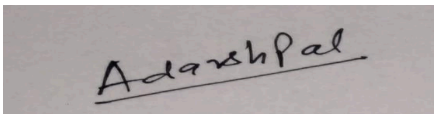
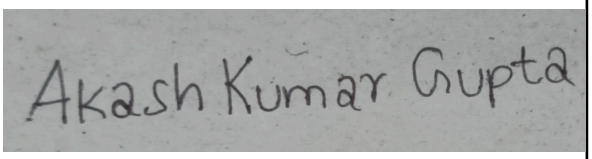
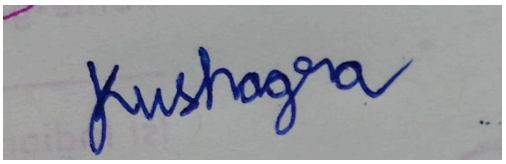
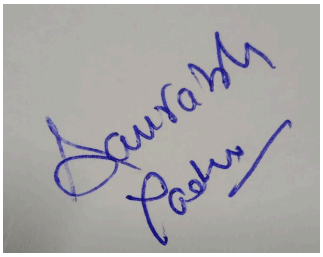
Abhijit Dalai	
Adarsh Pal	
Akash Kumar Gupta	
Kushagra Tiwari	
Saurabh Yadav	
Snehil Tripathi	
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