CHE261 PROCESS ANALYSIS

APPLICANT	Mollycule
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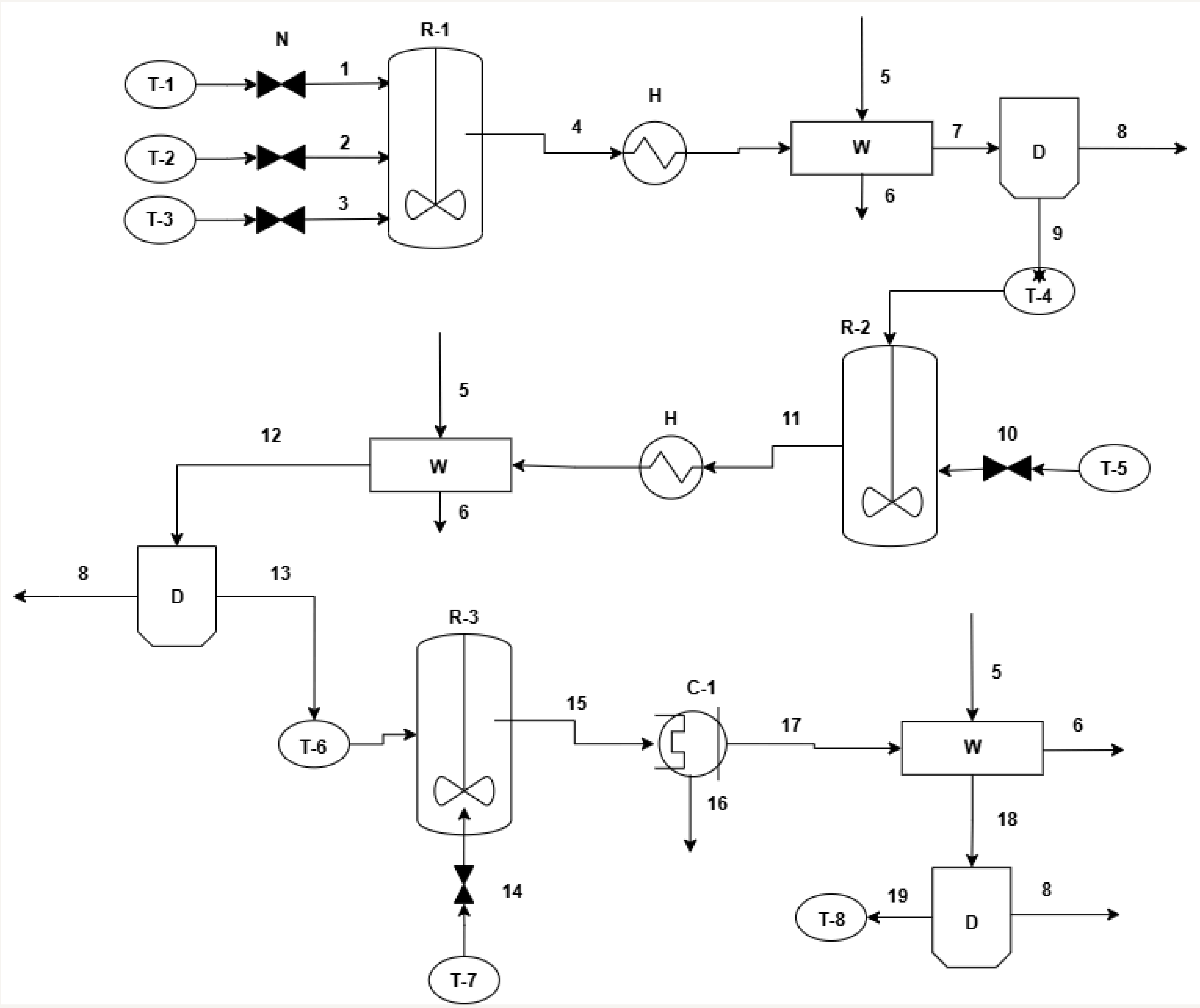
CHEMICAL FORMULA	$C_{10}H_{11}N_5O$.
CHEMICAL NAME	Pymetrozine
PROCESS TITLE	Synthesis of Pymetrozine

a) Block Diagram



1. Equipment List & Nomenclature

- T-1: Diethyl Carbonate Storage Tank
- T-2: Hydrazine Hydrate Storage Tank
- T-3: Solvent Storage Tank
- T-4: Carbodihydrazide Storage Tank
- T-5: 3-Formylpyridine Storage Tank
- T-6: Pyridyl Storage Tank
- T-7: Monochloroacetone Storage Tank
- T-8: Pymetrozine Storage Tank
- R-1: Hydrazidation Reactor (Jacketed Agitated)
- R-2: Condensation Reactor (Jacketed Agitated)
- R-3: Cyclization Reactor (Jacketed Agitated)
- C-1: Crystallizer Unit
- H: Heat Exchanger
- W: Washer
- D: Dryer

2. Process Stream List & Nomenclature

- 1: Carbonate Feed
- 2: Hydrazine Feed
- 3: Solvent Stream
- 4: Crude Carbodihydrazide Stream
- 5: Washing Solvent
- 6: waste/byproduct stream
- 7: Wet Carbodihydrazide Stream
- 8: Evaporative Loss Stream
- 9: Dried Carbodihydrazide Stream
- 10: 3-Formylpyridine Feed
- 11: Pyridinyl Hydrazide Mixture
- 12: Purified Pyridinyl Stream
- 13: Dry Pyridinyl Stream
- 14: Monochloroacetone Stream
- 15: Crude Pymetrozine Stream
- 16: Mother Liquor (Crystallization Waste)
- 17: Purified Pymetrozine Crystals
- 18: Washed Pymetrozine Crystals
- 19: Dried Pymetrozine

b) Unit Operations and Process Conditions

1. Raw Material Handling and Feeding

- Storage Tanks (Tanks-1 to Tanks-7)
  - Used for storing reactants, solvents, and catalysts.
- Pumps
  - Transfers raw materials from storage tanks to reactors.
- Flow Control Valves
  - Regulates feed flow into reactors.

2. Reaction Stages

- Reaction 1: Hydrazidation (Carbodihydrazide Synthesis)

$$(C_2H_5O)_2CO + 2N_2H_4 \cdot H_2O \rightarrow H_2N-NH-CO-NH-NH_2 + 2C_2H_5OH$$

  - Jacketed & Agitated Reactor-1
    - Reaction Type: Nucleophilic Substitution
    - Temperature: 75–80°C
    - Pressure: Atmospheric
    - Residence Time: 2–4 hours
    - Reactants: Dialkyl Carbonate + Hydrazine Hydrate
    - Solvent: Ethanol/Water
    - Byproducts: Alcohol (methanol or ethanol)

- Reaction 2: Condensation (Pyridin-3-ylmethylenecarbodihydrazide Synthesis)

$$CH_6N_4O + C_6H_5NO \rightarrow C_7N_5H_9O + H_2O$$

  - Jacketed & Agitated Reactor-2
    - Reaction Type: Schiff Base Condensation
    - Temperature: 50–70°C
    - Pressure: Atmospheric
    - Residence Time: 3–5 hours
    - Reactants: Carbodihydrazide + 3-Formylpyridine
    - Solvent: Ethanol/THF
    - Byproducts: Water

- Reaction 3: Cyclization (Pymetrozine Synthesis)

$$C_7H_9N_5O + C_3H_5ClO \rightarrow C_{10}H_{11}N_5O + HCl + H_2O$$

  - Jacketed & Agitated Reactor-3
    - Reaction Type: Cyclization
    - Temperature: 80–100°C
    - Pressure: Atmospheric or slight vacuum
    - Residence Time: 4–6 hours
    - Reactants: Pyridin-3-ylmethylenecarbodihydrazide + Monochloroacetone + Base (K_2CO_3/Na_2CO_3)
    - Solvent: Ethanol/THF
    - Byproducts: Salt, H_2O, excess reagents

3. **Post-Reaction Processing**

- Cooling
  - Heat Exchangers (1, 2)
    - Type: Shell & Tube or Plate
    - Cooling Medium: Chilled water or glycol
    - Exit Temperature: ~25–30°C

  - Crystallizer (C-1)
    - Function: Cools down the crude pymetrozine solution to induce crystallization
    - Cooling Medium: Chilled glycol or water jacket
    - Exit Temperature: Adjusted for optimal crystal formation

- Purification & Drying
  - Washers (1, 2, 3)
    - Type: Countercurrent Washing
    - Washing Medium: Water/Ethanol
    - Purpose: Removes impurities, residual reactants, and byproducts

  - Dryers (1, 2, 3)
    - Type: Vacuum Tray Dryer or Rotary Dryer
    - Temperature: 50–70°C
    - Vacuum Level: 50–100 mmHg
    - Purpose: Removes residual moisture from solid product

c) Material Balance

Mass balance:-

1. Preparation of Carbodihydrazide (III)

Materials (Before Reaction)

→ Ethanol = 200g
→ water = 200g

$\left.\begin{matrix}\text{Ethanol} = 200g \\ \text{water} = 200g\end{matrix}\right\}$ Total solvent A = 400g

Reactive reagents:-

- Diethyl carbonate (II): 118.1g (1 mol)
- 40% hydrazine hydrate: 275g (40% pure hydrazine)

$\Rightarrow (275)(0.4) = 110g$

$\Rightarrow$ water from hydrazine $= 275 - 110g = 165g$

* Solvent to reagent ratio:-

$$\text{Ratio} = \frac{400}{118.1} = 3.39$$ (lies between 3 - 7) acc. to RnD report.

Reaction:

$$(EtO)_2CO + 2N_2H_4 \longrightarrow (NHNH_2)_2CO + 2EtOH$$

Now, moles of $N_2H_4 = \frac{110}{32} \simeq \underline{3.44}$ mol

We assume 2.2 mol hydrazine (free basis) are available to react.

→ According to reaction 2 mol consumed $= 2 \times 32 = 64g$ consumed

→ 0.2 mol $\times$ 32 = 6.4g remains unreacted

- Reaction products:-

Dihydrazine carbonate $[(NHNH_2)_2CO]$: $\simeq 90g$ produced. (1 mol)

Ethanol produced = 92g

solvent + unreacted materials →

Ethanol = 200 + 92 = 292g

water = 200 + 165 = 365g

Excess hydrazine = 6.4g (0.2 mol) + (110 - 64) gets consumed.

c) Material Balance

Around Reactor-1 (mass balance) ②

Before Reaction :-

Component	Mass (g)	Note
Ethanol (solvent)	200g	Added as solvent
Water	200g	Added as solvent
Diethyl carbonate	118.1 g	1 mol
40% hydrazine hydrate	275g	110g hydrazine, 165 g water
Total	793.1g	

After reaction

Component	Mass (g)	Notes
Dihydrazine carbonate	90 g	1 mol product
ethanol	292g	200 → solvent, 92 → prod used
Water	365 g	200 → Added, 165 → hydrazine
Unreacted hydrazine	46 g	(110 − 64).
Total	793 g	

Washer & dryer :-

20g of water added to filter cake

Total mass after water wash addition = 793.1 + 20
= 813.1g

After drying product is obtained as 88.9 g of carbodihydrazide (III)

weight represents yield of 98.8%.

compared to theoretical product mass of about 90g

Liquid phase (Mother Liquor)

After removing dried solid = 813.1 − 88.9 = 724.2g

c) **Material Balance**

Mass balance :-

(Before workup)

Component	Mass (g)	Notes.
Reaction mixture	793.1g	total mass from rxn
wash water	20g	water used to wash filter cake
Total mass	813.1g	

After work-up

Component	Mass (g)	Notes
Solid product (carbodihydrazide)	88.9g	98.8% yield (theoretical ~90g)
Liquid phase	724.2g	contains solvents and soluble impurities
Total	813.1g	

Stage-2 : Synthesis of pyridin-3-ylmethylenecarbodihydrazide (IV)

- Before Reaction

Solvent B : Ethanol = 200g, water = 100g } Total solvent = 300g

Reactive reagents :-

Carbodihydrazide (III) = 45g (0.5 mol)

3-formylpyridine = 53.6g (0.5 mol)

Ratio of solvent to carbodihydrazide:-

* $= \frac{300}{45} = 6.67$ (lies between 5-10 range) acc. to RnD report.

Water elimination :-

For 0.5 mol of product, water eliminated $= 0.5 \times 18 = 9g$

c) Material Balance

Theoretical mass of condensation product: ⑦

→ total mass of condensing reactants - eliminated water

= 98.6 - 9 = 89.6 g

After reaction:-

Solid condensation product = 89.6g (rxn 100% yield completion)

water: 100g + 9.0g = 109g

* (Before Reaction)

Component	Mass (g)	Notes.
Ethanol	200 g	Added solvent
Water	100 g	Added solvent
Carbodihydrazide	45g.	0.5 mol (MW ≃ 90 g/mol)
3-formylpyridine	53.6g	0.5 mol (MW = 107.1 g/mol)
Total	398.6 g	

After reaction:

Component	Mass (g)	Notes.
Condensation product	89.6 g	98.6 g formed with 9 g of water elimination
Water eliminated (by product)	9 g	produced during condensation
Remaining liquid (Mother liquor)	309 g	Contains ethanol & water (100+9+200)
Total	398.6 g	

* Washer & dryer part:-

100g ethanol is added to dissolve 3-formylpyridine

Total mass before washer becomes = 398.6 + 100

≃ ~~498~~ 498g

c) Material Balance

30g of water is added to wash the filter cake

After drying 89 g of pyridin-3-ylmethylene carbonyl-dihydrazide (IV) obtained.

* Before washer & dryer

Component	Mass (g)	Notes
Reaction Mixture	498g	Contains the formed condensation product, solvent and water (eliminated) included
Wash water added	30g	used to wash filter cake
Total	528g	

After washer & Dryer:-

Component	Mass (g)	Notes Eg
Isolated, solid product	89g	product yield of compound (IV), yield = 99.9%
Mother liquor	439 g	Combined solvents and dissolved residues.
Total	528g	

* Stage-3: Preparation of pymetrozine:-

Compound (IV) is used: 71.6 g (0.4 mol)

Monochloroacetone is used: 40.7g (0.44 mol)

Rxn

Compound (IV) + Monochloroacetone ⟶ pymetrozine + HCl

HCl produced (≈0.4 mol, 14.6g) is neutralized by K_2CO_3.

$K_2CO_3 + 2HCl \longrightarrow 2KCl + H_2O + CO_2$

c) Material Balance

Molecular weight of pymetrozine ≈ 234.05 g/mol

for 0.4 mol ⇒ (0.4)(234.05) ≈ 93.6 g

Overall Input:- Compound (IV) = 71.6 g

Monochloroacetone = 40.7 g

K_2CO_3 = 34.5 g

Solvents (Ethanol + Water) = 350 g

Total ≈ 492.6

Solvent C :-

Ethanol = 200 g + 50 g ⌉ dropwise addition

Water = 100 g ⌋ 350 g = Total

Component	Mass (g)	Notes
Comp. (IV)	71.6 g	0.4 mol
Monochloroacetone	40.7 g	0.44 mol
K_2CO_3	34.5 g	0.25 mol
Ethanol	200 g	Solvent C
Water	100 g	Solvent C
Ethanol	50 g	Used to dissolve monochloroacetone
Total	≈ 492.6 g	

Mass balance After reaction:

Component	Mass (g)	Notes
~~Pymetrozine~~ (cyclized) product	93.6 g	After reaction
KCl	29.8	KCl produced.
Water	108.6	from neutralization + initial
Excess K_2CO_3	6.9	≈ 0.05 mol remaining
Ethanol	250 g	200 g initial + 50 g dropwise
CO_2	8.8 g	0.2 mol CO_2 released
Total	492.7 g	

c) Material Balance

Washer and dryer :-

(final solid product obtained = 83.9 g which is 96.6% of theoretical 86.8 g)

30 g of water used to wash filter cake

Before work-up

Component	Mass	Notes.
Reaction Mixt.	492.6	Remains as total mass after reaction
Wash water added	30g	used to wash filter cake
Total	522.6	

After work-up :-

Component	Mass	Notes
Dried product	83.9g	Final solid product obtained
Mother liquor	438.7g	Contains bulk of solvents, and by products
Total	522.6g	

Now scaling up to produce 1000 kg/day pymetrozine, the input required at stage 1 should be.

$$\text{Scale factor} = \frac{1000 \times 10^3}{83.9} = 11,918.$$

Ethanol = 200×11918 = 2383 kg

water = 200 × 11918 = 2383 kg

Diethyl carbonate = 118.1× 11918 = 1407.5 kg

40% Hydrazine hydrate = 275 × 11918 = 3277.4 kg

wash water for filtration = 20×11918 = 262 kg

c) <u>Material Balance</u>

* Scaling for stage 2:-

(8)

Scale factor =

89 g of (IV) produced from 45g ⇒ 89/45 = 1.978

Scaled stage 1 feed (9438 kg) yields (88.9 g per 793.1g) an output of

$$\left(\frac{88.9}{793.1}\right) \times 9438 \text{ kg} \simeq 1056.9 \text{ kg of (III)}$$

$$(\text{Scale factor})_2 = \frac{1056.9 \times 10^3}{45} = 23486$$

Required

→ Carbodihydrazide (III) = 45 × 23486 = 1056.9 kg

→ 3-formylpyridine = 53 × 23486 = 1244 kg

→ Ethanol = 200 × 23486 = 4697 kg

→ water = 100 × 23486 = 2349 kg.

→ Ethanol (in reagent) = 100 × 23486 = 2349 kg

Stage-3:-

Conversion 71.6 (IV) ⟶ 83.9 g (factor ≃ 1.171)

Stage (2) produce compound (IV) ~ 2089 kg

$$\text{Scale factor} = \frac{2089 \times 10^3}{71.6} \simeq 29{,}170$$

Required:-

→ Monochloroacetone = 1186 kg

→ Potassium Carbonate = 1007 kg

→ Solvents (Ethanol) = 250 × 29170 = 7293 kg

→ Solvent (water) = 100 × 29170 = 2917 kg

d) Reactor Sizing and Cost Estimation

Reactor Capacity Calculation

- The required reactor volumes are calculated using mass balance data and an densities of all the components. The actual reactor design capacity is determined considering only 70% of the total volume can be utilized.

- **Stage 1:**

Input:

Component	Mass (kg/day)
Diethyl Carbonate	1,404.50
Hydrazine Hydrate (40%)	3,279.4 (1,312 kg hydrazine + 1,967.4 kg water)
Ethanol	2,383
Water	2,383
Wash Water	262
Total Mass	9,712.90

d) Reactor Sizing and Cost Estimation

- **Stage 1:**

Volume Estimation:

Component	Mass (kg)	Density (kg/L)	Volume (L)
Diethyl Carbonate	1,404.50	~0.975	1,441.50
Hydrazine Hydrate (40%)	3,279.40	~1.032	3,176.40
Ethanol	2,383	~0.789	3,020.30
Water	2,383	~1.000	2,383.00
Wash Water	262	~1.000	262
Total Volume			10,283.20

Reactor Volume Calculation:

- Total Reactor Volume = (Total Estimated Volume)/0.7
  = 10,283.2/0.7
  = 14,690.3 L

d) Reactor Sizing and Cost Estimation

Reactor Capacity Calculation

- The required reactor volumes are calculated using mass balance data and an densities of all the components. The actual reactor design capacity is determined considering only 70% of the total volume can be utilized.

- **Stage 2:**

Input:

Component	Mass (kg/day)
Carbohydrazide (III)	1,056.9
3-Formylpyridine	1,244
Ethanol	4,697
Water	2,349
Ethanol (in exaqut)	2,349
Total Mass	11,695.9

d) Reactor Sizing and Cost Estimation

- **Stage 2:**

Volume Estimation:

Component	Mass (kg)	Density (kg/L)	Volume (L)
Ethanol	7,046	~0.789	8,929.7
Water	2,349	~1.000	2,349.0
Carbohydrazide & 3-Formylpyridine	2,300.9	~1.2	1,928.25
Total Volume			13,207.0

Reactor Volume Calculation:

- Total Reactor Volume = (Total Estimated Volume)/0.7
  = 13,207/0.7
  = 18,867.1 L

d) Reactor Sizing and Cost Estimation

Reactor Capacity Calculation

- The required reactor volumes are calculated using mass balance data and an densities of all the components. The actual reactor design capacity is determined considering only 70% of the total volume can be utilized.

- **Stage 3:**

Input:

Component	Mass (kg)
Monochloroacetone	1,188
Potassium Carbonate	1,007
Ethanol (Solvent)	7,293
Water (Solvent)	2,917
Total Mass	12,405

d) Reactor Sizing and Cost Estimation

- **Stage 3:**

Volume Estimation:

Component	Mass (kg)	Density (kg/L)	Volume (L)
Ethanol	7,293	~0.789	9,243.4
Water	2,917	~1.000	2,917.0
Monochloroacetone & Potassium Carbonate	2,195	~1.2	1,829.2
Total Volume			13,989.6

Reactor Volume Calculation:

- Total Reactor Volume = (Total Estimated Volume)/0.7
  = 13,989/0.7
  = 19,985.1 L

d) Reactor Sizing and Cost Estimation

Reactor Volume Estimation Table for all 3 reactors:

Reactor	Total Mass in Reactor (kg/day)	Estimated Volume (L)	Design Capacity (L) (Based on 70% usage)
Reactor 1	9,711.9	10,283.2	14,690.3
Reactor 2	11,695.9	13,207 L	18,867
Reactor 3	12,405	13,989.6	19,985.1

d) Reactor Sizing and Cost Estimation

Capital Cost Estimation

- The cost estimation is based on the Matche Equipment Cost Calculator and we are utilizing Jacketed and Agitated Reactor in each with material as Glass Lined CS and pressure set between atmospheric to 25 psi.

  Capital Cost Table:

Equipment	Design Capacity (gallons)	No. of Units	Cost/unit ($)
Reactor 1 (Jacketed, Agitated, Glass-lined CS)	3880.7	1	96,300
Reactor 2 (Jacketed, Agitated, Glass-lined CS)	4984.13	1	110,000
Reactor 3 (Jacketed, Agitated, Glass-lined CS)	5279.5	1	113,400

Total Cost: $ 319,700 = ₹ 2,73.53,116

References:

- https://patents.google.com/patent/CN104844574A/en
- https://www.matche.com/equipcost/Reactor.html

Contribution of each member

Shreyas Gupta (230991)

- Designed the Process Flow Diagram (PFD), incorporating all unit operations such as reactors, washers, dryers, crystallizers, and heat exchangers.
- Defined key process conditions (temperature, pressure, solvent recovery, waste handling) for efficient operation.
- Sized the reactors based on process conditions, ensuring 70% of total volume utilization for reaction mixtures.
- Conducted a capital cost estimation, doing cost analysis of Glass-Lined Carbon Steel (GLCS) reactors.

Ankit Yadav(231181)

- Performed a detailed material balance for the scaled-up process plant (1000 kg/day).
- Determined input and output flow rates for all process streams and unit operations.
- Established assumptions for simplified yet accurate calculations, ensuring precise mass flow tracking.
- Optimized reactant consumption and efficiency, reducing material losses and improving yield.

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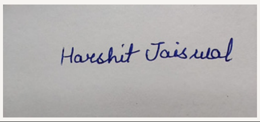
HARSHITJAISWAL	230460	
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