Technical Team

Nature of Invention: Process Flow Diagram and Mass Balance

Applicant: ChemEverse

Inventors: Tanvi Manhas, Harshvardhan Agarwal

Chemical Formula: CH2=C(R)-COO-(CH2CH2O)nR’

[R = H or CH_3 (from acrylic or methacrylic acid backbone)]

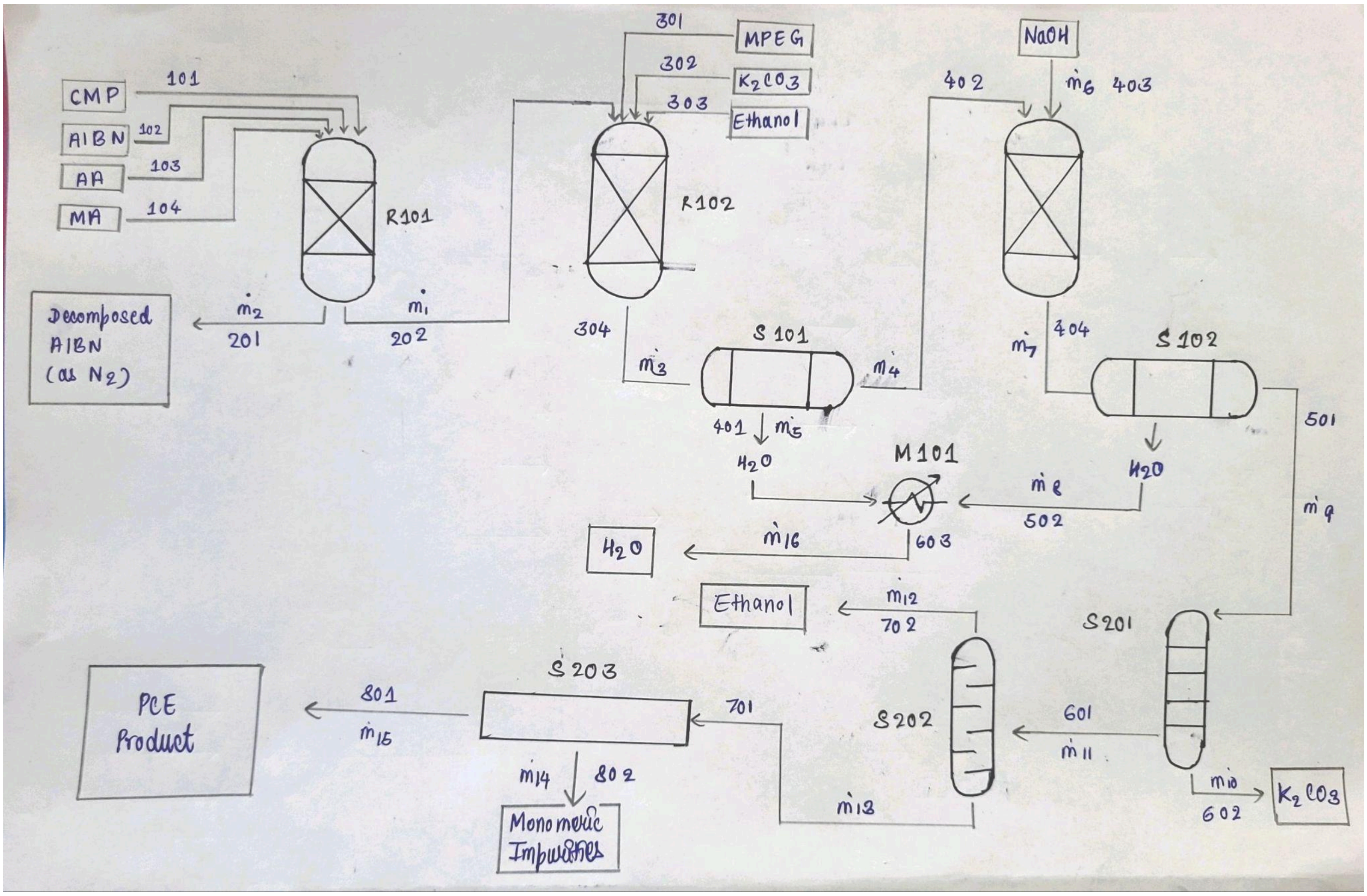
[R' = End group, often an alkyl or ether group]

Chemical Name : Polycarboxylate Ether

Process Title: Two-Step Synthesis of Polycarboxylate Ether with Neutralization

Process Description:

1. **Block Diagram**



Unit Operations and Process Conditions :

- R101 - Polymerisation Reaction

  Process Conditions : Requires controlled temperature (around 70°C) and N2 atmosphere to prevent oxidation. The synthesis temperature is critical, with optimal conditions typically around 70°C for the main chain formation.

- R102 - Esterification Reaction

  Process Conditions : Requires controlled heating & continuous N_2 purge to remove byproduct water.

- R103 - Neutralisation Reaction

  Process Conditions : Requires pH control to ensure complete ionization of the polycarboxylate groups, typically around pH 6-7.

- S101 - Phase Separation (Decantation)
- S102 - Phase Separation (Decantation)
- S201 - Filtration (Solid-Liquid Filtration)
- S202 - Evaporation (Vacuum DIstillation)
- S203 - Purification (Membrane Filtration)
- M101 - Condenser

Material Naming Convention :

- AA - Acrylic Acid
- CMP - 3-Chloro-2-methyl-1-propene
- MA - Methacrylic Acid
- AIBN - Azobisisobutyronitrile
- MPEG - Methoxy Poly Ethylene Glycol

Time : Reaction times can vary from 6 to 8 hours depending on the specific step and conditions.

2. Material Balance for a scaled-up Process Plant with capacity of 1000 kg/day

i) **Material Balance about R101**

Input Streams :

- Stream 101 - 100 g CMP
- Stream 102 - 0.5 g AIBN
- Stream 103 - 300 g AA
- Stream 104 - 100 g MA

Reaction :

$$4\,C_3H_4O_2 + CH_2{=}C(CH_3)\text{-}CH_2Cl + CH_2{=}C(CH_3)\text{-}COOH \xrightarrow{\text{AIBN, Heat}} [\text{-}CH_2\text{-}CH(COOH)\text{-}]_4\text{-}[\text{-}CH_2\text{-}C(CH_3)\text{-}CH_2Cl]\text{-}[\text{-}CH_2\text{-}C(CH_3)\text{-}COOH]\text{-}$$

Calculations:

Conversion of AA = 96%

Unreacted AA = 300 - 0.96*300 = 12 g

AA reacted = 288 g = 288/72 = 4 mol

AA is the limiting reagent. 4 mol AA will react with 1 mol CMP and 1 mol MA to give 1 mol of Intermediate Polymer.

1 mol CMP = 90.5 g

1 mol AA = 72 g

1 mol MA = 86 g

Total mass of reactants = 288 + 90.5 + 86 = 464.5 g

Total mass of Reactants = Mass of Intermediate Polymer = 464.5g

Unreacted compounds :

- AA : 300 - 288 = 12 g
- MA : 100 - 86 = 14 g
- CMP : 100 - 90.5 = 9.5 g

Output Streams :

Stream 201 : m2 = 0.5g

Stream 202 :

- Intermediate Polymer : 464.5 g
- AA : 12 g
- MA : 14 g
- CMP : 9.5 g

m1 = 464.5 + 12 + 14 + 9.5 = 500 g

ii) **Material Balance about R102**

Input Streams :

- Stream 301 - 10,000 g MPEG
- Stream 302 - 2.5 g K2CO3

- Stream 303 - 500 g Ethanol
- Stream 304 - N2 (continuous purge stream)
- Stream 202 - 500 g

Reaction :

$$\text{-COOH} + \text{CH}_3\text{O-(CH}_2\text{CH}_2\text{O)}_n\text{-H} \xrightarrow{\text{K}_2\text{CO}_3} \text{-COO-(CH}_2\text{CH}_2\text{O)}_n\text{-CH}_3 + \text{H}_2\text{O}$$

Calculations:

In each Intermediate Polymer, there are 5 -COOH groups. 1 mol Polymer will require 5 mol MPEG to esterify it, giving 1 mol PCE, and 4 mol H2O

Efficiency of esterification = 80%

Moles of Intermediate Polymer esterified = 0.8 * 1 = 0.8 mol. Mass = 0.8 * 464.5 = 371.6 g.

Moles of Intermediate Polymer unreacted = 1 - 0.8 = 0.2 mol. Mass = 464.65 - 371.6 = 92.9 g

Mols of MPEG required = 0.8 * 5 = 4 mol. Molar mass of MPEG = 2000 g/mol. Total mass = 4 * 2000 = 8000 g. Now, we can see that we have excess MPEG. Therefore, unreacted MPEG = 10,000 - 8000 = 2000 g.

Moles of H2O formed = 4 * 0.8 = 3.2 mol. Mass = 3.2 * 18 = 57.6 g.

Moles of PCE formed = 0.8 mol. Mass = Mass (Reactants) - Mass(H2O) = 371.6 + 8000 - 57.6 = 8314 g.

Output Streams :

Stream 304 :

- PCE = 8314 g
- H2O = 57.6 g
- Intermediate Polymer = 92.9 g
- MPEG = 2000 g
- Ethanol = 500 g
- K2CO3 = 2.5 g
- AA = 12 g
- CMP = 9.5g
- MA = 14 g

m3 = 8314 + 57.6 + 92.9 + 2000 + 500 + 2.5 + 12 + 9.5 + 14 = 11002.5 g

iii) **Material Balance about S101**

Input Streams: Stream 304

All water is removed from this stream.

Output Streams:

- Stream 401 : m5 = 57.6 g H_2O
- Stream 402 : m4 = 11002.5 - 57.6 = 10944.9 g

iv) **Material Balance about R103**

Input Streams :

- Stream 402 - 10,944.9 g
- Stream 403 - m6 g

Reaction :

$$\text{-COOH} + \text{NaOH} \rightarrow \text{-COONa} + H_2O$$

Calculations :

Intermediate Polymer = 92.9 g = 0.2 mol. Each polymer molecule has 5 -COOH groups. 1 mol of Polymer will react with 5 mol NaOH to give 1 mol Sodium Polycarboxylate and 5 mol H_2O.

Moles of NaOH required = 0.2 * 5 = 1 mol. Mass = 40 g = m6

Moles of H_2O formed = 0.2 * 5 = 1 mol. Mass = 18 g

Moles of Sodium Polycarboxylate formed = 0.2. Mass = 92.9 + 40 - 18 = 114.9 g

Output Streams :
Stream 404

- PCE = 8314 g
- H_2O = 18 g
- Sodium Polycarboxylate = 114.9 g
- MPEG = 2000 g
- Ethanol = 500 g
- K_2CO_3 = 2.5 g
- AA = 12 g
- CMP = 9.5 g
- MA = 14 g

m7 = 10,984.9 g

v) **Material Balance about S102**

Input Streams: Stream 404

All water is removed from this stream.

Output Streams:

- Stream 502: m8 = 18 g H_2O
- Stream 501 : m9 = 10,984.9 - 18 = 10,966.9 g

v) **Material Balance about M101**

Input Streams:

- Stream 401 : m5 = 57.6 g H_2O
- Stream 502 : m8 = 18 g H_2O

All water is condensed and removed from the plant.

Output Streams:

Stream 603 : m16 = 75.6 g

vi) **Material Balance about S201**

Input Streams: Stream 501

K_2CO_3 is filtered out from this stream.

Output Streams:

- Stream 602: m10 = 2.5 g K_2CO_3
- Stream 601 : m11 = 10.966.9 - 2.5 = 10,964.4 g

vii) **Material Balance about S202**

Input Streams: Stream 601

Ethanol is evaporated from the stream.

Output Streams:

- Stream 702: m12 = 500 g Ethanol
- Stream 701 : m13 = 10,964.4 - 500 = 10,464.4 g

viii) **Material Balance about S203**

Input Streams: Stream 701

Stream is purified, removing all the monomeric impurities and unreacted compounds.

Output Streams:

Stream 802:

- MPEG = 2000 g
- AA = 12 g
- CMP = 9.5 g
- MA = 14 g

m14 = 2035.5 g

Stream 801:

- PCE = 8314 g
- Sodium Polycarboxylate = 114.9 g

m15 = 8428.9 g

ix) **Scaling up for 1000 kg/day product**

Scaling Factor = 1000 kg / 8428.9 g = 118.64

We will scale the process up by a factor of **118.64**

x) **Final Input Streams Required for the production of 1000 kg/day**

Stream 101 : 0.1 * 118.64 = **11.864 kg/day CMP**

Stream 102 : 0.0005 * 118.64 = **0.05932 kg/day AIBN**

Stream 103 : 0.3 * 118.64 = **35.502 kg/day AA**

Stream 104 : 0.1 * 118.64 = **11.864 kg/day MA**

Stream 301 : 10 * 118.64 = **118.64 kg/day MPEG**

Stream 302 : 0.0025 * 118.64 = **0.2966 kg/day K2CO3**

Stream 303 : 0.5 * 118.64 = **59.32 kg/day Ethanol**

Stream 403 : 0.04 * 118.64 = **4.7456 kg/day NaOH**

xi) Final Product Streams

Stream 801 : **1000 kg/day**

- **986.37 kg/day PCE**
- **13.63 kg/day Sodium Polycarboxylate**

3. Energy Balance for a scaled-up Process Plant with capacity of 1000 kg/day

1) Balance Across Co-Polymerization Unit

Assumption:- Superheated Steam (200C and 1 atm) is used to heat up the reactors. The energy associated with temperature change is miniscule compared to the heat of reactions so they will be ignored.

Input Streams :- AA :- 4.304×10^{-4} kg/s

CMP :- 1.435×10^{-4} kg/s

MA :- 1.435×10^{-4} kg/s

AIBN :- 7.135×10^{-7} kg/s

Output Streams :- Intermediate Polymer :- 6.664×10^{-4} kg/s

Unreacted AA :- 1.7216×10^{-5} kg/s

Unreacted CMP :- 1.363×10^{-5} kg/s

AIBN :- 7.135×10^{-7} kg/s

Heat of Reaction = ΔH°rxn = -55 kJ/mol

Cp $_{steam}$ = 1.996 kJ/kg-K

Extent of Reaction = Reacted Quantity of CMP = 1.434×10^{-3} mol/s

So :- **Overall Heat of Reaction** = ΔH°rxn * Extent = -78.87 J/s

2) Energy Required to Keep the reactor at 70°C

Cp $_{carbon\ steel}$ = 0.49 kJ/kg-K

So, on a unit mass basis, Q = Cp * (70-25) = **22.05 kJ/kg**

Temperature Drop of Per Mass Superheated Steam,

T = 200 - Q/Cp, T = 188.95 °C/kg

3) Balance Across Esterification Unit

No Temperature Changes are Involved in this Reaction

Heat of Reaction = ΔH°rxn = +15kJ/mol

Extent = 496 mols/day

Total Heat Required for Reaction = ΔH°rxn * Extent = 7440 kJ/day

Change in Temperature of Steam

Assumption :- Assuming Steam Flow to be 100 kg/day

7440 = 1.996 * 100 * (200-T)

T = 162.725 °C

4) **Balance Across Neutralization Unit**

Once Again, No Temperature change involved in this Reaction

Heat of Reaction = ΔH°rxn = -60 kJ/mol

Extent = NaOH consumed = 24.8 mols/day

Total Heat Lost by Reaction = ΔH°rxn * Extent = -1488 kJ/day

4. Reactor Volumes

Design of Reactor R101:- This is a relatively small scale reactor only producing 59.32 kg of Effluent per day. Dividing by the value of density (1.051 kg/L) gives us 56.44 L of required space. Assuming that only 70% of the reactor can be filled at a time, we go with a reactor space of 80.62 L.

Design of Reactor R102:- The effluent of this reactor contains about 1305.3366 kg of components per day, majorly consisting of Non-Neutralised PCE. The density of PCE is found to be about 1.11 kg/L. So the approximate volume required for this reactor would be 1175.98 L. Assuming that only 70% of the reactor can be filled at a time, we go with a reactor space of 1679.97 L

Design of Reactor R103:- 1000 kg of PCE with density of 1.11 kg/L would require 900.9 L of Reactor space. Since we are assuming only 70% of the reactor can be filled at a time, we go with a reactor space of 1285.714 L

Capital cost (only for the reactor):

Equipment	**Design Capacity (L)**	**No. of units**	**Cost/unit ($ for year 2014)**	**Total Cost ($ for year 2014)**
Reactor R101 :- (Jacketed reactor, agitated, Glass Lined Carbon steel, atm. pressure)	80.62	1	6,100	6,100
Reactor R102 :- (Jacketed reactor, agitated, Glass Lined Carbon steel, atm. pressure)	1679.97	1	30,500	30,500
Reactor R103 :- (Jacketed reactor, non agitated, Glass Lined Carbon steel, atm. pressure)	1285.714	1	4,800	4,800
Total				41,400 USD

References:

1. http://www.matche.com/equipcost/Reactor.html
2. *"Concrete Admixtures Handbook - Properties, Science and Technology"* by V.S. Ramachandran
3. Production of Modified Superplasticizer by Two-Step Synthesis of Polycarboxylate Ether, Advanced Journal of Chemistry, Section B, 2024.
4. POLY CARBOXYL ETHER (PCE) PROJECT OF 18,000 T/Y, Environmental Clearance Document.
5. Ether polycarboxylate superplasticizer and preparation method thereof, Patent CN104261720A.

List the contributions of each author:

Tanvi Manhas :

- Researched the upscaling of the process and determined optimal process conditions.
- Studied and verified the exact reactions involved based on previous reports.
- Identified the specific unit operations and equipment required for the process.
- Designed a feasible Process Flow Diagram integrating reactions and unit operations.
- Analyzed reaction efficiencies and yields to optimize production.
- Performed the Material Balance, accounting for all catalysts, solvents, side products, and impurities.

Harshvardhan Agarwal :

- Using the stream data from Mass Balance, derived an Energy Balance with appropriate approximations.
- Researched the values of various physical quantities of PCE in order to determine Energy and Reactor Costs.
- Estimated the Volume requirements of each Reactor.
- Researched the types of Reactors that would suit the needs of our Industrial Process making sure that it is Cost-Effective.
- Found out the estimated costs of all reactors suited to the needs of this Process.

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Name	Roll No	Signature
Anshika Agrawal (CEO)	230160	Anshika
Tanvi Manhas	231084	Manhas
Harshvardhan Agarwal	230466	Harsh