Polymers

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Outline

- ***Industrial Process for synthesis of***

1. ***Polyethylene***
2. ***Acrylonitrile Polymers***
3. ***Acrylate & Methacrylate polymers***

- ***Biomedical Polymer***
- ***Polymer Processing***
- ***Plasticizers & Anti-oxidants for polymers***

Industrial Process for Manufacturing of Polyethylene

- Originally prepared by decomposition of diazohydrocarbons
- Action of Sodium on decamethyl bromide (Fischer-Tropsch synthesis)
- Reduction of Polyvinyl chloride
- Polymerization of ethylene (Major Process for Industrial production)
- The products are liquid, greases, hard & soft waxes, thermoplastic solids.
- Here we discuss only high m. w. thermoplastic solids only.
- Prepared by **High pressure & Low pressure processes.**

High Pressure Process for Manufacturing of Polyethylene

- *This polymerization process is carried out in high pressure autoclave at pressures 15000-30000 psi and tempt of 150-300°C.*
- ***Produces LDPE***
- ***Process:***

✓ *High purity ethylene is required to manufacture Polyethylene.*

✓ *This high purity ethylene is mixed with small percentage of Oxygen (0.02-0.08 %) which serves as catalyst.*

✓ *The mixture is then heated to 150-300°C & fed to* ***SS tabular reactor*** *where tempt is maintained to 150-300°C.*

✓ *The effluent from the reactor passes to* ***Separator*** *in which unconverted gaseous ethylene is removed & recycled to an intermediate stage of the process.*

- ✓ *The liquid from the separator is Polyethylene*
- ✓ *It is chilled quickly & solidified product is chopped passed for milling, rolling, compounding, palletizing.*
- ✓ *The polymerization reactions are highly exothermic & require strict control in order to prevent explosive decomposition of the ethylene.*
- ✓ *The M. W. of the polymer can be controlled by the reaction conditions.*
- ✓ *Purer the ethylene & higher the pressure higher the M. W. built up and higher the M. P.*
- ✓ *Higher the oxygen content & tempt more vigorous the polymerization and lower the degree of polymerization.*

- ❑ **Other Catalyst:** *Peroxy comp, ozonides, azo comp, azines, amine oxides, oximes, hydrazines, hypohalites, etc.*

High Pressure Process for Manufacturing of Polyethylene

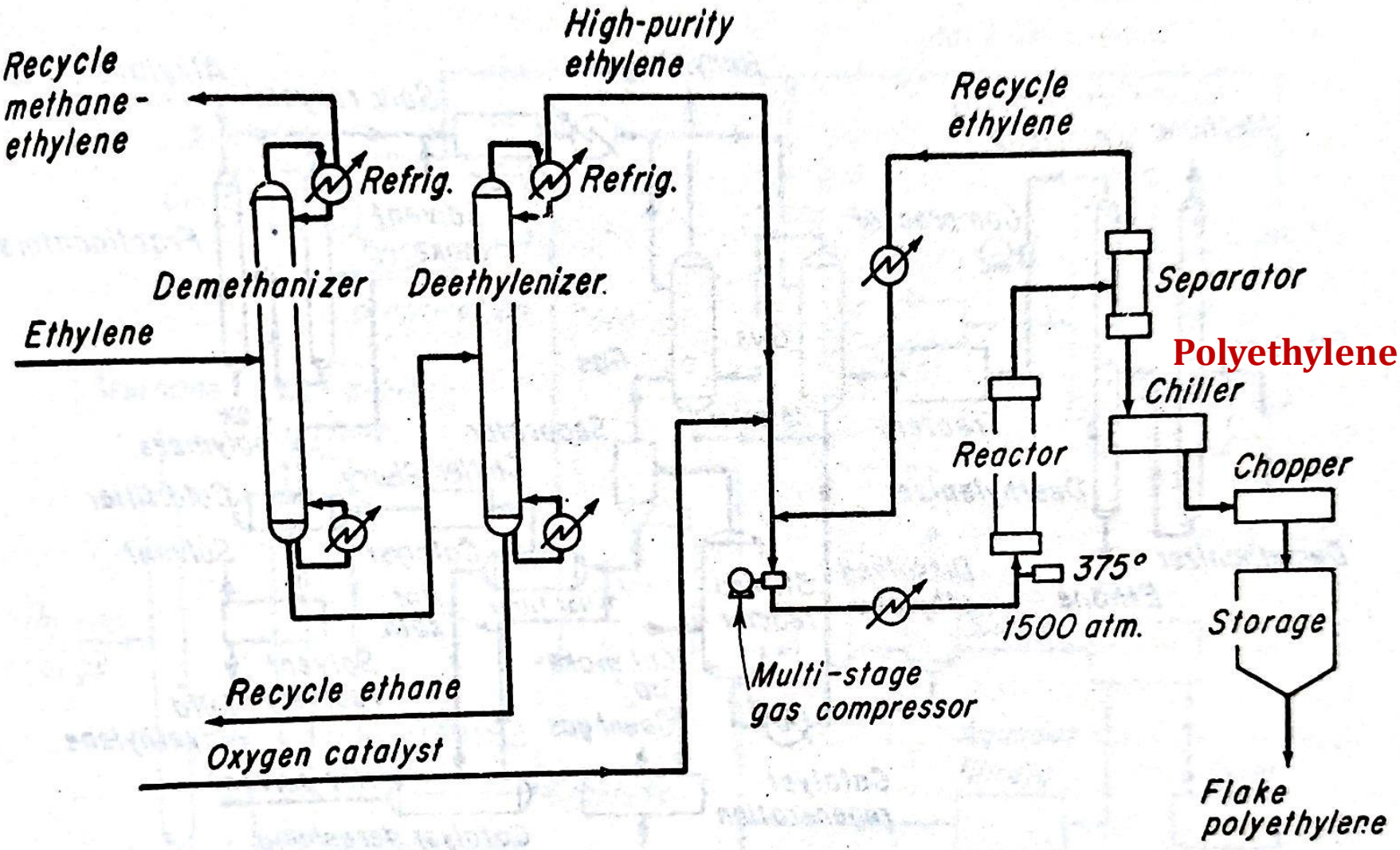

FIG. 15-32. High-pressure polyethylene process. (*Courtesy Koppers Co.*)

Low Pressure Process for Manufacturing of Polyethylene

- *This polymerization process is carried out at relatively low pressures 100-500 psi & tempt 90-180°C in either fixed bed or slurry type operations.*
- ***Catalyst:*** *3 types of Catalyst can be used: Ziegler/Natta, Cr/Mo oxide, Metallocene*
- ***HDPE*** *is formed by this process.*

Process: Ziegler type ethylene polymerization

- ✓ *Ziegler catalyst is prepared by adding diethyl aluminium chloride* ***(Activator)*** *& titanium tetra chloride* ***(Co catalyst)*** *to a dry hydrocarbon solvent under inert atmosphere.*
- ✓ *This catalyst is subsequently transferred to a dry, well purged 5 litre flask & diluted with more solvent.*

Low Pressure Process for Manufacturing of Polyethylene

- ✓ A small amt of dual catalyst, prepared in dried paraffinic solvent is charged to the reactor.
- ✓ High purity ethylene is then charged to the reactor and maintained pressure of reactor in the range 15-100 psi.
- ✓ The tempt rises from 20°C to 60-70°C in about 10 minutes and maintained for 30 -40 min.
- ✓ *After 30-40 min alcohol is added to deactivate the catalyst & Polyethylene powder is separated from the solvent by filtration and drying.*

Low Pressure Process for Manufacturing of Polyethylene

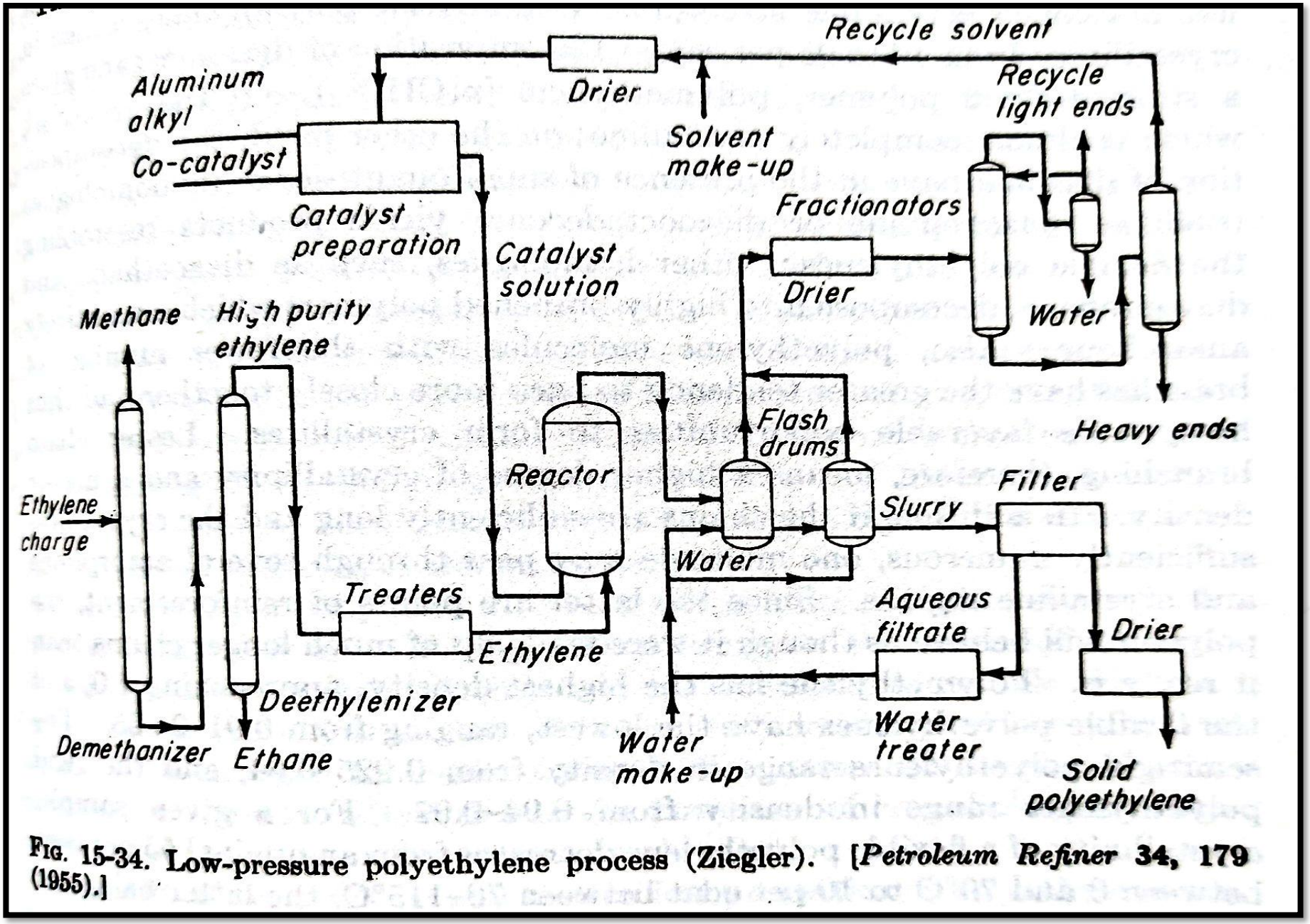

FIG. 15-34. Low-pressure polyethylene process (Ziegler). [*Petroleum Refiner* 34, 179 (1955).]

Low Pressure Process for Manufacturing of Polyethylene

- ✓ The reactor product is sent to the series of flash drums to remove the solvent & precipitate the polymer.
- ✓ Water is added to flash the drum to destroy the residual catalyst & remove the polyethylene as a slurry.
- ✓ The polymer is removed from this slurry by filtration and dried.
- ✓ The semirigid to rigid polyethylene have densities in the range from 0.93-0.96.

- ✓ ***Other Activators:*** *Hydrides, Alkyls or aryls of beryllium, aluminium. Gallium, indium, lithium, magnesium and zinc.*
- ✓ ***Other Cocatalysts:*** *Comp of transition series of 4, 5 & 6*

Manufacturing of Acrylonitrile Polymers

- ✓ There are many synthetic methods for the production of Polyacrylonitrile.
- ✓ But only two methods have been important commercially.

1. Catalytic Dehydration of ethylene cyanohydrin
2. Addition of HCN to acetylene in catalyst solution.

Manufacturing of Acrylonitrile Polymers

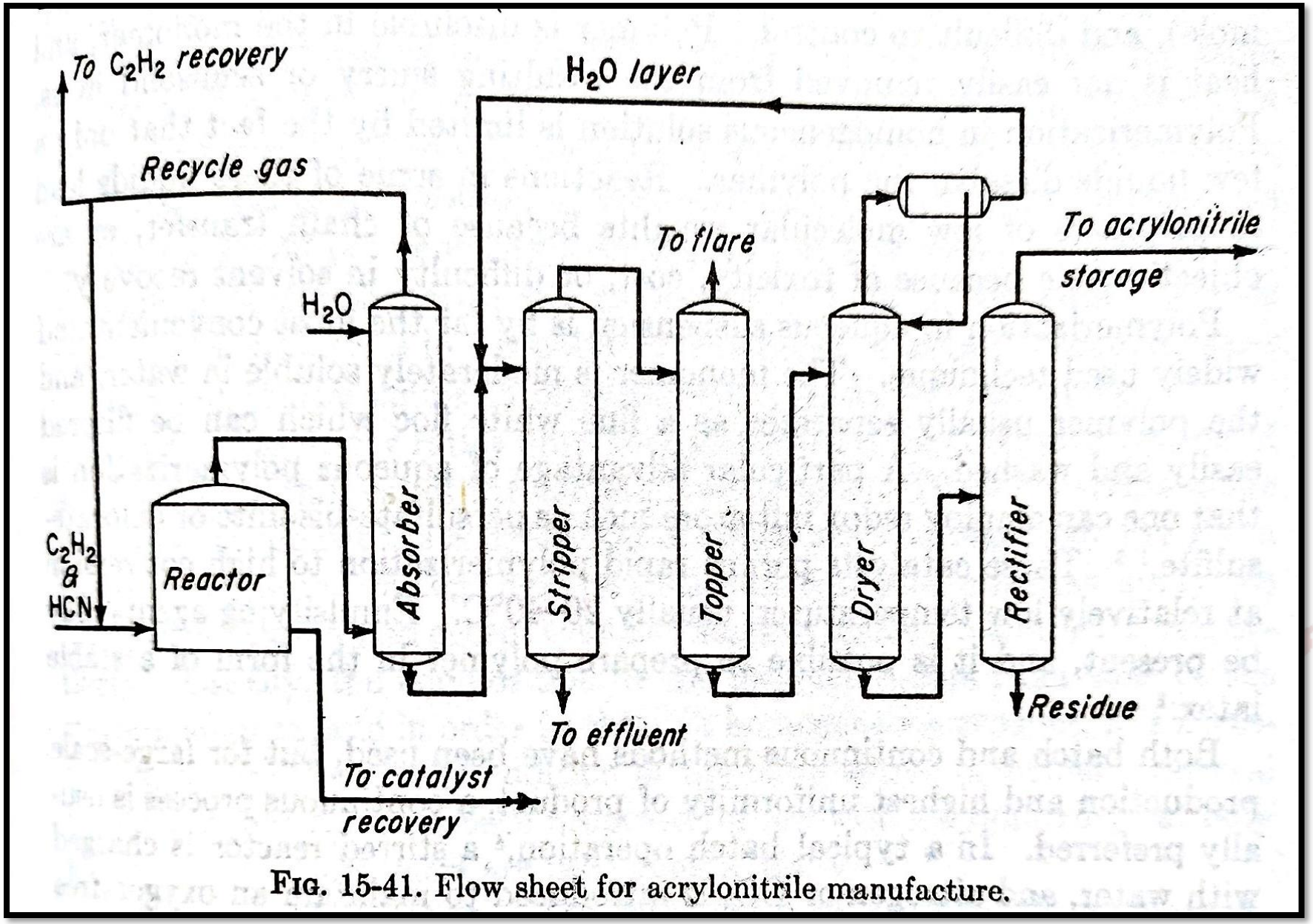

FIG. 15-41. Flow sheet for acrylonitrile manufacture.

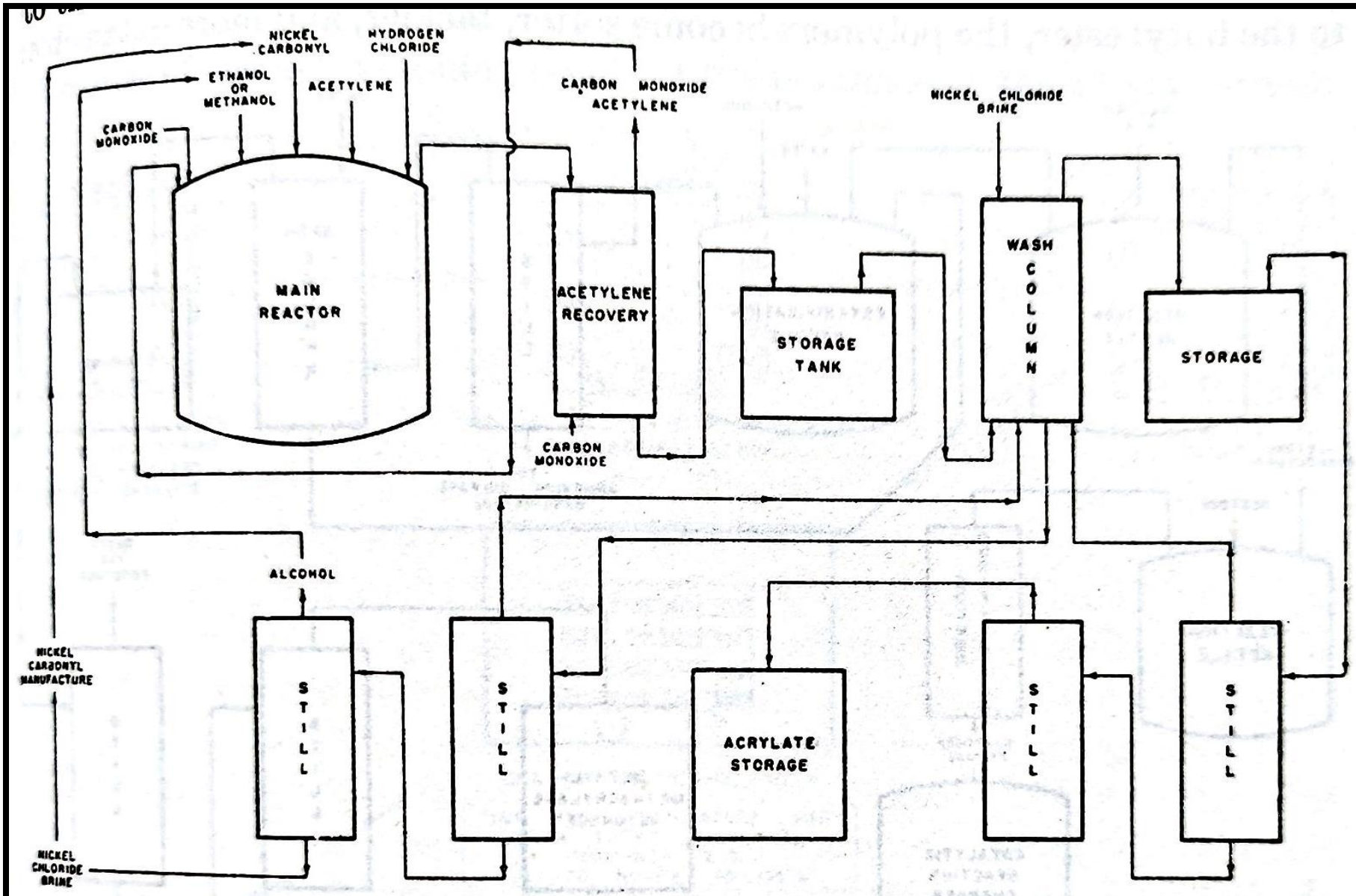

FIG. 15-38. Flow diagram: production of methyl or ethyl acrylate.

Schematic of TET

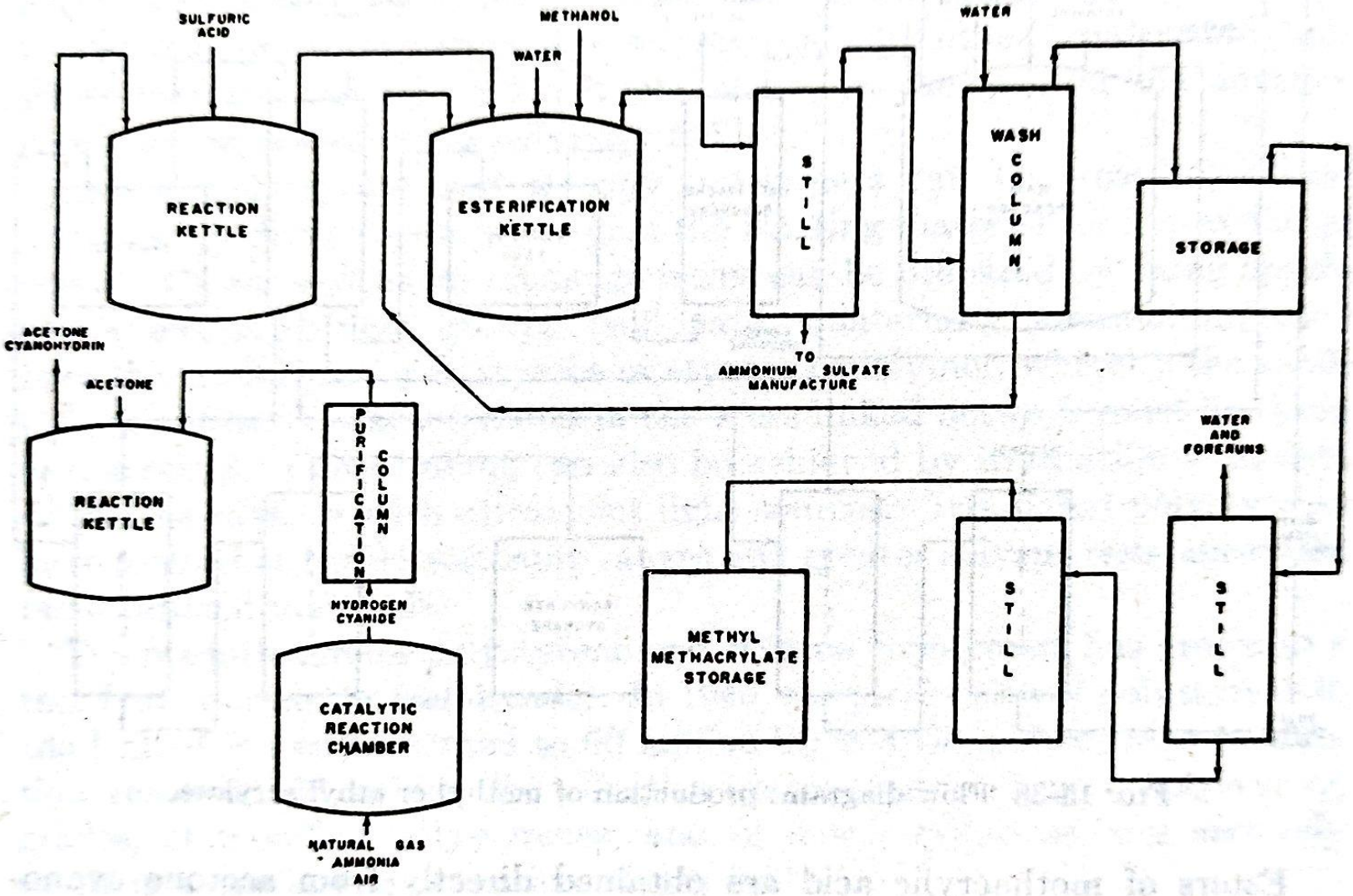

FIG. 15-39. Flow diagram: production of methyl methacrylate.

:::::Thank You:::::