

# Lecture 14. The production of plastics.

## Production of polyethylene and others polymer.

### Process parameters. Catalysts.

Industrially polymers are classified into two main classes – **plastics** and **elastomers**.

**Plastics** are moldable organic resins. These are either natural or synthetic, and are processed by forming or molding into shapes. Plastics are important engineering materials for many reasons.

*Light weight, wide range of colors, low thermal and electrical conductivity, less brittle, good toughness, good resistance to acids, bases and moisture, high dielectric strength (use in electrical insulation), etc.*

- Plastics are again classified in two groups depending on their mechanical and thermal behavior as **thermoplasts** and **thermosets**.

# Thermoplasts

These plastics soften when heated and harden when cooled – processes that are totally reversible and may be repeated. These materials are normally fabricated by the simultaneous application of heat and pressure. They are linear polymers without any cross-linking in structure where long molecular chains are bonded to each other by secondary bonds and/or inter-wined. They have the property of increasing plasticity with increasing temperature which breaks the secondary bonds between individual chains.

*Acrylics, Polyvinyl chloride, nylons, polypropylene, polystyrene, polymethyl methacrylate, etc.*

# Thermosets

These plastics require heat and pressure to mold them into shape. They are formed into a permanent shape and cured or 'set' by chemical reactions such as extensive cross-linking. They cannot be re-melted or reformed into another shape but decompose upon being heated to too high a temperature. Thus thermosets cannot be recycled, whereas thermoplasts can be recycled.

*Epoxies, vulcanized rubbers, phenolics, unsaturated polyester resins, and amino resins.*

# Elastomers

Also known as rubbers, these are polymers which can undergo large elongations under load, at room temperature, and return to their original shape when the load is released. There are number of man-made elastomers in addition to natural rubber. These consist of coil-like polymer chains those can reversibly stretch by applying a force.

*Polyurethanes, Silicones.*

Most of polymer properties are intrinsic i.e. characteristic of a specific polymer. Foreign substances called additives are intentionally introduced to enhance or modify these properties. These include – *fillers, plasticizers, stabilizers, colorants, and flame retardants*.

**Fillers** are used to improve tensile and compressive strength, abrasion resistance, dimensional stability etc. Wood flour, sand, clay, talc etc are example for fillers.

**Plasticizers** aid in improving flexibility, ductility and toughness of polymers by lowering glass transition temperature of a polymer. These are generally liquids of low molecular weight.

**Stabilizers** are additives which counteract deteriorative processes such as oxidation, radiation, and environmental deterioration.

**Colorants** impart a specific color to a polymer, added in form of either dyes (dissolves) or pigments (remains as a separate phase).

**Flame retardants** are used to enhance flammability resistance of combustible polymers. They serve the purpose by interfering with the combustion through the gas phase or chemical reaction.

# The manufacture of polyethylene

**Polymer Chemistry:** The manufacture of polyethylene follows addition polymerization kinetics involving catalysis of purified ethylene. Its molecular formula is  $-(\text{CH}_2-\text{CH}_2)_n-$  with a molecular weight of 1,500 to 100,000. Its melting point is 85 – 110 °C. its density is 0.91 -0.93 , when produced by high pressure process and 0.96, when produced by low pressure process.

# Technology

There are three processes by which polyethylene is manufactured –

**a. High Pressure Process:** This process was developed in the UK. It uses peroxide catalyst at 100-300 °C and produces low density randomly oriented polymer which have a low melting point. The process is run at pressure of 1000 – 2500 atms. This process yields Low Density Polyethylene (LDPE).

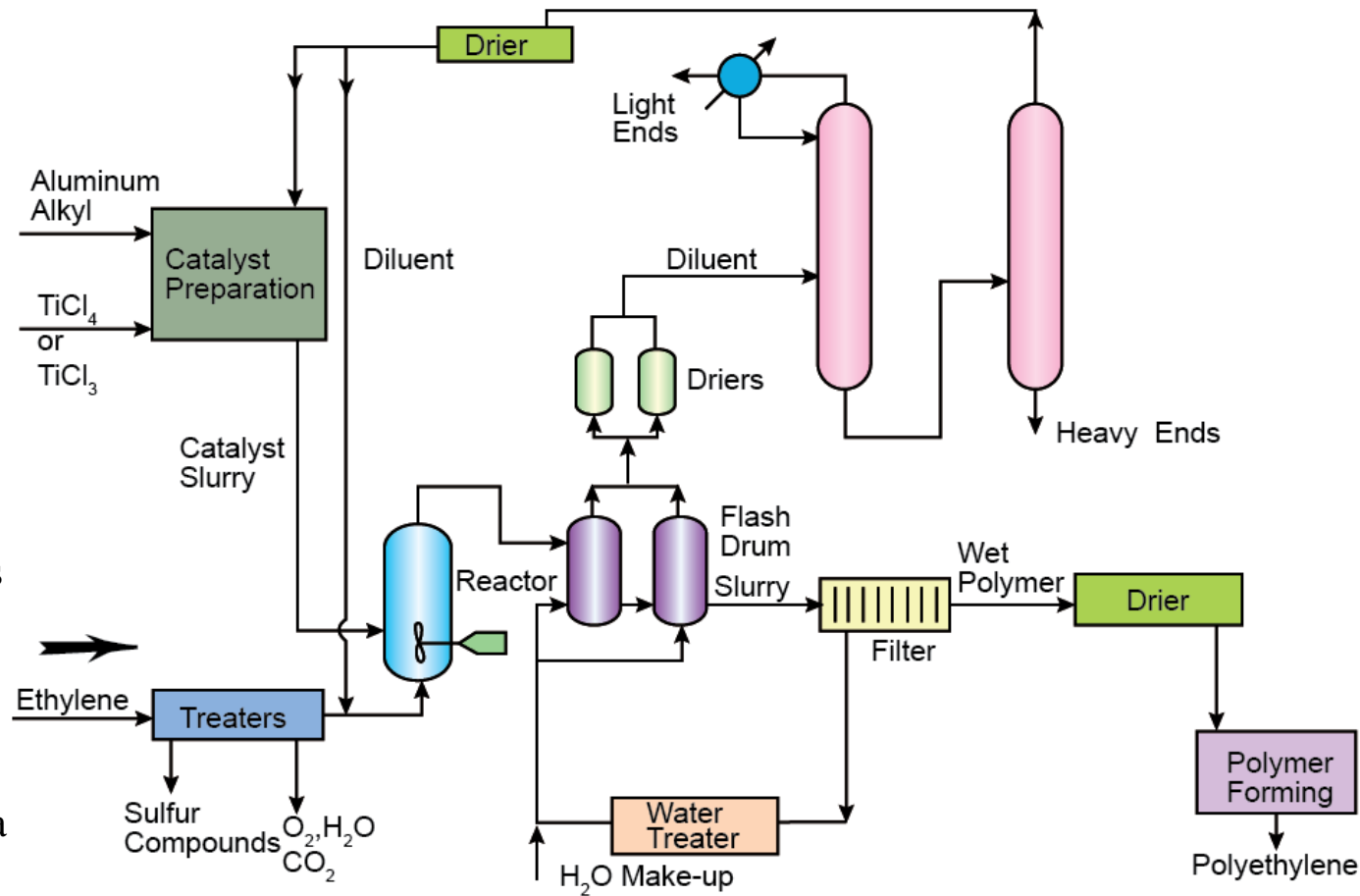
**b. Intermediate Pressure Process:** This process was developed in the USA. For preparing high density polymer with increased rigidity, crystallinity, tensile strength and softening point. The process uses MoO<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> on alumina as catalyst and is operated at 30 – 100 atms.

**c. Low Pressure Process:** This process was originally developed in Germany for preparing high density polyethylene (HDPE). The catalyst used in this process consists of aluminium triethylactivated with heavy metal derivatives such as TiCl<sub>4</sub>.



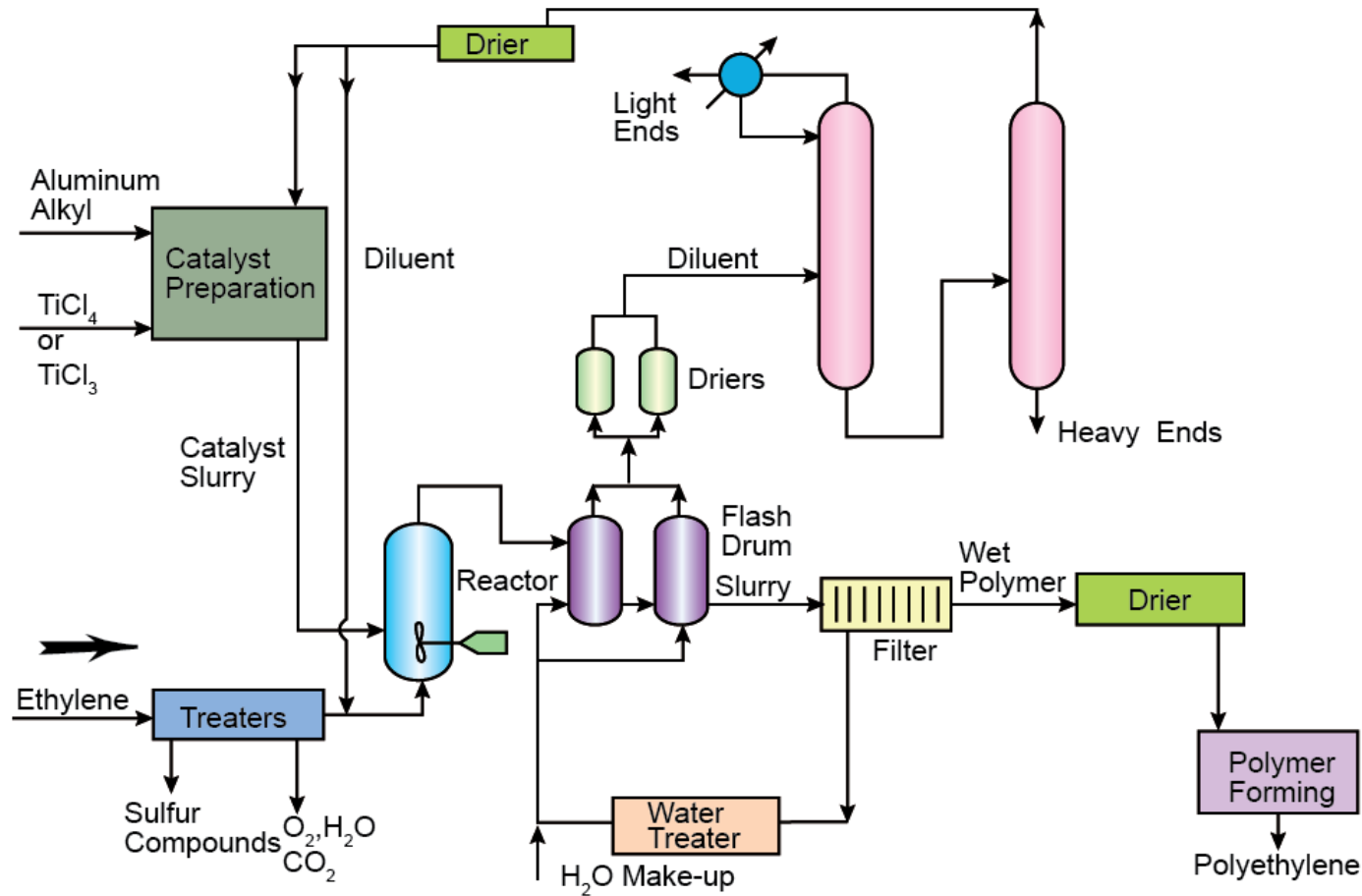
# The flow sheet of Low Pressure Ziegler Process to produce polyethylene

At the very onset, through the process of desulphurization and removal of light ends, high purity ethylene is prepared. The ethylene is further treated to remove traces of oxygen and its compounds which can possibly deactivate the catalyst. The ethylene is first pumped into a reactor where it is mixed with catalyst diluents stream. The optimum temperature and pressure maintained should be 70 °C and 7 atms. The effluent stream then follows across a series of flash drums in order to remove the solvent from the catalyst.



# The flow sheet of Low Pressure Ziegler Process to produce polyethylene

The residual catalyst at this point is removed by adding water. The flashed solvent is thereafter recycled to the catalyst make-up unit after appropriate drying and redistillation. The slurry which results is then centrifuged to remove the water, and the water is treated to remove the catalyst before recycle. The final products of polyethylene solids are then dried, extruded and given the required final forms.



# The manufacture of Polyvinyl Chloride (PVC)

**Polymer Chemistry:** The manufacture of Polyvinyl Chloride (PVC) follows addition type kinetics and produces linear polymers. The vinyl chloride monomer (VCM) has a boiling point of 13.4 °C and is a gas at room temperature and pressure. The vapor pressure of VCM over the typical polymerization temperature range of 50 °C to 70 °C is 800 – 1250 KPa.

# Technology

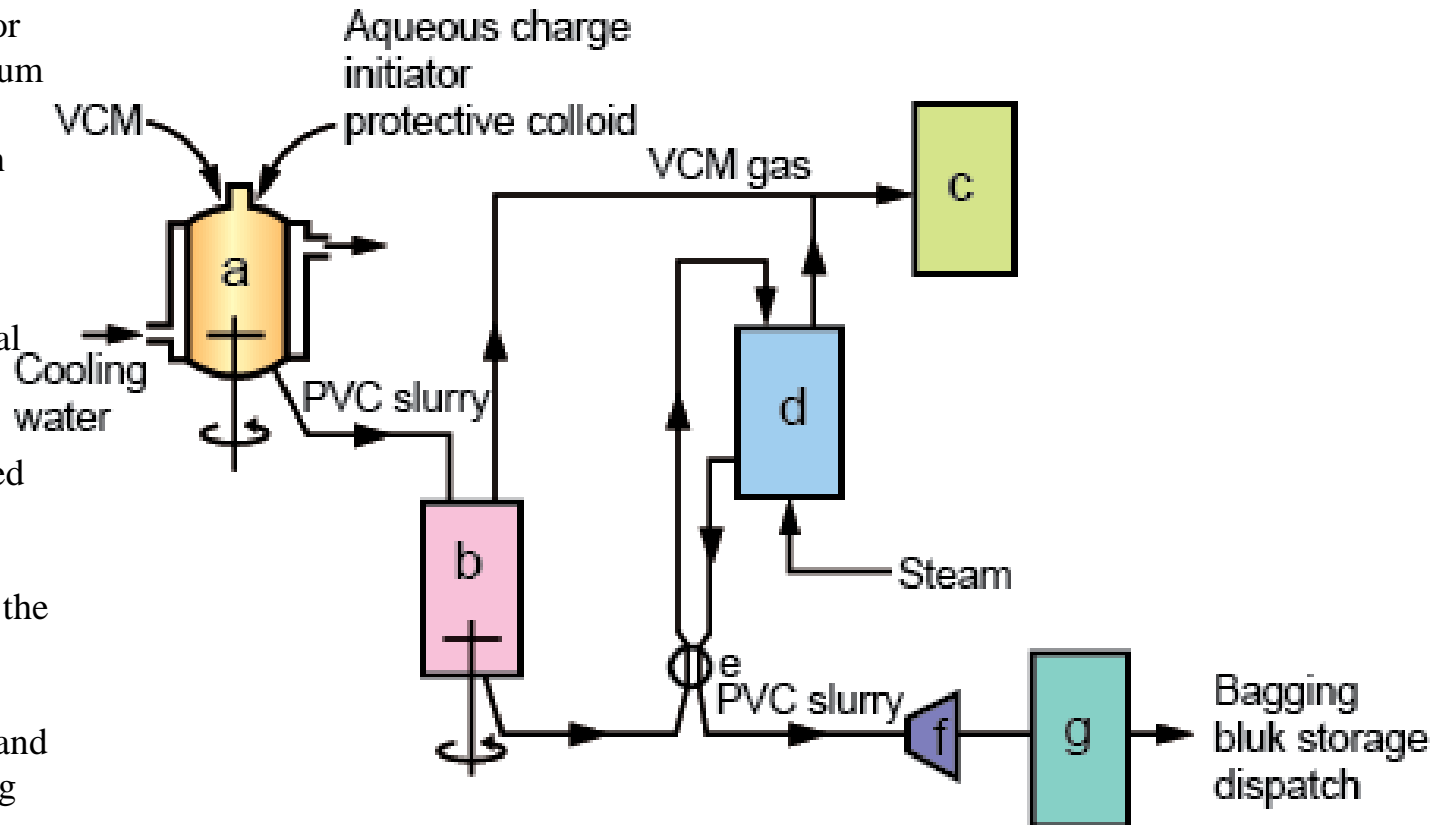
The two most commercially use methods for the manufacture of PVC are *Emulsion Polymerization* and *Suspension Polymerization*.

The Suspension Polymerization process provides 80 % of the world production. The Suspension Polymerization process is actually a bulk polymerization process which is carried out in millions of droplets . Each of these droplets act as small reactors.

# Manufacture of Poly(Vinyl Chloride)

The liquid vinyl chloride is dispersed in water by vigorous stirring in a reactor. The reactor is fitted with baffles for optimum agitation and also has a condenser for heat removal. In the reactor, small droplets of size 30 - 40 $\mu$ m diameter are formed.

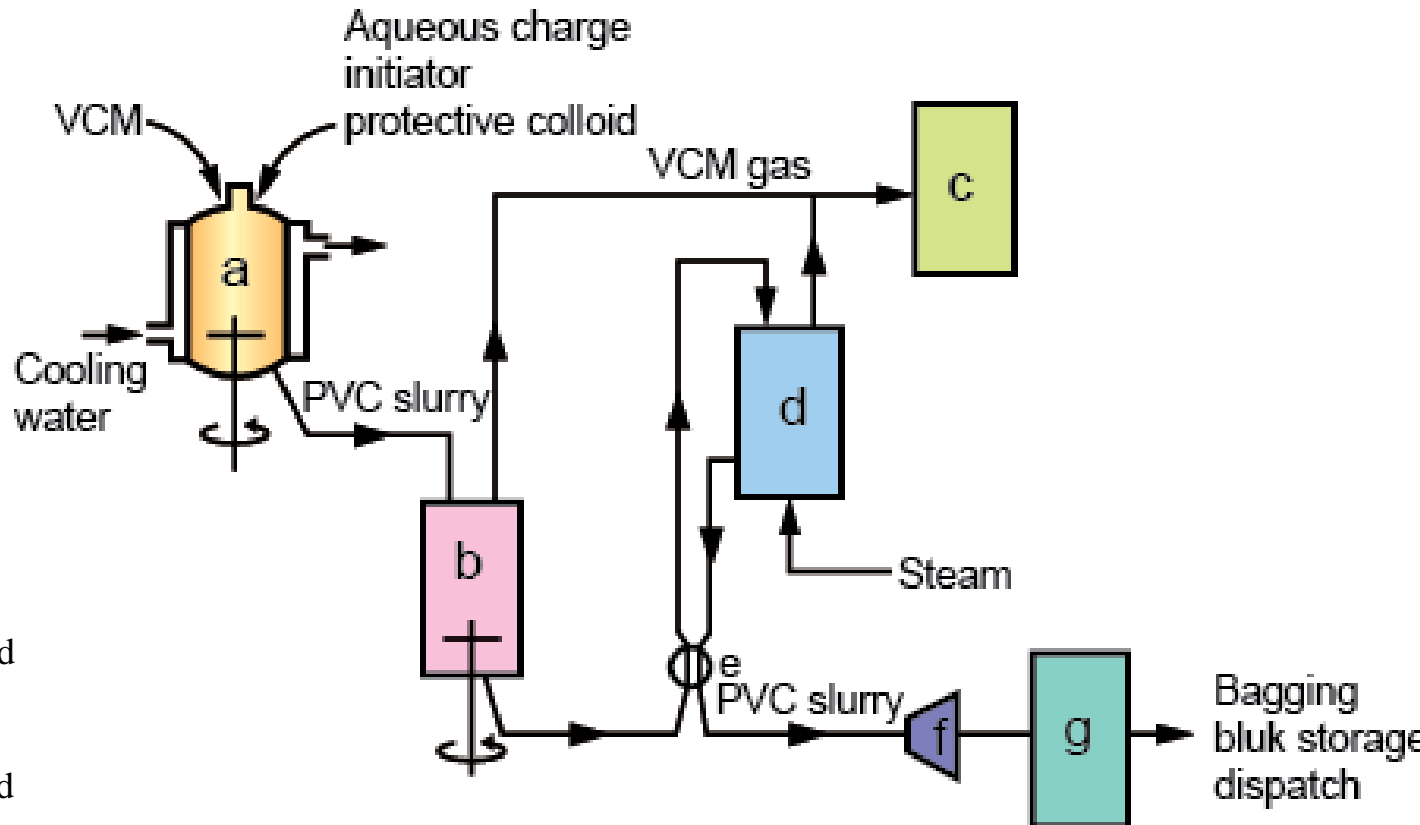
A monomer soluble free radical initiator is charged into the reactors. After charging, the reactor temperature is increased to 45–75 °C. The heat decomposes some of the initiators to free radicals, and the monomers in these droplets begin to polymerize., the reaction is highly exothermic and the heat is removed via cooling jackets or by boil – off to the condenser. Thereafter, the condensed monomer is returned to the reactor.



a) Reactor; b) Blowdown Vessel; c) VCM Recovery Plant;  
d) Stripping Column; e) Heat Exchanger; f) Centrifuge; g) Driers

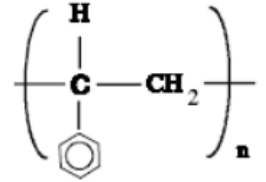
# Manufacture of Poly(Vinyl Chloride)

Although the PVC is insoluble in its monomer, it is swollen by VCM to form a coherent gel. Even in the gel phase, the polymerization continues. The polymerization is rapid at first, but slowly, as the conversion reaches 80–85 %, the rate is reduced due to monomer starvation. At a predetermined pressure, the reaction is ended by adding a chain terminator or by venting the unreacted monomer to a recovery plant. Even after venting, the aqueous slurry contains 2–3 % unreacted monomer, which is then removed by stripping in a Stripping Column. The unreacted monomer is recovered and stored for later polymerization stages. The slurry is then passed through a heat exchanger and is passed through a continuous centrifuge to give a wet cake with 20–30 % moisture.



a) Reactor; b) Blowdown Vessel; c) VCM Recovery Plant; d) Stripping Column; e) Heat Exchanger; f) Centrifuge; g) Driers

# The manufacture of Polystyrene



**Polymer Chemistry:** Styrene readily polymerizes to polystyrene by a relatively conventional free radical chain mechanism. Either heat or initiators will begin the polymerization. Typically initiators used in the suspension process include benzoyl peroxide and di-tert-butyl perbenzoate. Potassium persulfate is a typical initiator used in emulsion polymerizations.

Polystyrene is an odorless, tasteless, rigid thermoplastic.

# Technology

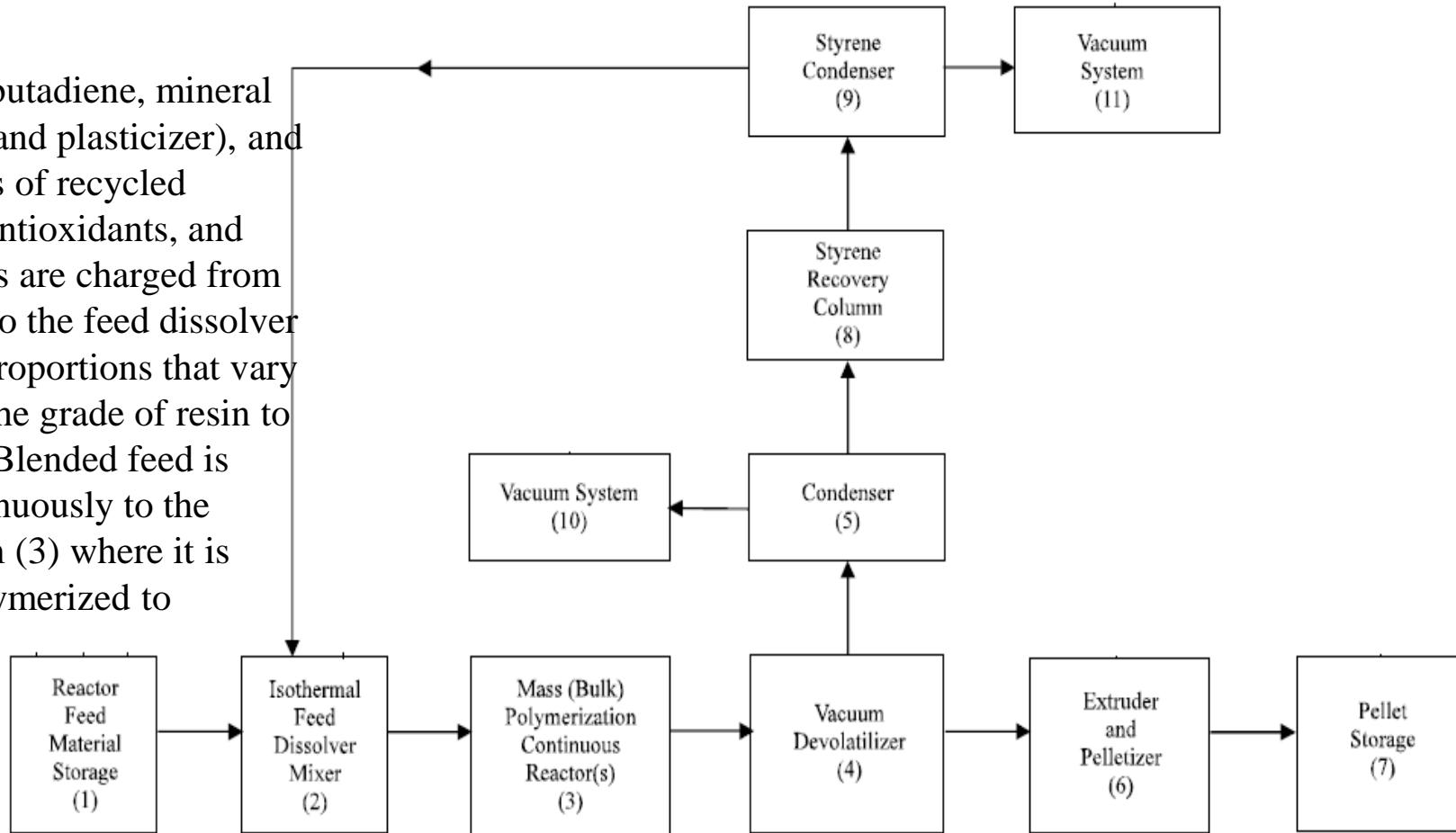
Polystyrene can be produced by *bulk (or mass), solution (a modified bulk), suspension, or emulsion polymerization techniques.*

**The bulk (mass) process** is the most widely used process for polystyrene today. The suspension process is also common, especially in the production of expandable beads. Use of the emulsion process for producing styrene homopolymer has decreased significantly since the mid-1940s.



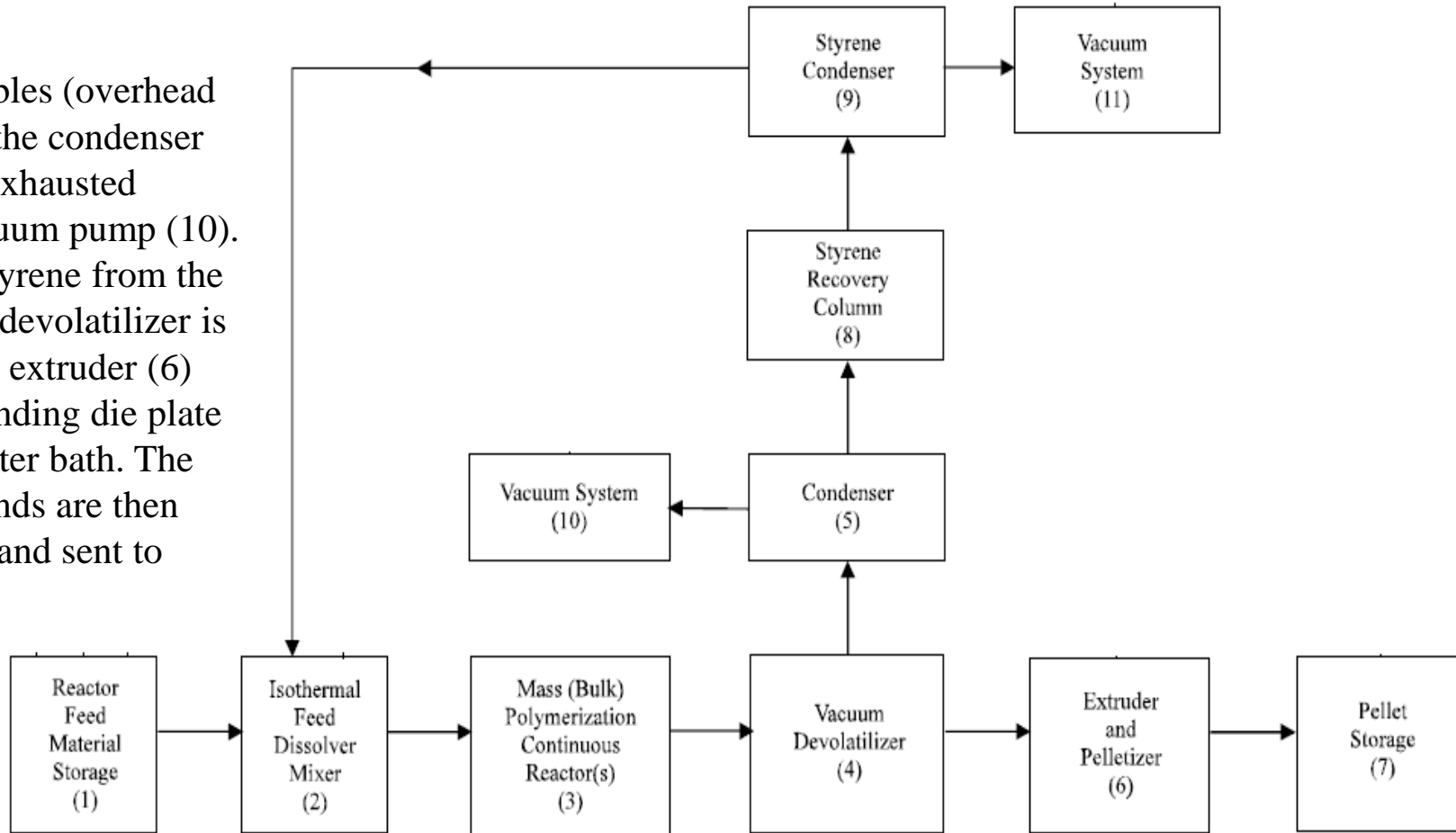
# Manufacture of Polystyrene

Styrene, polybutadiene, mineral oil (lubricant and plasticizer), and small amounts of recycled polystyrene, antioxidants, and other additives are charged from storage (1) into the feed dissolver mixer (2) in proportions that vary according to the grade of resin to be produced. Blended feed is pumped continuously to the reactor system (3) where it is thermally polymerized to polystyrene.



A process line usually employs more than one reactor in series. Some polymerization occurs in the initial reactor, often referred to as the prepolymerizer. Polymerization to successively higher levels occurs in subsequent reactors in the series, either stirred autoclaves or tower reactors. The polymer melt, which contains unreacted styrene monomer, ethylbenzene (an impurity from the styrene feed), and low molecular weight polymers, is pumped to a vacuum devolatilizer (4). Here, most of the monomer, ethylbenzene, and low molecular weight polymers are removed, condensed (5), and sent to the styrene recovery unit (8 and 9).

# Manufacture of Polystyrene



Noncondensables (overhead vapors) from the condenser typically are exhausted through a vacuum pump (10). Molten polystyrene from the bottom of the devolatilizer is pumped by an extruder (6) through a stranding die plate into a cold water bath. The solidified strands are then pelletized (6) and sent to storage (7).

In the styrene recovery unit, the crude styrene monomer recovered from the condenser (5) is purified in a distillation column (8). The styrene overhead from the tower is condensed (9) and returned to the feed dissolver mixer. Noncondensables are vented through a vacuum system (11). Column bottoms containing low molecular weight polymers are used sometimes as a fuel supplement.