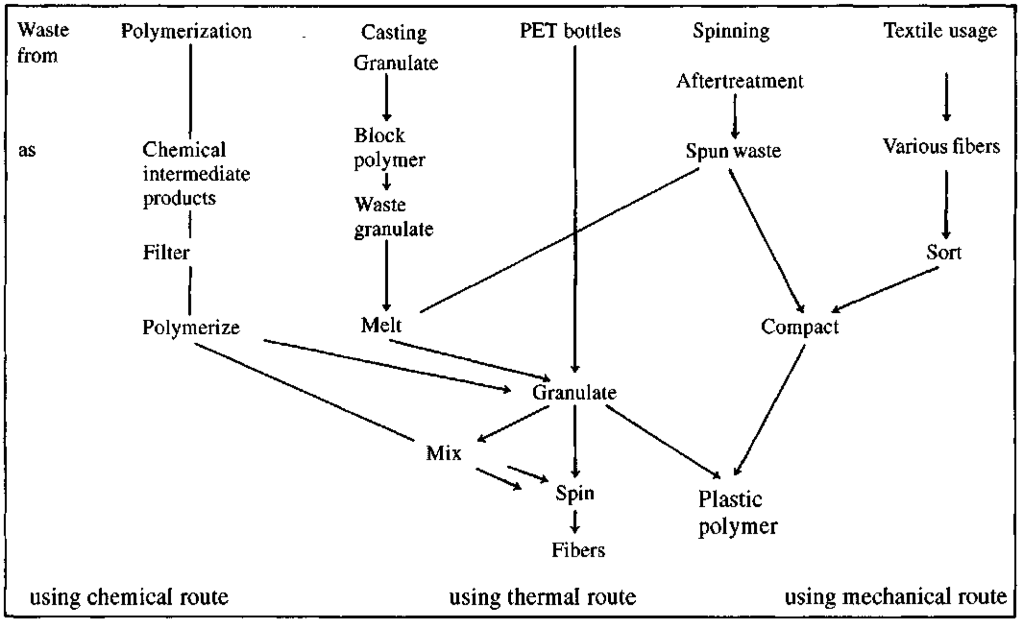
8 Waste Processing and Recovery (Recycling)

8.1 Overview

In 1970, one could still expect 5 ... 7% waste from polymerization to finished staple or yarn. Falkai [1] reported in 1981 up to 15% waste and low quality product for some processes. Owing to advances in the quality of intermediate materials and automation, including continuous processing, modern plants today produce only about 3 ... 4% waste. This waste consists of lumps of oxidized polymer and low bulk density filament waste, undrawn, partly drawn and fully drawn. 2 ... 3% waste is normal in fiber production. In the case of 2 staple fiber lines each producing 200 t/d, this equates to 500 kg/h waste—which, valued at 1 DM/kg—results in an annual cost of approximately 4 000 000 DM, thus justifying the argument for recycling. The filament waste, valued at 0.30 DM/kg, is worth approximately 900 000 DM p.a.; selling this waste does not recover its true cost. Recovery of starting materials, intermediate products or end products is nowadays significantly more economical. Table 8.1 shows production routes where waste arises and possibilities of re-using such waste. Additionally, certain production routes permit the recovery of intermediate products or auxiliary agents and their re-use, which may be necessary to make these processes economically viable.

Table 8.1 Recovery and Utilization of Waste



Extruded solid polymer waste is almost always oxidized on the surface. Yarn and fiber waste is mostly dressed with spin finish. Solvents and intermediate products are more or less strongly contaminated with other chemical substances, e.g., degradation products, or are strongly diluted with water or precipitation agents, which may make evaporation or distillation necessary. This complexity necessitates recovery being examined on a case by case basis; the sections following can only give advice regarding some important recovery processes.

8.2 Chemical Processing of PA 6 Waste

8.2.1 Recovery of Caprolactam from PA 6 by Thermal Decomposition

The temperature-dependent equilibrium between polyamide 6 and lactam:

$$\mathrm{HN{-}(CH_2)_5{-}CO} + \mathrm{H_2O} \underset{\text{decomposition}}{\overset{\text{polycondensation}}{\rightleftharpoons}} \mathrm{H[OH{-}(CH_2)_5{-}CO]_n{-}OH} + \text{equilibrium lactam}$$

can be exploited to recover lactam from PA6 waste; this lactam can be removed by an excess of water or by vacuum [2]. In practice, an autoclave is filled to ca. 75% capacity with about (0.15 × volume [l]) kg of size-reduced PA6 waste, and 1.7…3.5 w/w% phosphoric acid is added. After about 0.5…1 h, one obtains a 30% condensate. The maximum amount of lactam is obtained at 280…300 °C. On refilling with the same amount of polyamide and somewhat less phosphoric acid, ca. 50 charges can be processed. The recovered lactam is extracted by centrifuging and concentrated by evaporation and distillation under a high vacuum to obtain pure lactam, as shown in Fig. 8.1 [1].

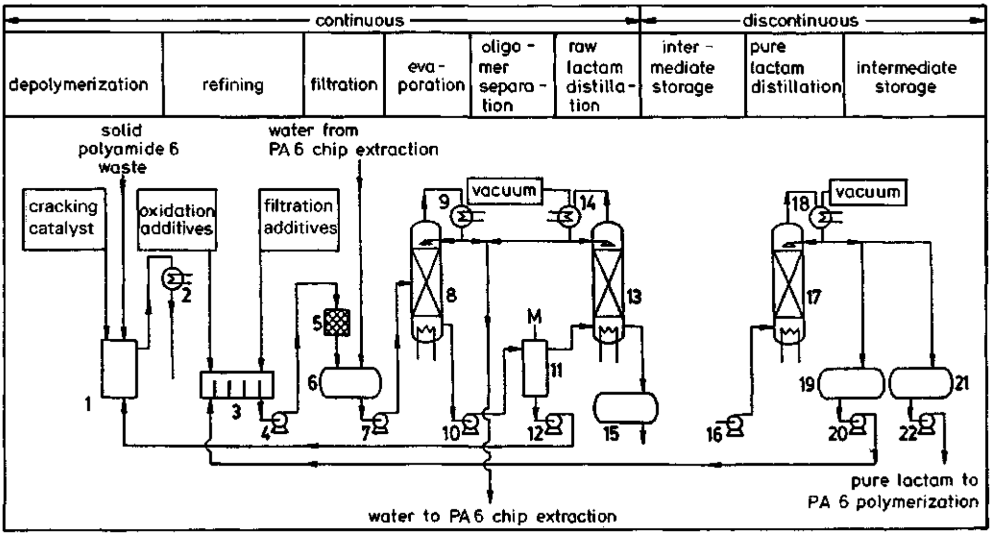


Figure 8.1 Process schematic of a lactam recovery plant [1]

1 Cracker (cracking vessel)
2, 9, 14, 18 Condenser
3 Refining
4, 7, 10, 12, 16, 20, 22 Pumps
5 Filtration
6, 15, 19, 21 Vessels, storage tanks
8 Evaporator stage
11 Thin film evaporator
13 Raw lactam column
17 Pure lactam column

8.2.2 PA 6 Recovery through Depolymerization-Filtration-Re-Polymerization [3]

Using this process, even contaminated PA 6 waste can be recovered. Figure 8.2 shows a process having, e.g., a 2 m^3 autoclave (2) which is filled with ca. 500 kg PA 6 waste from which spin finish, if present, has been removed by washing. After adding ca. 200 kg water, the autoclave is heated to 220...225 °C at 2 bar pressure. Higher temperatures and a greater quantity of water increase the caprolactam content during depolymerization, but reduce the capacity and increase the pressure, making the autoclave uneconomical. The resulting solution is forced through a very fine (quality-determining) large area filter (3) into the re-polymerization vessel (5) (which could also be a pressureless VK tube), where it is polymerized at 257...280 °C (as described in Section 2.2.3.6). Contamination and oxygen present during the depolymerization result in slight yellowing. This can only be avoided by using pure input material, by evacuation and by purging with pure nitrogen in the melt autoclave (2). A further disadvantage of this process is the long processing time of 24 h per charge.

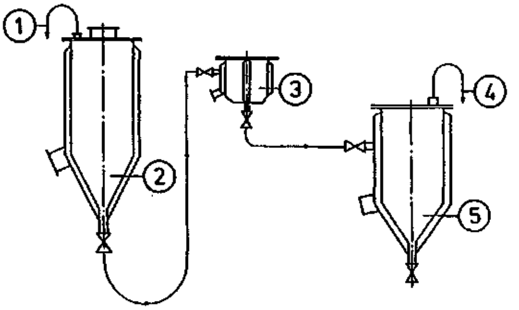


Figure 8.2 Depolymerization-filtration-repolymerization process [3]
1 Exhaust vapor
2 Depolymerization pressure vessel
3 Filter
4 Exhaust steam and exhaust gas (to a condensor)
5 Polymerization pressure vessel

8.2.3 Recovery through Reprecipitation of PA 6 [4,5]

The waste is dissolved in caprolactam at 170 °C, and the solution is extruded into water [6]. One can also use hydrochloric acid, sulfuric acid, calcium chloride or phenol at slightly higher tmperature. The most economical process is that using hydrochloric acid. A yield of up to 80% is possible. The product has an ash content of 0.04...0.2% and contains 0.03...0.1% chlorine, 5...10 mg iron/100 g and 1...2% water; a solution viscosity of 2.0 to 2.3 is achievable. After extrusion into water and granulation, the recovered product can be blended with new granulate at up to 5% loading.

8.2.4 Lactam Recovery across the Entire Production Process

In a production plant, waste, monomer and oligomer arise at various stages, as illustrated in Fig. 8.3. The main arisings are:

- from the vacuum stage in polymerization (highly concentrated) (1)
- granulate- or fiber tow washing water, of 5...10% conc. (2)
- monomer from monomer aspiration (3) and
- sublimation products from the quench chamber upper inner wall (3)
- oxidized polymer waste from spinning start-up, spin pump- and pack changes (4)
- yarn waste from spinning start-up, etc. (5)
- yarn waste from spinning start-up from aspirators (6, 7)
- yarn waste containing spin finish, from spun packages and doffing (8)
- yarn waste from further processing
- waste yarn cut from short packages, package residues or from yarn segregation

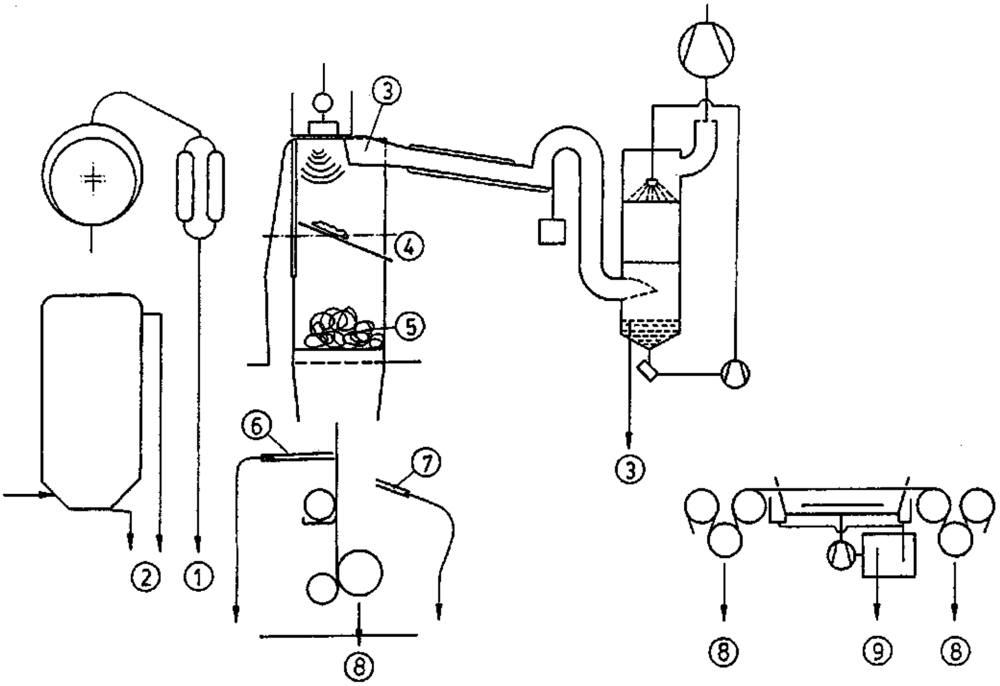


Figure 8.3 Waste generation at polycondensation, spinning and further-processing

1 Monomer condensate from the vacuum finisher, or
2 Extraction water from granulate washing
3 Monomer exhaust gas and monomer washing water
4 Polymer waste from spin pack change (lumps)
5 Spinning start-up waste (filament)
6 Yarn suction waste from machine-mounted aspirator
7 Yarn suction waste from hand aspirator gun
8 Yarn or filament waste
9 Extraction water or drawing bath water, possibly contaminated with solvent and/or spin finish

- spray water from the monomer aspiration circuit, of very low concentration and strongly oxidized
- from drawstands (8) and
- extractables in washing and drawing water (9).

Unless used for shoddy, this waste should be chemically recovered, sometimes after evaporation. Polymer lumps (hard waste) should first be size-reduced.

During PA 6 spinning, monomer and its associated derivatives of concentration 0.1 ... 0.5% in air are aspirated by the monomer extraction, the amount of monomer depending on the monomer content of the granulate or melt; in the case of PP, the monomer content is 0.3 ... 0.8% w/w. Provided that it does not condense on the quench chamber sidewalls, the monomer is exhausted to atmosphere by the suction hood, the monomer concentration being 0.1 ... 0.5% in air. When using heated extractor hoods, followed by a pipe air extract velocity of 10 m/s, the monomer/air mixture is led to a spray tower where the monomer is precipitated by water. It is not economical to recover any materials here. Non-heated monomer extractor hoods must be changed weekly for cleaning.

If one ignores recovery of the above waste, there are three further sources worth considering:

- highly-concentrated waste, such as melt, lumps, yarn with or without spin finish, etc. (hard and soft waste). These should be size-reduced or compacted, then depolymerized.
- waste in solution, usually of between 4 and 10% concentration, typically granulate washing water, etc. These solutions are concentrated via multi-stage evaporation.

- spray water from the monomer extraction system. Concentration is mostly not economical, but—for environmental reasons—it should be treated in a purification plant.

Because of the low lactam concentration, evaporation requires a very high energy input. The investment and energy costs have been roughly estimated [35]:

Process	Investment	Energy costs
2 stage	average	average
3 stage	high	low
1 stage with mechanical vapor concentration	high	very low
1 stage with steam jet vapor concentration	low	average

For middle-sized plants, the mechanical vapor concentration has proved to be the most economical.

Distillation is purposely carried out batchwise to cope with the variable throughputs at polymerization. A three stage program of residual water evaporation, pre-distillation and oligomer separation, as well as fine distillation, ensures an optimal lactam quality. The oligomers are pumped off for cracking, the pure lactam is sent directly to the polymerizer and the distillation waste products can be burnt.

8.3 Chemical Processing of PA66 Waste

The monomers are recovered by means of hydrolysis; there are many possibilities:

- The waste is treated with 50% H_2SO_4 at 115...120 °C in an autoclave. After separation of the dicarboxylic acid, the hydrolyzed solution is neutralized with a paste made from caustic lime and water at 90 °C. Water and diamine are then distilled off, after which the condensate is rectified [8].
- In the alkaline hydrolysis process [9,11], the waste is treated with 10...15% alkali under pressure at 200 °C, followed by extraction of the diamine from the hydrolyzed solution using an organic solvent, or
  - distillation of the diamine from the hydrolyzed solution in the presence of an alkaline salt of the dicarboxylic acid, or
  - acidification of the dicarboxylic acid salt, after removal of diamine, using a strong mineral acid, and separation of the carboxylic acid by means of crystallization.
- Total hydrolysis in water [10] using a strongly acidic ion exchanger. The previously size-reduced PA is brought to reaction by the water and the ion exchanger at between 50 and 150 °C, after which the ion exchanger is separated from the water, and the monomer adhering to it is dissolved using reagents of appropriate pH (e.g., aqueous ammonia at increased temperature)
- Hydrolysis in the presence of the original acid [12], i.e., the dicarboxylic acid used in the polymerization of the polyamide. After complete hydrolysis, the excess acid is neutralized by the original diamine, and the resulting salt solution can be directly used for renewed polymerization.
- In production polycondensation there are problems with contamination of the HMD (hexamethylene diamine) solution. This problem is relatively easy to solve when using solid AH salt or HMD and adipic acid as starting materials, since a rectification stage can be built into the intermediate evaporation stage, from where the condensate of the distillate can be either taken to the salt-dissolving vessel or to neutralization and then re-used. If, however, the production process involves an AH salt solution, the condensate from the evaporation stage must go into the waste water. This results in a very expensive distillation stage, as—on the one hand—the HMD must be recovered, and on the other hand as little HMD as possible must end up in the waste water, since it is both toxic and difficult to bio-degrade [35].
- The solid deposits in the neighborhood of the spinneret, particularly on the upper, inner walls of the quench chamber, need to be mechanically scraped off from time to time if they are to be recovered, as described at the beginning of this chapter. Such waste constitutes 0.5...0.75% of the spun PA66-throughput.

8.4 Depolymerization of Polyester

For trouble-free re-use of polyester waste, only decomposition to the original monomers is practicable; here there are three possibilities:

- Hydrolysis using water (alkalis or acids)
- Alcoholysis using methanol or glycol
- Decomposition using glycol, followed by conversion to DMT

8.4.1 Conversion of Polyester to TPA or DMT

The plant required for depolymerization (Fig. 8.4) is quite simple: a 2- to 10-fold excess of water is added to the waste in a pressure vessel, which is heated for 3...5 h at 230...250 °C under a pressure of 30 bar. The depolymerization vessel (3), of, e.g., 1000 l volume, is charged with 250 kg PET waste and 500 kg water from the vessel (2), and is then heated for 2 h at 230 °C/30 bar without stirring. The heating is then switched off and the vessel is slowly stirred by an anchor-shaped agitator. After a cooling down time of 3 h, the contents reach 90 °C; the reaction mixture is pumped into the cold vessel (1), where the temperature is allowed to fall to 20...30 °C. The drained and centrifuged product then contains ca. 205 kg TPA of 98...99% purity. If followed by a pressurized esterification using methanol and vacuum distillation, a pure DMT of yield ca. 95% is obtained.

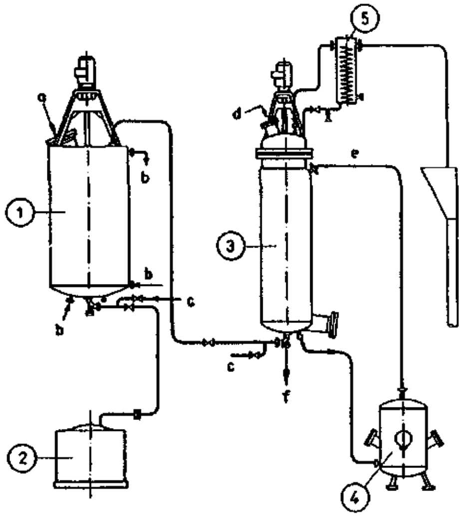


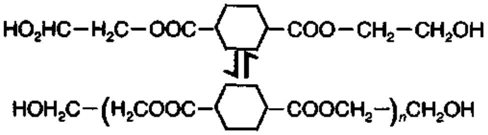
Figure 8.4 Schematic of apparatus for regenerating terephthalic acid from PET
1 Stirring vessel (cold)
2 Centrifuge
3 Autoclave for pi = 35 atm.
4 Dowtherm (Diphyl) evaporator
5 Reflux cooler
a) Waste
b) Washing water
c) Steam
d) Waste from (2)
e) Dowtherm (Diphyl) vapor
f) Raw TPA

A change in the PET/water ratio between 1 : 2 and 1 : 12 has no effect on the yield. Already after 2 h cooling time a yield of 92% crystalline TPA is achieved. An acidic hydrolysis using 50% concentration nitric acid, sulfuric acid or phosphoric acid is also possible, but—owing to the high acid costs—has found no industrial application.

Solution of 5 parts (w/w) PET in 12 parts (w/w) 15% NaOH at 180 °C and 6...8 bar for a max. time of 6 h also produces a product which, after boiling with 50 parts (v/v) of water, can be crystallized at 80...90 °C by adding 16 parts (v/v) n-HCl to yield 95% (of theoretical) crystalline TPA.

8.4.2 DMT Recovery via Glycolysis of PET

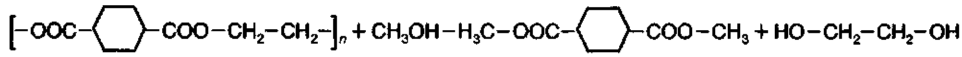
One obtains diglycol terephthalate by means of non-pressurized treatment of PET in ethylene glycol, or by means of pressure using an ethylene glycol solution [18]. At the end of the glycolysis an equilibrium (with $n = 1$) prevails:



The equilibrium concentration of this diol ester, in the presence of a small quantity of water, shifts with temperature until the temperature has fallen to half its value. On further cooling, crystals of the diglycol ester (Bp = 111 °C) precipitate in quantitative yield. Although this process appears to be very advantageous, in practice it is very difficult, as the necessary purity for recycling is difficult to achieve. Even after frequent recrystallization, the product retains a slight yellowish color.

8.4.3 Recovery of DMT via Polyester Methanolysis

DMT is directly generated according to the formula:



Methanol vapor, superheated to 240 °C, converts PET directly to DMT + ethylene glycol in the presence of phosphoric acid as catalyst [16]; the product is contaminated with 2 … 7% monomethyl ester. Pressurized methanolysis in the presence of an aryl sulfonic acid (e.g., benzene- or naphthalene sulfonic acid) is more favorable. Uniform addition of DMT accelerates the decomposition [17]. Use of 0.0027 mol zinc acetate as catalyst at 20 … 30 bar results in a yield of 85 … 88% after ca. 2.5 h [14].

8.4.4 Gaseous Byproducts in PET Production

Acetaldehyde, residual glycol, methanol and oligomer are released mainly in the exhaust gases of the vacuum system and partly beneath the spinneret. They are, however, present in such low concentration that they are sensibly mixed with the combustion air of the central heat transfer oil burner and incinerated or are catalytically burnt in an after-burner.

If, however, the vacuum system operates with glycol and glycol vapor, the impure glycol arising can be treated in the central glycol recovery plant.

In the TPA-PET esterification process, one tries to lose as little glycol as possible with the water arising from cracking. By the use of very expensive distillation columns to purify the water/glycol vapor directly, glycol (the sump product) can be re-directed back into the esterification reactor [35].

The byproduct methanol can be sufficiently concentrated by integrated rectification columns that it need not be re-distilled before re-use [35].

8.5 Mechanical Waste Processing

The state of the waste determines the form of processing. Hard waste (polymer blocks) and PET bottles are granulated, filament waste is compacted, and drawn filament waste is shredded or cut. The first-mentioned can be melted and processed as such, the last-mentioned can be recycled as textile staple, usually of lower quality. Textile material comprising more than one polymer and/or natural fibers can only be processed to shoddy. Mixtures of some polymers can often be reformed into large plastic parts. If the waste is dressed with spin finish, it should be scoured free of finish, then dried.

In all the above processes, metal parts must be removed, e.g., by magnetic separators. Depending on the starting material, one of the following processes is used.

8.5.1 Polyester Bottle Granulate

Polyester bottles are available in large quantities. The paper labels must be removed, after which the bottles are washed and granulated. Like PET granulate, the bottle chips are crystallized, dried and melt-spun using an extruder. Large area product filters and Dowtherm-heated spinning beams are appropriate for spinning staple fiber, fiberfill or non-wovens for further processing.

8.5.2 Polymer Blocks (Solid Waste and PET Bottles)

According to [19], size reduction occurs between the rotary knife of the granulator and the sieve, through which the granulate is forced (Fig. 8.5). The motor sizes have been optimized for the available machine types, and determine the throughputs (Fig. 8.6). If these limits are exceeded, the material to be ground can become too warm and can stick together. The machine rotor in Fig. 8.7 (a) serves to size-reduce compact pieces; the open rotor (b) is for bulky material, hollow pieces and filament waste, among others. Highly-drawn yarn can, however, cause problems here. (C) is used for working large lumps of waste [20].

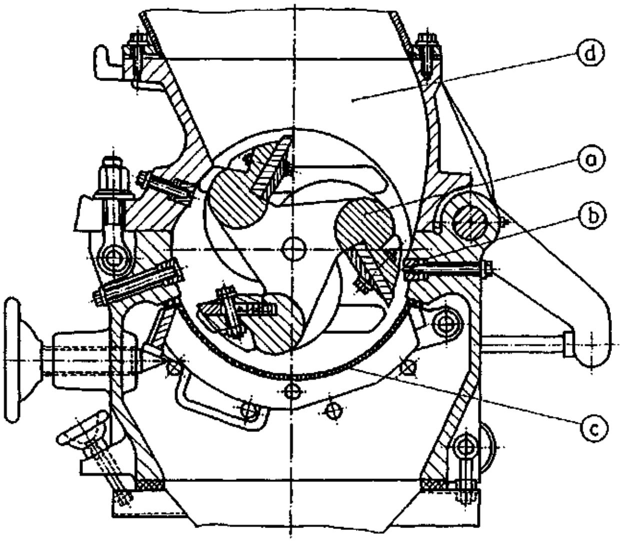


Figure 8.5
Cutting mill, having a horizontal axis and an openable top
a) Open rotor
b) Stator knife
c) Sieve insertion
d) Feeding zone

The machines are made operator-safe by having the inlet hopper large or high and/or by automatic charging of feedstock. Ease of cleaning is equally important.

The processed granulate should have a chip size of between 3 and 6 mm, and should be dust-free. Electrostatic charge can be almost totally eliminated by the use of a water mist spray to produce almost saturated air. The (pneumatically) transported granulate can be cleaned by cyclones, separators, etc.

8.5.3 Compaction of Filament Waste [24–26]

The filament waste is cut in a cutting mill granulator, between a rotary knife (as in Fig. 8.7 b) and a fixed knife. The sieve insert, having a square mesh opening of 12...20 mm, determines the size of the waste granulate which is pneumatically transported away. A speed-regulated stuffing screw (a) (Fig. 8.8) presses

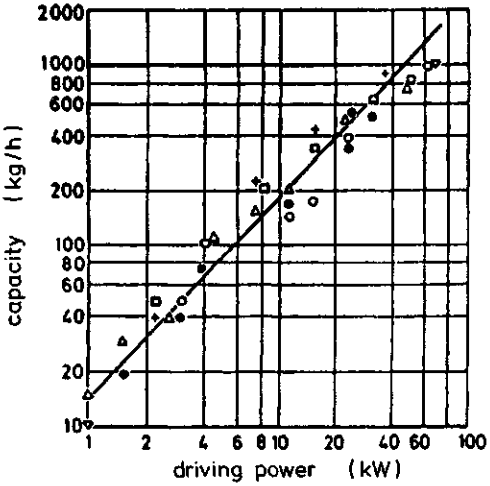


Figure 8.6 Throughput of a cutting mill as a function of the installed power

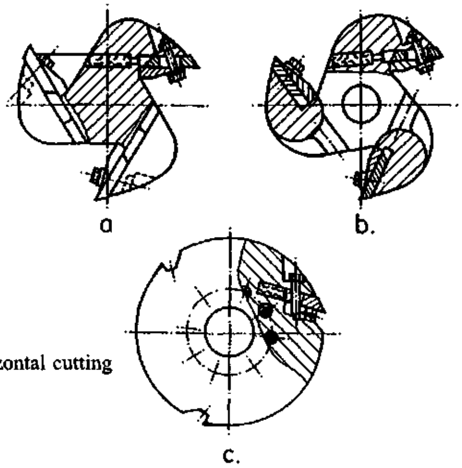


Figure 8.7
Rotor design for horizontal cutting mill
a) Solid rotor
b) Open rotor
c) Milling rotor

material from the compacting zone centrally against a pair of disks (Fig 8.9), one being a stator and the other a rotor—from inside to outside. In the first part of the shearing zone, the material is accelerated radially and tangentially, causing its bulk density to increase. This is followed by a kneading zone and a rolling zone, and thereafter an external cooling-, relaxation- and exit zone. By means of motorized adjustment of the gap between the two disks, the frictional heat and thereby the temperature of the material can be adjusted, enabling one to achieve the optimal plasticizing temperature in the neighborhood of the softening point, but below the melting point. Figure 8.9 shows the various conditions. The sintered agglomerate is fed to a second cutting mill granulator having a 4 . . . 8 mm sieve opening in the sieve insert and a large housing which can be air- or water cooled. A cyclone in the pneumatic transport line removes dust and fine particles.

The waste yarn to be processed can have up to 7% moisture content. Any spin finish present is largely evaporated by the temperatures which arise during processing. There is no danger of thermal degradation, as the sintering temperature is always well below the melting point. Any moisture remaining after processing can be removed by vacuum drying. The bulk density of the compacted granulate is given in Table 8.2.

A compactor disk size of 500 mm diameter is optimal, permitting a throughput of 400–500 kg/h, depending on the feedstock. The required power would be 90–110 kW.

8.5.4 Yarn to Staple Processing

There are small specialist firms which buy yarn waste, sorted or unsorted, and convert it to staple. Spun or POY yarn residues on tube can be taken off overhead from a creel, plied, drawn and crimped in a one stage process. During processing, new waste packages can be knotted—or spliced into the running tow. Here the "Lummus" staple cutter has proved itself useful (section 4.13.12). After cutting, the staple is pneumatically conveyed to a bale press, where it is compressed, baled and strapped.

Waste packages from draw texturizing machines, after pre-tensioning, can be knotted into the above-described tow and thus processed as above.

Yarn cut off from waste packages is compressed and cut to small size in a guillotine. It is then used as staple or flock.

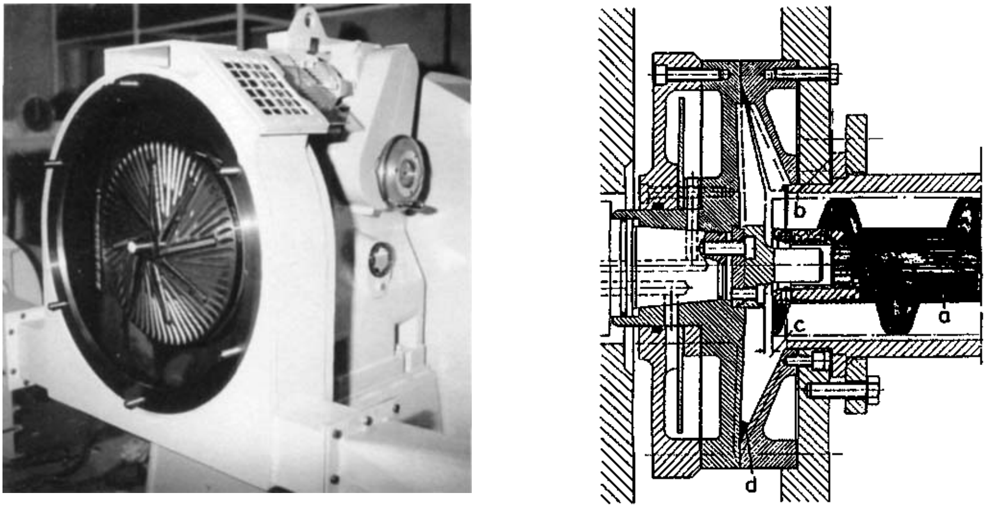


Figure 8.8 Design of a compactor having a stator-rotor as central processing unit of the plant, and upgrading photograph (opened)
a) Supply screw
b) Compression zone
c) Kneading zone
d) Relaxation zone

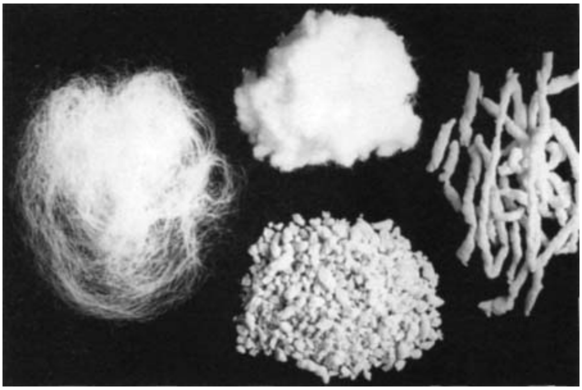


Figure 8.9
Polyester fiber shown at various stages of compression during processing
a) Loose fibers
b) Compressed fibers
c) Agglomerate
d) Compacted granulate

Table 8.2 Bulk Density of Granulate after Compaction

Feedstock	Comparative throughput kg/h	Bulk density g/l
PE film	450...500	335...350
PP film	400	350
PP staple	320	345
PA film	300	470
PA 6 staple	350	420
PA 66 staple	350	450
PET film or staple	350	600

The staple so made can vary considerably in cut length, tenacity and elongation. One therefore tries to set an average staple length of 70 . . . 90 mm so that the staple can be used in worsted yarn, possibly only as a blend component.

8.6 Direct Extruder Processing of Yarn and Film Waste

As long as the waste material is of one type, e.g., only PP or only PET, it can be reprocessed to granulate or chip by an extruder modified for the purpose. It is possible to add up to ca. 5% of the regranulate to fresh granulate without noticeably affecting the quality of the staple fiber. Here, however, the following questions need to be clarified:

- how much degradation (in η_{rel}, $[\eta]$ or MFI) is permissible in the recovery process, both in the regranulate and in the final product as mixture?
- how high a % of regranulate is permissible in the final product when particular final properties, e.g., viscosity, tenacity and elongation, should not be negatively affected?
- which, and how much, contamination is allowable in the regenerated granulate, and which melt filtration should be used?
- if the desired final product properties have not been achieved, is it possible to improve them by means of another process stage or by additional further processing?

The pre-treatment of the waste comprises sorting, metal removal, washing, possibly crystallization and drying. The spin finish can be satisfactorily removed by using an extruder with two de-gassing zones. The extruder throat has an entry funnel fitted with a stuffing screw, which—because of the low bulk density—begins in the conical part of the hopper (Fig. 8.10) and continues (as a cone) in the main screw, covering the first 4 pitches (diameter ratio 1 : 2.5 to 1 : 3).

A good measure of the plastification and homogenization is the shear work:

for a single screw extruder

$$\frac{d\sigma}{dx} = \frac{v_0}{t}$$

for a twin screw extruder [34]

$$\frac{dv}{dx} = \frac{v_0 - v_a}{S_k}$$

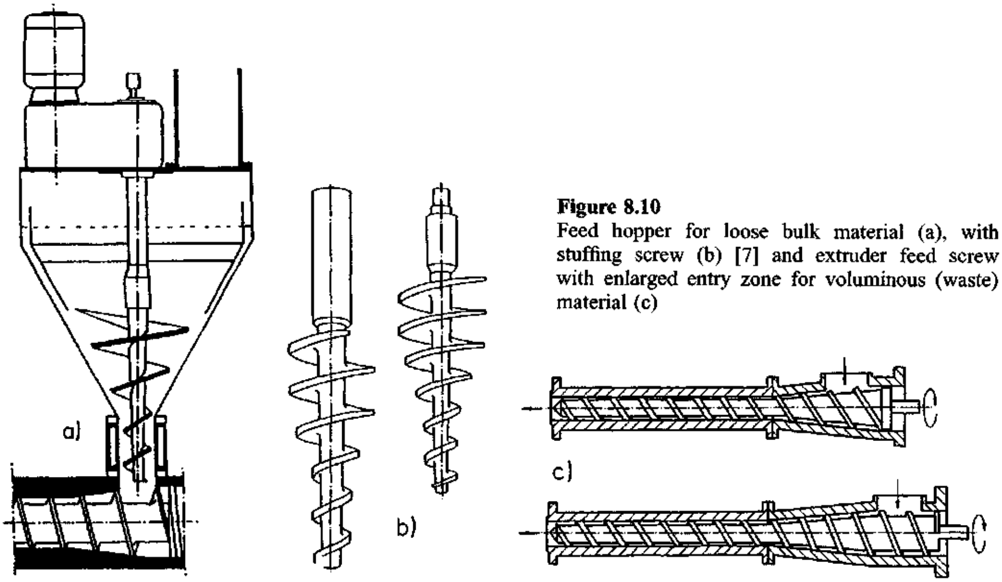


Figure 8.10
Feed hopper for loose bulk material (a), with stuffing screw (b) [7] and extruder feed screw with enlarged entry zone for voluminous (waste) material (c)

where v_o = circumferential speed of the screw root, v_a = circumferential speed of the screw outside diameter, S_k = the gap between the above parts and t = screw depth.

Single screw extruders have good axial mixing, counter-rotating twin screw extruders poor axial mixing and co-rotating twin screws the best mixing. To evaporate the moisture absorbed by PA and the spin finish, one de-gassing zone may suffice, but two de-gassing zones are preferable. With co-rotating twin screws, the incomplete filling results in a suitable surface being formed for satisfactory functioning of the vacuum.

For effecitve de-gassing, the following is important:

- long residence time under vacuum at the highest possible temperature
- increasing shear deformation
- low filled volume, i.e., large polymer surface in the degassing zone
- good pre-drying, as described in Section 4.5

Although the counter-rotating twin screw extruder provides optimal conditions for degassing, satisfactory results can almost always be obtained with the single screw extruder when using one or two de-gassing zones [27].

The quality of the product is also determined by the filtration. Here large area product filters having a pore fineness of 20—or sometimes even 10 μm—are fitted. From experience, clean material (only aspirated waste) contains $\leq 0.01\%$ inpurities, finish-dressed fiber up to 2% and slightly soiled residues up to 4%.

Finally, the recovered product can either be granulated, possibly crystallized and dried and then mixed with fresh granulate or be spun as a 100% recycled product of lower quality; in the case of PET one must expect $\geq 10\%$ $[\eta]$ reduction. Direct spinning to staple fiber gives a somewhat better quality, but the product is by no means of prime quality. Figure 8.11 shows a plant for converting filament waste to granulate.

Type	A	B	C	D	E	F
HKS 120/70/1	2300	1200	1800	2895	4040	ca. 7900
HKS 140/90/1	2800	1800	1800	3550	4690	ca. 9000

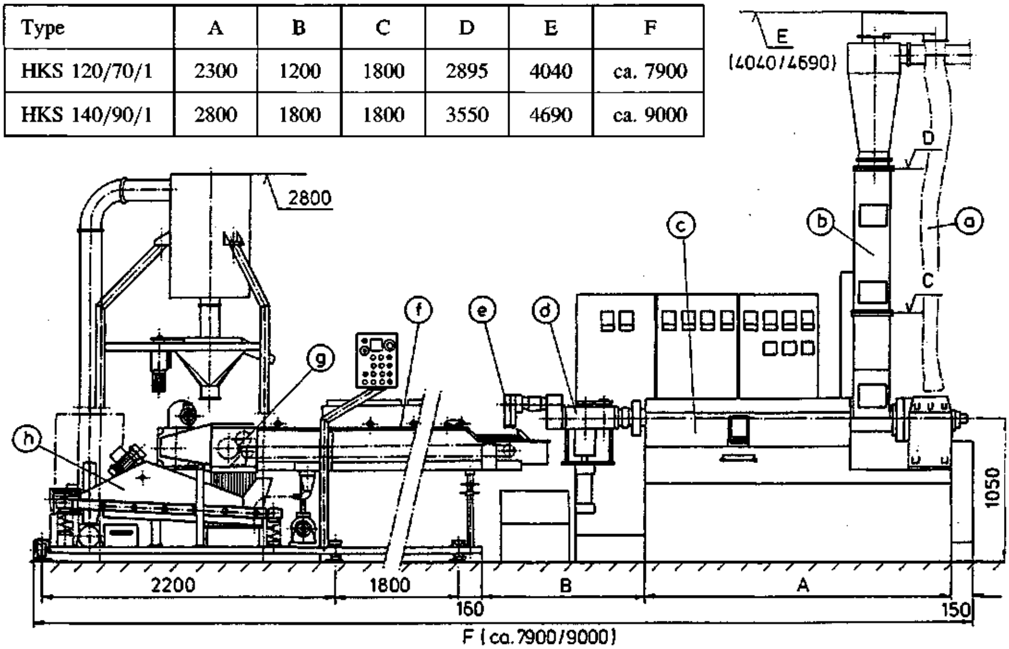


Figure 8.11 Extruder-based plant for converting yarn waste to granulate [27]
a) Pneumatic suction of waste chaff (raffia)
b) Waste buffer storage
c) Degassing extruder
d) Continuous change filter
e) Extrusion head
f) Cooling conveyor with water spray
g) Granulator
h) Dewatering and granulate transport

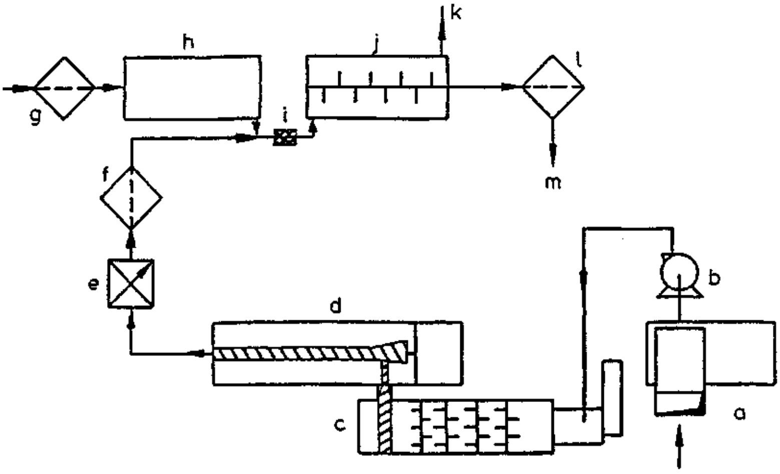


Figure 8.12 Hydrolytic degradation of polyester and injection of the depolymerized product into a continuous polymerizer [7, 14]

a) Cutting mill
b) Fan
c) Washing unit, and
d) Charging apparatus and single screw extruder with enlarged feed zone (= depolymerizing zone)
e) High viscosity pump
f) Filter
g) Prefilter in polycondensation stage, for pre-product
h) Static mixer
i) Static mixer
j) Finisher (for waste melt)
k) Reactor (= finisher, 275°C/6 h/0.3 mbar)
l) PET melt filter
m) PET melt to spinning or strand extrusion (for chips)

If the producer has a PET polycondensation plant, the waste can be deliberately decomposed in an extruder and, after good filtration, pumped into the main stream before the finishing reactor via a static mixer (Fig. 8.12). The end product retains its value.

8.7 Recovery and Cleaning of Gases and Fluids

Spinning and further processing which employ solvents and involve wet processing only become economic when the components are recovered, and are only ecologically acceptable when process water and exhaust gases are cleaned. If one takes the solvent price as being half the polymer price, and reckons on a 25% polymer solution, the cost case becomes clear. Protective gas (e.g., N_2), too, is expensive, and must be recovered and re-used in the dry spinning process. Exhaust gases laden with solvent also need to be aspirated, both for health reasons and to avoid explosion hazard.

Figure 8.13a shows a gas and solvent flow diagram for a PAN dry spinning process. N_2 protective gas is heated to 330 ... 350 °C in a Dowtherm vapor-heated heat exchanger and flows to each spinning tube head, where it is individually superheated to an exact temperature, e.g. 352 ± 2 °C. During the fiber transit down the tube, the DMF concentration increases from 40 to ca. 400 g/m^3. Simultaneously the spinning gas cools down, being at ca. 250 °C somewhat below the spinneret and at 150 °C on exiting the end of the tubes. This exhaust gas is used to preheat the regenerated gas from 20 ... 25 °C to 100 °C. After cooling down, the DMF concentration decreases to about 40 g/m^3. Part of this gas stream is diverted through an active carbon filter for purification.

Losses are compensated by fresh nitrogen, which is pumped through the heat exchanger previously mentioned into the main gas circuit (Fig. 8.13b and c).

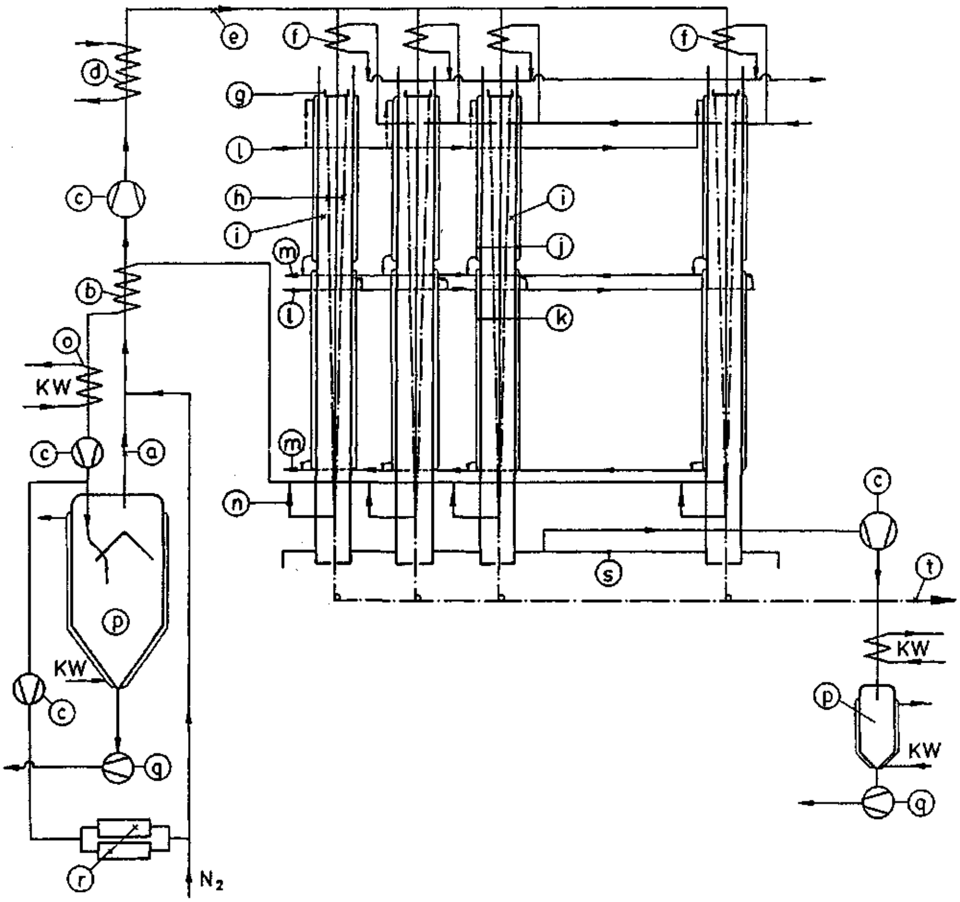


Figure 8.13a Flow sheet of a plant for purifying the spinning gas of a PAN dry spinning machine [36]
a) Fresh gas containing 60 g/m^3 of DMF (depends on the cooling watertemperature)
b) Gas/gas heat exchanger (serving a) and n), ca. 140 °C)
c) Fresh gas pump (fan)
d) Dowtherm (Diphyl) vapor-heated gas heater (up to 350 °C)
e) Hot gas manifold
f) Gas booster heater (one per spinning head tube) with Dowtherm (as per d)
g) Spin pack(s) (mostly annular spinnerets)
h) Yarn bundle
i) Spinning tube, with
j), *k*) Jacketed heating zones for liquid heating
l) Inlet for heat transfer medium (above: up to 350 °C; below: mostly 200 ... 250 °C)
m) Outlet for heat transfer medium (above: mostly between 250 and 200 °C; below: well above the boiling point of the solvent)
n) Spinning gas aspiration (one per tube)
o) Gas-cold water heat exchanger (serving c) = return gas fan
p) (Spray) condensor
q) Condensate pump for recovery
r) Active carbon filter for gas part-stream (with fan c)
s) Extractor hood
t) Plied spun cable
KW) Cold water (as low a temperature as possible)

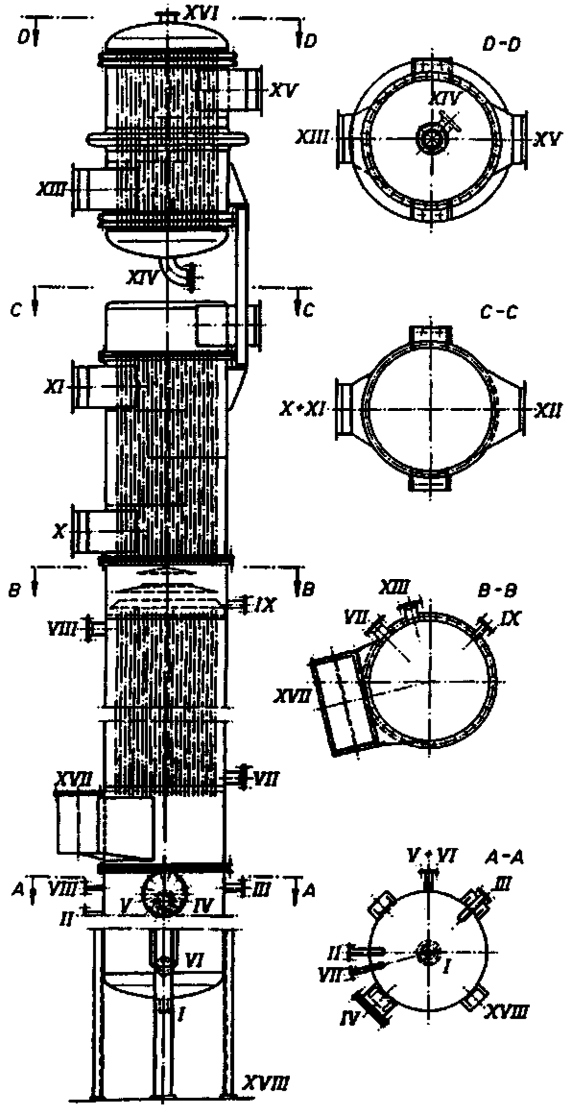


Figure 8.13b
Spinning gas purification column belonging to flow sheet Fig. 8.13 [36]

I Condensate outlet
VI Sump
XI Spinning gas return to gas/gas heat exchanger
X Spinning gas return to
VIII Gas/water heat exchanger
XVII (Cold) spinning gas inlet to gas/gas heat exchanger
XII Pre-heated spinning gas Dowtherm (Diphyl) vapor/gas heat exchanger
XV Hot spinning gas

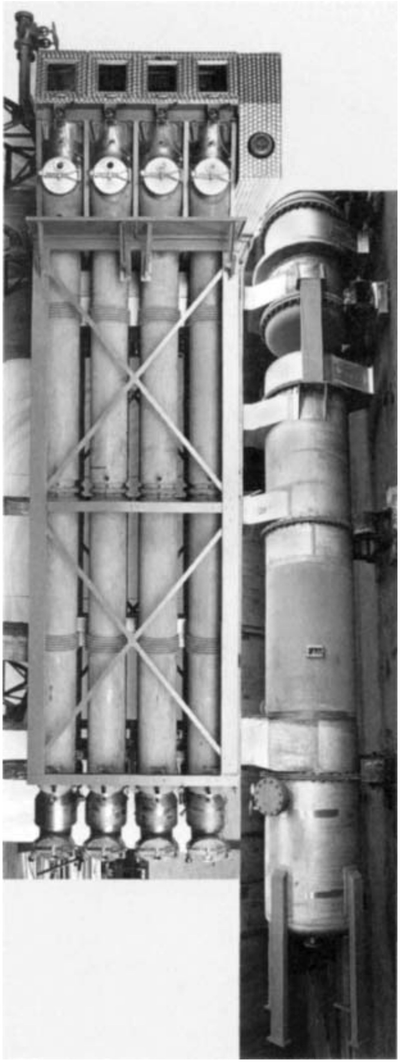


Figure 8.13c
Photograph of a PAN dry spinning machine (double-sided, 2 × 4 spinning tubes) and the included spinning gas recovery unit (for 32 positions [36])

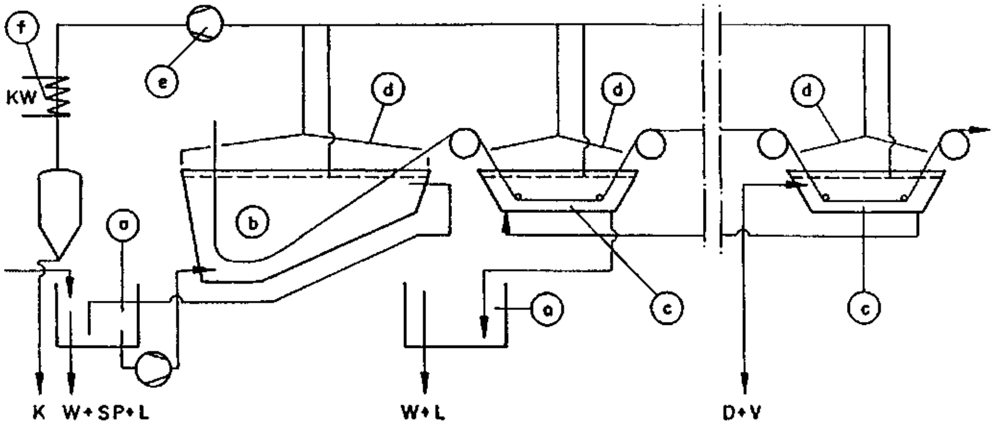


Figure 8.14 Bath- and vapor recovery system of a wet spinning and/or further processing line

a) Bath reservoir tank
b) Spinning bath with surface aspiration
c) Drawing-and post-treatment baths
d) Fume extractor hoods
e) Fan
f) Condenser

W Water
KW Cold water
SP Spinning bath
L Solvent
K Condensate

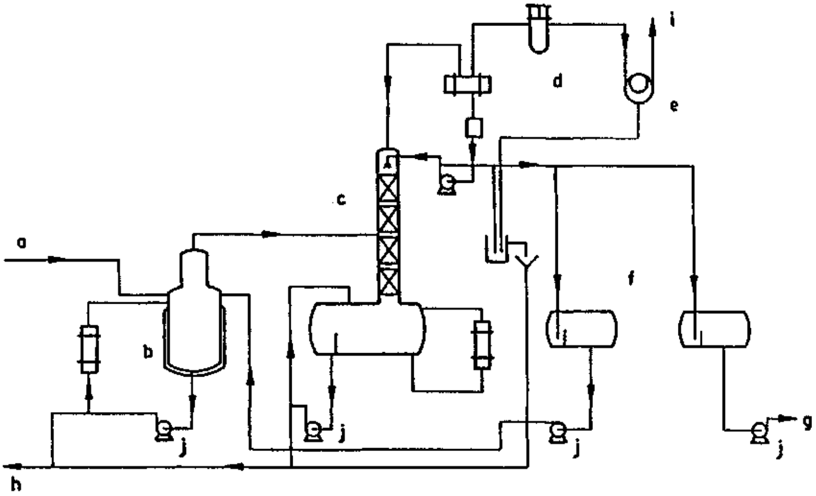


Figure 8.15 Recovery plant for glycol, methanol, etc. [34, 35]

a) Cracked glycol from the polycondensation
b) Pre-evaporation
c) Distillation
d) Condensation
e) Vacuum generation

f) Intermediate storage
g) Recovered glycol to polycondensation
h) Residue to incineration
j) Pumps

The DMF condensate formed as a result of cooling, mixed with a small amount of water, is pumped from the sump to a regenerator; after distillation, it is re-used as solvent. The PAN cable emerging from the spinning tube still contains 7 . . . 9% of DMF. As the tube is at a slight overpressure, some DMF vapor escapes with the tow on exiting the tube. Together with the aspirated air, this vapor is condensed in a cold water heat exchanger and led to the recovery unit.

In a wet spinning and after-processing plant (irrespective of whether the PAN has been dissolved in DMF or DMAC), demineralized water is fed into the last washing bath; it flows countercurrent backwards to the first drawing bath, becoming enriched by about 10% solvent, then flows via a storage tank to evaporation and recovery. In addition, the solvent vapor above each bath surface is aspirated via slits close to the bath surface (Fig. 4.336, pos. i); these vapors are condensed in a cold water heat exchanger and returned to the recovery unit (Fig. 8.14).

In the glycol recovery plant shown in Fig. 8.15, the use of two stage distillation enables a high quality, pure glycol to be obtained at 98% yield; the plant is very flexible. Methanol and DEG can also be recovered by such a plant provided the design has made allowance for such application. The products of cracking from the polymerizer are pumped into the pre-evaporator. Low boiling point components, as well as glycol and DEG, pass into the distillation column; the low boiling point components distil off at the top, while glycol and DEG collect in the bottom. In the second distillation, the column settings are optimized for the separation of DEG and (mono-) glycol.

The low boiling point fraction and the bottoms from the pre-evaporator and distillation column are mixed and incinerated in the central heat transfer fluid burner. The exhaust gas from the glycol ring main pumps of the vacuum generator of the vacuum plant, as well as the exhaust gas from the polycondensation plant, can also be sent to the heating plant for combustion [35].

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