

COMPARISON OF DEVOLATILIZATION TECHNOLOGIES FOR VISCOUS POLYMERS

*Dr. Pierre-Alain Fleury
Dr. Daniel Witte
Helmut Schildknecht
List Group*

Abstract

Devolatilization of solvents from viscous polymer cement is realized through stripping of solvent with steam in stirred vessels or directly by evaporating the solvent from the polymer. The later so-called direct desolventizing is realized in extruders or high volume kneaders. All 3 methods involve additional energy to drive out solvent either by partial pressure through additional steam (steam stripping), building and releasing pressure in order to explode the polymer bulk (extruder) or dynamic surface renewal (kneader).

Introduction

Polymer devolatilization is a separation process in which “volatiles” are to be removed from a final polymer. The “volatiles” are mainly solvents and small amount of rest monomer(s). The final amount of “volatiles” in the polymer after the devolatilization is generally between 100 and 1000 ppm. Based on the following study, we will see that the devolatilization process is mainly defined by the reaction step and polymer properties:

1. The reaction is normally carried out in tank reactors (diluted process) needing a high solvent concentration to ensure good mixing behavior and to control the reaction temperature. For some particular cases, the reaction is carried out in kneader reactors (high viscous process) under evaporative cooling at low solvent concentration or no solvent at all. As a consequence, the reaction step defines the amount of solvent to be separated.

2. The chemical properties of the polymer define the maximum allowable temperature to avoid undesired crosslinking between polymer chains or depolymerization.

In order to consider the influence of the reaction on the devolatilization we need to introduce a new step between the reactor and the devolatilizer: the main evaporation. For the diluted process working with a typical polymer concentration of 15% in the reaction step the main

evaporation has to remove large amount of solvents and the devolatilization focuses on the last solvent separation in the diffusion domain. In the case of the high viscous process the main evaporation can be simply eliminated.

The maximum allowable temperature has an impact on the design of the main evaporator and of the devolatilizer.

The main evaporation and devolatilization steps can not be dissociated and are discussed in this paper based on two different technologies:

- Steam Stripping Process (dewatering screw, belt dryer and cooler)
- Direct Separation Process (extruder / kneader)

Steam Stripping Process

This commonly used process for solvent removal from polymer cement uses steam both as energy source for the main evaporation of the solvent as well as stripping media for the final devolatilization. Superheated steam is injected into a hot water bath in which the polymer solution is suspended. While the solvent is removed, the polymer concentrates and is coagulated to polymer particles. If the polymer does not coagulate spontaneously, appropriate coagulation substances have to be added. Since steam is the energy source for evaporation and the water does not necessarily condense, the superheating of the steam has to provide the evaporation duty for the solvent. The solvent and steam off gas is separated in a second step by condensing and distillation. For these reasons a multiple of the solvent evaporation duty is needed to perform the evaporation by steam. The finishing step also requires excess steam, because the partial pressure of the steam is the only driving force of this diffusion-limited process. The water has to be dried off after the steam stripping process itself using a dewatering screw and belt dryer.

From an equipment and scale-up standpoint, the steam stripping process is simple using only stirred vessel in which the rubber/water/solvent mixture floats at low

viscosity. The upset of this process is the huge amount of energy required to provide the steam (up to 7 times more than direct devolatilization). The steam duty increases with required lower final solvent content in the polymer. In this case the number of consecutive stripping steps can be up to 5. Polymers, which sticks to the jacket of the stripping vessel or strongly foaming polymers cannot be steam stripped.

The final water removal from the polymer is often performed by hot air, no longer requiring ex-proof equipment. Rest solvent may be stripped off into environment because there may be some remaining solvents in the polymer.

Direct Separation Process

The main evaporation and the direct devolatilization are separation processes to pre-concentrate diluted polymer solutions and to separate remaining volatiles from the final polymer. They offer a highly economical alternative to conventional steam stripping process.

Main Evaporation

The reaction step delivers the polymer generally in a diluted phase or applying a new process in a high viscous phase. Therefore, two cases are to be considered for the main evaporation:

1. Diluted Process

The solution (co-)polymerization is carried out in CSTR(s) in the presence of 10-20 % polymer concentration. A main evaporation step is therefore needed to pre-concentrate this diluted polymer solution prior to the devolatilization.

- a. For (co-)polymers allowing heating above 200 °C the main evaporation is carried out with a series of flash pots ending in a pre-concentrated polymer solution containing 80-90 % polymer. The pre-concentrated polymer solution is then flashed into the devolatilizer to reduce residuals to 200-800 ppm (see Direct Devolatilization). **Figure 1a** shows the process flow diagram.
- b. The new technology for temperature sensitive polymers (below 200 °C) consists of a main evaporator followed by a devolatilizer (**Figure 1b'**). The new main evaporator applies mechanical energy

at low shear rates to pre-concentrate the polymer solution up to 80-95 % polymer concentration. Therefore, contact heat transfer is not needed any more. This eliminates local overheating and gel/specks formation. The pre-concentrated polymer solution is then flashed into the devolatilizer to further reduce volatiles down to 200-800 ppm (see Direct Devolatilization). **Figure 1b'** shows typical polymer capacities as a function of size of main evaporator for three polymer grades from low to high Mooney values. **Figure 1b'** demonstrates how compact the main evaporator can be even at high evaporation capacities. The well known foaming problem is also eliminated by using this technology.

2. High Viscous Process

Today kneader reactors are successfully applied to handle continuous bulk or solution (co-)polymerization reactions (**Figure 2 and 3**). High monomer conversions are achieved both above or below the glass transition temperature of the polymer. Surface renewal, evaporative cooling and efficient mixing allow optimal heat and mass transfer with the following results:

- Precise control of the product temperature and of the molecular weight even in presence of Trommsdorff's effect.
- Gel formation due to local high temperatures is avoided
- Easy feeding and incorporation of additives to the polymer.

The main advantage to carry out the continuous polymerization in a kneader reactor is to reach an end polymer mass having at least 80% polymer content. In some cases polymer concentrations close to 100% are also feasible. This makes the technology especially attractive to replace conventional processes where polymer contents of the reaction mixture are from 10% to 20% requiring costly solvent evaporation steps and subsequent treatment to remove water traces (to prevent catalyst poisoning). Therefore, by using this technology in which very little or no solvent is present, the conventional main evaporation step is not required. The final polymer mass with a concentration of at least 80% polymer can be flashed directly into the subsequent devolatilizer (see "Direct Devolatilization"). This devolatilization step reduces the remaining volatile content of the polymer to 200-800 ppm.

Direct Devolatilization

The high volume kneader is well suited for high-residence-time applications such as diffusion-limited

processes. Working under low vacuum, the polymer solution flashes into the kneader - devolatilizer. This technology provides a dynamic renewal of the exposed surface area between polymer melt and gas room for efficient mass transfer of solvent/ monomer(s) to the gas phase.

In comparison, extruder has very short residence time due to small internal volume and must therefore explode the polymer mass in order to increase the exposed area. For this purpose the shaft geometry depends on the polymer grade and must be changed/adapted for the production of another grade.

Compared to extruders for devolatilization, kneader - devolatilizers have four major advantages:

- Much lower shear rates to prevent break down of shear sensitive polymers.
- Much higher turn down ratio giving the flexibility to move from partial to full capacity within seconds.
- Much larger cross-sectional areas eliminating dome plugging (gas velocities max 5 m/s).
- Much lower maintenance costs (no wear on kneading elements).
- All polymer grades can be processed with one shaft configuration.

The typical rest solvent/monomer(s) content are as low as 200 ppm for low Mooney grades and 800 ppm for high Mooney grades at a capacity of up to 12,000 kg per hour and unit. Therefore, in addition to its higher flexibility and economic efficiency (lower production costs), the processing in a kneader insures the best polymer quality at low residual volatile contents.

The temperature sensitivity of the polymer is of important consideration for the devolatilization step. In order to control the polymer temperature operation parameters of the kneader - devolatilizer can be adjusted to limit the dissipated mechanical power going into the polymer mass. This adjustment permits to granulate the polymer in a reversible mode to get a high polymer interface area for mass transfer of "volatiles" to the gas phase. Being granulated, the polymer does not receive mechanical stress anymore and can be devolatilized in the high volume kneader under vacuum conditions.

Conclusion

The conventional Steam Stripping process and the Direct Separation process are compared in terms of specific energy consumptions (**Table 1**).

Steam Stripping delivers a good polymer quality even in case of temperature sensitivity. But this technology has a very high energy consumption (7 times more compared to Direct Separation) and does not work for all polymer grades (some stick or strongly foam).

Direct Separation process has been successfully implemented for non temperature sensitive polymers. Low energy consumptions and zero emission to the atmosphere have been confirmed.

Polymers, which are temperature sensitive can now be processed by Direct Separation using the new main evaporator working mainly with mechanical heat input at low shear rates.

The extruder or the high volume kneader is used for the final devolatilization step in the Direct Separation process. Extruders are well established in the domain but the kneader can improve the process work mainly in terms of better turn down ratio, polymer break down and dome plugging.

Typical applications for the Direct Separation process are : PB, BR, butyl rubber, poly(isoprene), SBR, SBS, SIS, SEBS, bi-and triblock polymers, EPDM, EPM, EOM, crosslinkable (co-)polymers, elastomer solutions, polymer solutions and other comparable products.

Key Words

Polymer devolatilization, comparison, stripping, diffusion, kneader, extruder, high viscosity, rubber, foam.

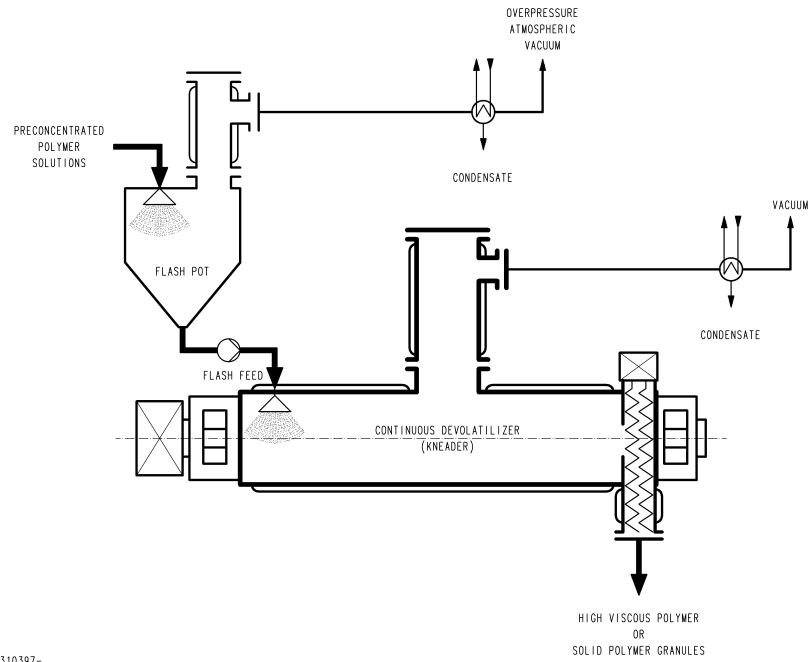


Figure 1a : Diluted Process; $T > 200^{\circ}\text{C}$

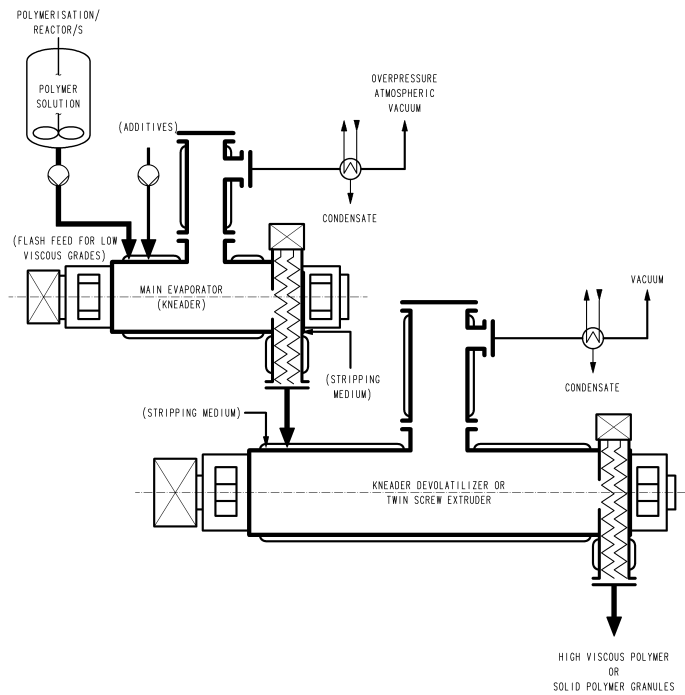


Figure 1b' : Diluted Process; $T < 200^{\circ}\text{C}$

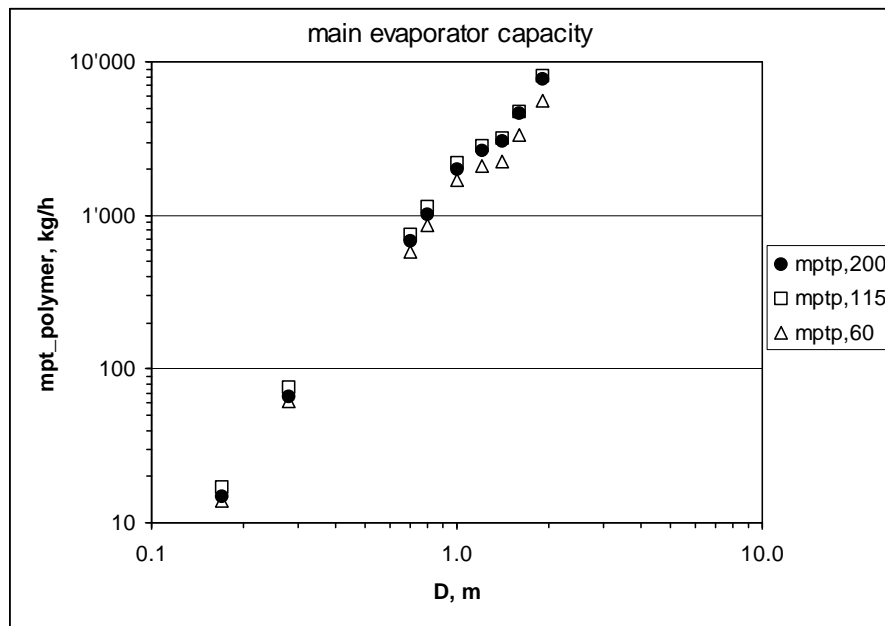
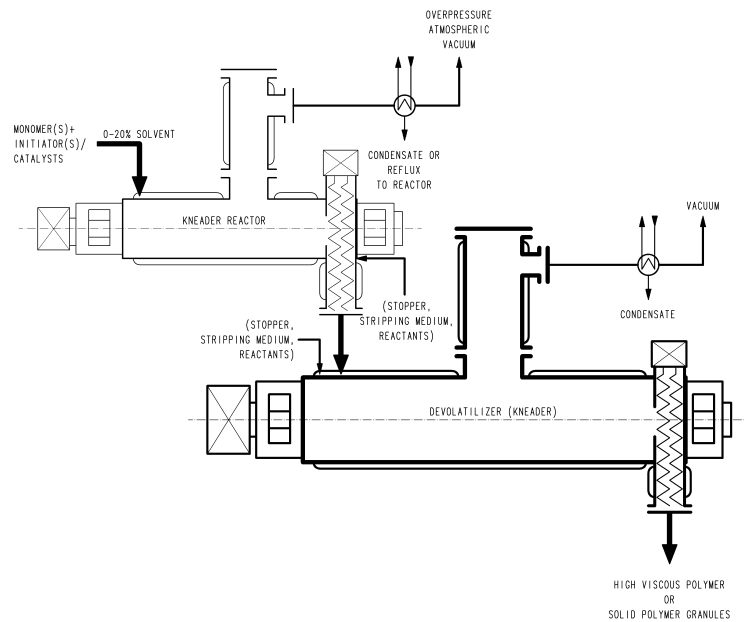


Figure 1b : Typical capacities for the main evaporation as a function of evaporator's diameter. The capacity refers to the pure polymer. Three polymer grades are calculated: 200, 115 and 60 kg/mol for the molecular weight in weight. The feed polymer concentration to the evaporator is respectively 15, 18 and 23% to target same viscosity in tank reactor. The discharge polymer concentration of the evaporator is respectively 85, 87 and 90%. The product temperature is 160 °C for all grades.



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Figure 2 : High Viscous Process: The (co-)polymerization can be carried out in a kneader reactor without or with the presence of up to 20 % solvent concentration with high monomer conversion. This concentrated polymer solution is then directly flashed into the devolatilizer to reduce residuals down to 200-800 ppm (see Direct Devolatilization). The main evaporation step in between is in this case not necessary.

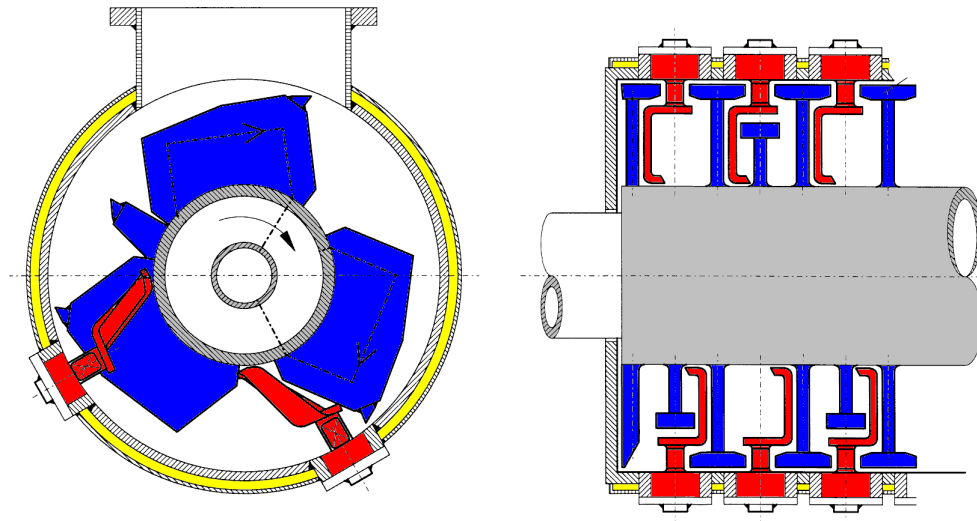


Figure 3: High Viscosity Kneader

Specific Energy Consumptions	Steam Stripping	Direct Separation	
		Flash evaporation	Mechanical evaporation
MJ/kg final polymer	11	1.7	1.7
Solvent purification	High demand	No demand	No demand
Environment impact	Contamination	Clean	Clean

Table 1 : Comparison between two separation technologies. The Specific Energy Consumptions are given for the main evaporation and devolatilization steps. Most of catalytic systems are killed by water: this requires a high demanding purification process in the case of Steam Stripping.