

# Transfer Phenomena During the Extraction of Polyamide 6 Granules

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## ABSTRACT

The heat and mass transfer has been studied in the case of solid/liquid extraction applied to polyamide 6 granules. A solution being proposed for the intensification of heat and mass transfer involving recirculation of the extraction waters by inducing a sinusoidal, low amplitude and high frequency velocity. The hydrodynamic calculations performed, evidenced an eight times increase in each of the individual heat transfer coefficient and an over five times increase in each of the individual mass transfer coefficient. Also, all attempts aimed at the optimization of the process have been materialized in the elaboration of a new spinning tube model as well as in the selection of a thermal agent suitable for the obtention of desired temperature profile in the extractor.

**Key Words:** solid/liquid extraction, heat and mass transfer, temperature profile, microrecirculation, polyamide 6

## INTRODUCTION

The solid/liquid extraction has constituted the topic of numerous investigations, devoted to mass and heat transfer phenomena accompanying this operation.

The studies on the influence of various factors upon such processes, and also the elaboration of some physical models of extraction permitted the establishment of the transfer equations characteristic to different types of devices, as well as the optimization of their transfer processes.

In the obtainment of polyamide 6, the

extraction phase represents an important stage, as influencing essentially the polymer's quality, and therefore, its development in optimization conditions is mainly considered by the producers.

One of the important factors in polyamide extraction is the polymer's morphology. Sudden cooling in a cooling bath causes macromolecules to freeze in a metastable state, characterized by a much higher free energy, comparatively with that corresponding to the equilibrium state. Consequently, a polymer with an amorphous-crystalline structure with voids between the crystallites results in favourizing the polymer diffusion. On heating,

the macromolecular chains acquire a certain mobility and the free energy in excess contributing to rearrangement of the neighbouring segments, so that exceeding of the superior glass transition temperature causes the macromolecules rearrangement as a compact structure, unfavourable for extraction.

## RESULTS AND DISCUSSION

### Intensification of heat and mass transfer

The parallel calculation of the individual coefficients of heat and mass transfer leads to the following results:

Heat transfer

$$\alpha = \frac{Nu \lambda}{d_{eq}}$$

$$Nu = C Re^m Pr^n$$

$$Pr = \frac{C_p \eta}{\lambda} \quad Re = \frac{w d_{eq} \rho}{\eta}$$

Mass transfer

$$k_L = \frac{ShD}{d_{eq}}$$

$$Sh = C Re^p Sc^q$$

$$Sc = \frac{\eta}{\rho D}$$

Under constant temperature conditions, the synthetic expressions of the individual transfer coefficients in which fluids velocity is the only remaining operation variable, may be written as follows:

$$\alpha = Aw^m \tag{1}$$

$$k_L = Bw^p \tag{2}$$

where A and B are coefficients resulted by grouping of the physical parameters of the systems with following expressions:

$$A = \frac{C}{d_{eq}^{1-m}} \rho^n \eta^{n-m} \lambda^{1-n}$$

$$B = \frac{C}{d_{eq}^{1-p}} \frac{\rho^{p-q}}{\eta} D^{1-q}$$

while  $m = 0.8$  and  $p = 0.66$ , as recommended in literature [1].

Equations (1) and (2) evidence clearly that the only means of intensifying the heat and the

mass transfer is by increasing the liquid velocity.

The liquid velocity depends on the technological parameters and also on the installation geometrical characteristic. Consequently, for an extractor on  $n_t$  pipe with the diameter  $d$ , the velocity is given by relation:

$$w = \frac{4G}{n_t \pi d^2 \rho} \tag{3}$$

Increase of the solvent velocity through increase of the solvent flow rate or through reducing the diameter and number of pipes is not possible without perturbing the process of fabrication. That is why, different solutions should be considered, such as: recirculation or micro-recirculation of the extraction waters through the inducement of an alternative velocity, of low amplitude and high frequency. As the former solution requires designing of a new extraction device, microrecirculation seems more attractive.

Such movement of the liquid transforms the device which under normal conditions, involves shifting into a system of N extractors with intense stirring, placed in series. Essentially, recirculation occurs at microfluid scale, being developed on N recirculation regions. Its practical realization assumed joining of a pump, equipped with a piston, without valves, on the solvent supply pipe, so that the solvent flow rate remains the same as during normal operation, being given by velocity's continuous component, while the average velocity is much higher, as due to the velocity's alternative component.

The volume of solvent, V, shifted in time  $\tau$  is:

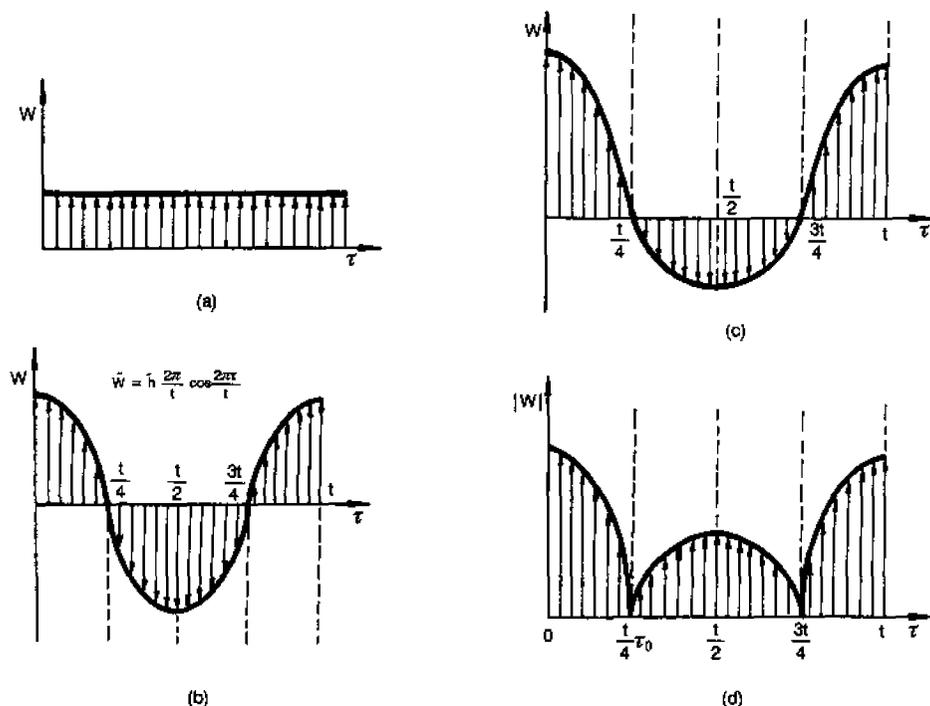
$$V = \bar{V}_s \tau + \tilde{V} \sin \frac{2\pi\tau}{t} \tag{4}$$

where  $\bar{V}_s$  is the flow rate of the solvent in  $m^3/s$  and  $\tilde{V}$  is the volume fluctuation in  $m^3$ , with period  $t$  (s).

The instantaneous flow rate will be given by relation:

$$V_s = \frac{dV}{d\tau} = \bar{V}_s + \frac{2\pi}{t} \tilde{V} \cos \frac{2\pi\tau}{t} \tag{5}$$

while the instantaneous velocity,  $w = V_s/S$ , will be:



**Figure 1.** Time variation of the liquid velocity under various operating conditions: (a) in the absence of the alternative component; (b) in the presence of pulsations and the absence of the continuous component; (c) in working conditions involving the presence of continuous and alternative components; (d) velocity modulus under working conditions.

$$w = \bar{w} + \hat{\lambda} \frac{2\pi}{t} \cos \frac{2\pi\tau}{t} \quad (6)$$

where  $\bar{w} = \bar{V}_s/S$  and  $\hat{\lambda} = \hat{V}/S$ .

It was demonstrated [2] that the average apparent flow rate, defined by:

$$V_{s(av)} = \frac{1}{nt} \int_0^{nt} V_s d\tau$$

is equal with the solvent flow rate,  $\bar{V}_s$ .

The average velocity is calculated by integrating equation (6):

$$w_{av} = \frac{1}{nt} \int_0^{nt} w d\tau \quad (7)$$

As in the hydrodynamics process, the direction of velocity vector has no importance, and only its

modulus being of interest, and the function being periodical with period  $t$ , symmetrical to  $t/2$ , integral (7) becomes:

$$w_{av} = \frac{2}{t} \left[ \int_0^{\tau_0} |w| d\tau + \int_{\tau_0}^{t/2} |w| d\tau \right] \quad (8)$$

where  $\tau_0$  being the root of function  $|w| = f(\tau)$ , over the  $[0 - t/2]$  interval (Figure 1). The expression of this root results from condition  $|w| = 0$ , applied to equation (6):

$$\tau_0 = \frac{t}{2\pi} \arccos \left( -\frac{\bar{w}t}{2\pi\hat{\lambda}} \right) \quad (9)$$

The calculations performed, under such conditions, on equation (8) lead to the following final expression of the extraction liquid average

velocity, in conditions of microcirculation:

$$w_{av} = \bar{w} \left[ \frac{2}{\pi} \arccos \left( -\frac{wl}{2\pi\lambda} - 1 \right) + \frac{4\lambda}{l} \sin \left[ \arccos \left( -\frac{wl}{2\pi\lambda} \right) \right] \right] \quad (10)$$

In the practical situation of an extractor with 17 pipes with an inner diameter  $d = 0.207$  m, in each pipe 3 L/min extraction water being circulated, to which microcirculation is applied by oscillations with period  $t = 0.4$  s, corresponding to a frequency  $\nu = 2.5$  Hz, and an amplitude  $\lambda = 2$  mm, the following velocity values resulted:

$$w = 1.486 \cdot 10^{-3} \text{ m/s}$$

and

$$w_{av} = 0.02 \text{ m/s}$$

By applying equations (1) and (2) for the recirculation of extraction water, when the liquid velocity is  $w_{av}$ , the following ratios of the individual heat and, respectively, mass transfer coefficients result:

$$\frac{\alpha^1}{\alpha} = \frac{A w_{av}^m}{A w^m} = 8.002 \quad (11)$$

$$\frac{k_l^1}{k_l} = \frac{B w_{av}^p}{B w^p} = 5.56 \quad (12)$$

Expressions (11) and (12) evidence an eight times increase of the individual heat transfer coefficient and an over five times increase of the individual mass transfer coefficient, which demonstrates the efficiency of microcirculating extraction waters in processes of extracting polyamide 6 granules.

#### Operating Parameters and Optimization Criteria

The equation expressing the kinetics of mass transfer is:

$$m = KS_s V (1 - \varepsilon) \Delta C \tau \quad (13)$$

where,  $m$  is the amount of extracted monomer (kg);  $K$  is the universal coefficient of mass transfer ( $\text{kg}/\text{m}^2\text{h}$ );  $S_s$  is the specific surface of granules ( $\text{m}^2/\text{m}^3$ );  $V$  is the volume of the device ( $\text{m}^3$ );  $\varepsilon$  is

the fraction of voids;  $\Delta C$  is the average difference of concentration in the extractor (%);  $\tau$  is the duration of extraction (h).

Equation (13) may suggest a possible maximization of the amount extracted through increase in each of the factors constituting it. Apparently, this is simple, if neglecting its interdependence with the other technological phases that do not permit the increase over certain limits of the factors involved. That is why, finding some values not exactly maximum but optimum of selected parameters becomes essential.

The interdependence established between the variables  $K$ ,  $S_s$ ,  $V$ ,  $\varepsilon$ ,  $\Delta C$  and  $\tau$  are the following:

Duration of standing in the installation,  $\tau$ , leads to increasing the extraction yield as, at a minimum volume of extraction water, the desired demonomerization occurs, and a solution concentrated in lactam would result that induces reduced consumption of steam in the evaporation stage, which, nevertheless, induces a considerable reduction in the extractor productivity. Optimization of the standing duration consists in bringing together the extractor productivity with the lowest yield of the operations succeeding the extraction, usually spinning or drawing.

The extraction process driving force and the average difference of concentration might be increased by increasing the specific consumption of extraction water, which is accompanied by unfavourable consequences, such as a high specific consumption of demineralized water, a much higher specific consumption of thermic agent for heating the extractor, and also a high specific consumption of steam in the phase of monomer recovery. Another means of increasing  $\Delta C$  would be optimization of the polymerization phase, so that to obtain granules with low monomer content.

The fraction of voids influences extraction by the fact that decrease of  $\varepsilon$  induces concurrent increase of the extraction yield (equation 13), in parallel with intensification of the fluid flow among the granules.

From this point of view it is indicated to extract granules with as low dimensions as possible

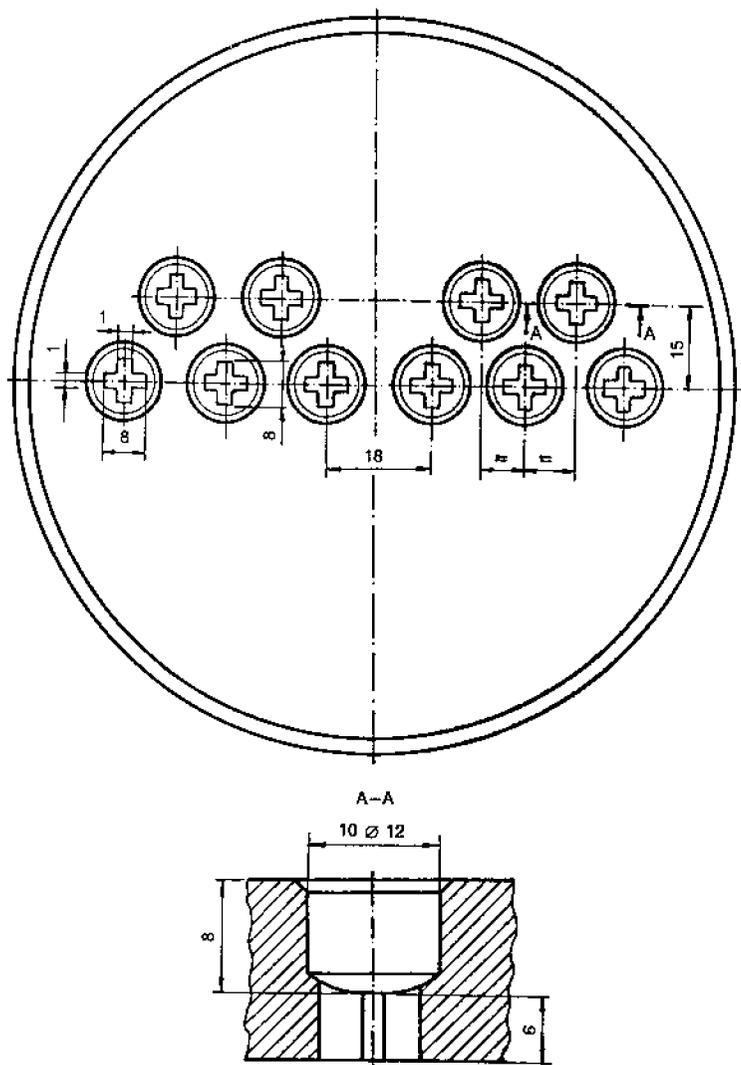


Figure 2. Spinning device of polyamide 6.

and as closer as possible to the spherical or cylindrical shape, with a unitary diameter/height, which as far as possible induces compact arrangement in the extractor.

The volume of the device may be increased

by the utilization of pipes with as high diameter as possible, or by the utilization of an increased number of pipes, which actually means replacement of the extractor with a one of a higher capacity.

The specific surface,  $S_s$ , is reversely proportional to the diameter of polyamide granules, so that to permit action upon the spinning device, which results in the obtainment of polyamidic cables, either shaped or with lumen. The solution given in a patent [3] involves a spinning device (Figure 2) that produces granules with a 30% higher specific surface.

The universal coefficient of mass transfer may be increased on acting either upon the hydrodynamics of the extraction process through increasing the fluid circulation velocity (as already discussed in a previous section) or by increasing temperature and attainment of temperature profiles along the extractor, for a highly efficient utilization of the device total height.

Figure 3 plots various temperature profiles along the extractor's height, corresponding to the utilization of various heating agents.

Especially important in this case are curves 4 and 5, corresponding to a temperature profile quasiconstant over the whole length of the device, at a temperature of about 100 °C, which favors an intense extraction. This explains, however, the technologists' option for the utilization of hot water with an initial temperature of 98 °C as a heating agent.

Study of the heat transfer between the extraction agent and the polyamide granules

considered as spherical permitted [4,5] calculation of temperature in the center of the granule, at various time intervals (Figure 4).

The observation made, that after about 30 s. the polyamide granules attain practically the temperature of the extraction medium permitted to consider that once the extraction time in the device is of hours in any point of the extractor, the granules temperature is equal to that of the extraction agent.

### CONCLUSION

Study of the physical model of solid/liquid extraction applied to a polymeric granule permitted to find some new means of intensifying mass and heat transfer accompanying this operation.

The extraction liquid velocity has a special influence upon the individual coefficients of heat and, respectively, mass transfer, so that a convenient solution for increasing this velocity will be reflected correspondingly in the  $\alpha$  and  $k_L$  values. To this end, microcirculation of the extraction waters by inducing a sinusoidal velocity of low amplitude and high frequency was proposed; a solution requiring no essential modification of the existing installation for obtaining polyamide 6.

The calculations performed in hydrodynamic conditions selected for a tubular extractor utilized in an industrial installation evidenced a

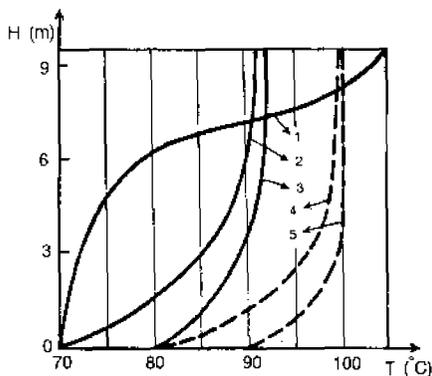


Figure 3. Temperature profile along the extractor when using various heating agents: (1) by 6 atm steam. (2) and (3) by hot water at 98 °C and (4) and (5) by 0.5 atm steam.

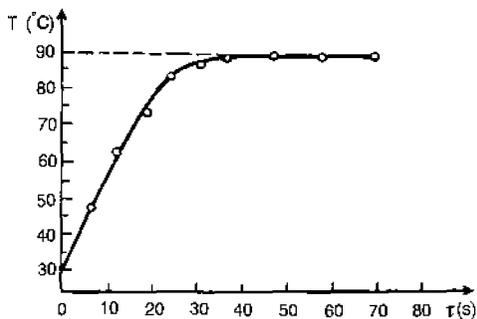


Figure 4. Time variation of temperature in the center of the polyamide 6 granule (the upper line corresponds to the temperature of the extraction liquid).

considerable increase of the heat and mass transfer, so that the values of the ratios between the individual transfer coefficients, in the normal and pulsatory recirculation conditions, are equal to 8 for the heat transfer and, respectively, 5.56 for the mass transfer.

Study of the mass transfer kinetics during polyamide granules extraction permitted the analysis of the operating parameters that may contribute to the intensification of transfer phenomena, in view of optimizing the extraction conditions. To this end, a solution for a substantial increase of the granules specific surface has been suggested, involving a corresponding modification of the spinning device.

The thermal calculations performed on the extractor heated with hot water at 98 °C, permitted the obtainment of the temperature profile on the device height; the values of which demonstrate that the extraction waters maintain, under such conditions, a constant temperature along the extractor thus providing a polymer with a constant percent of nonextracted monomer.

## NOMENCLATURE

C	Coefficient in criterial equations.
$C_p$	Specific heat of the liquid (J/kgK).
d	Diameter of the extractor pipe (m).
$d_{eq}$	Equivalent diameter (m).
D	Diffusion coefficient ( $m^2/s$ ).

G	Mass flow rate of the liquid (kg/s).
$k_L$	Individual coefficient of mass transfer in liquid phase.
$n_p$	Number of pipes in the extractor.
Pr	Prandtl number.
Re	Reynolds number.
S	Section surface ( $m^2$ ).
Sc	Schmidt number.
Sh	Sherwood number.
$V_s$	Volumetric flow rate ( $m^3/s$ ).
w	Velocity (m/s).
$\alpha$	Individual coefficient of heat transfer ( $w/m^2K$ ).
$\eta$	Dynamic viscosity of the liquid (Pa.s).
$\lambda$	Thermal conductivity of the liquid (w/mK).
$\rho$	Density of the liquid ( $kg/m^3$ ).
$\tau$	Time.

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