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New Falling Film Reactor for Melt Polycondensation Process

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Summary: A grid falling film tower (GFFT) has been invented as an ideal polycondensation reactor. In this reactor, polymer melt flows through multi-layers grids from top to bottom to form falling film owing to gravity without agitation and shear; large gas-liquid interfacial area is generated; the grids are perpendicular between adjacent layers to ensure film renewal and to achieve uniformly flowing. The fluid flow in this reactor has little back-mixing and dead zone, which is near to plug flow. All melts are under the state of thin film which avoids the negative effect of hydrostatic head on the mass transfer impetus. Furthermore, the GFFT has wide operation flexibility as well as adjustable configuration parameters to meet different demands. A pilot scale GFFT with the height of 4.0 meters has been applied to polyester polycondensation process. The intrinsic viscosity of polyethylene terephthalate increased from 0.45 dl/g to 0.8–0.9 dl/g successfully. GFFT is supposed to be an universal apparatus for many devolatilization processes.

Keywords: devolatilization; falling film; grid; polycondensation; reactor

Introduction

Condensation polymerization, proceeding by the reaction of two functional groups, usually is a reversible reaction with the formation of a volatile by-product. This by-product must be removed in order to drive the polymerization forward reaction toward completion, with the formation of polymers having high molecular weights. So reaction and devolatilization are coupled during the polycondensation process. With the progress of polycondensation, the melt viscosity often increases by about 2–4 orders of magnitude, which is expected to influence the diffusion of small volatile by-product molecules out of reaction media.[1] The viscosity of bulk melt increases so dramatically that mass transfer may become rate controlling step of whole process. Therefore, the mass transfer have to be intensified to remove the by-product timely in the polycondensation process.[2]

In order to remove by-products from polymeric solution effectively, the polycondensation apparatus should have a gas–liquid interface as large as possible. It is well known that a combination of high vacuum and thin film exposure could improve the reaction time for equivalent molecular weight buildup during the polycondensation process. The film phase with deficient volatiles should be remixed periodically with the bulk phase in order to maintain a favorable equilibrium reaction to give a desirable degree of polymerization.[3] Due to the need for a large surface area for the removal of by-products through high viscous polymer melt, some special film-forming devices that make use of mechanical means for surface area generation are used commonly, and the devices also have a rapid mixing of the polymeric solution to reach mass transfer at the favorable conditions of short exposure times.[4] Typically, horizontal rotating disc

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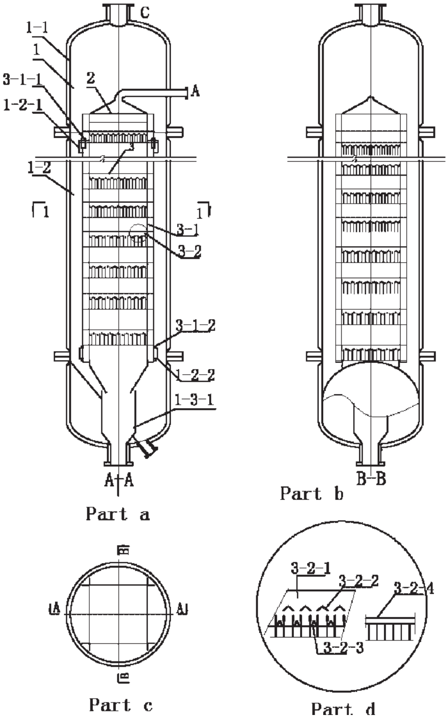


Figure 1.
The structural diagram of GFFT. Part a: Cutaway view of plane (A-A); Part b: Cutaway view of plane (B-B) perpendicular to plane (A-A); Part c: Vertical view of plane (1–1); Part d: Part sectional enlarged view of grids.

reactors or wiped-film devices are used. But there are some drawbacks for the horizontal rotating disc reactors: the specific interfacial area is limited by the bridging of melt between adjacent discs; over 50% melt is at the bottom of reactor with 0.1–0.2 times of reactor diameter level, the hydrostatic head which has negative effect on the reversible polycondensation reaction keeps accordingly; there exists 8–10% dead zone in the reactor; a part of melt is not easy discharged during shutdown period that may mean much more new materials will be needed to replace the existing ones when start-up again; it is easy to leak air at the sealing of agitating shaft because of bending, which is the result of heavy melt loading on the discs; and so on.

This paper relates to an innovational grid falling film tower (GFFT) reactor, the primary purpose is to make a recommendation of application of this new reactor to bulk polycondensation reactions. There are miscellaneous liquid-state polycondensation, such as nylons, polyethylene terephthalate (PET), polybutylene terephthalate (PBT), polyurea, polycarbonate, etc. The characteristic of fluid flow, mixing, film forming and renewal of this new reactor have been preliminary studied. The PET with higher molecular weight manufacture process has also been realized in this new GFFT polycondensation reactor.

Configuration of GFFT

The GFFT has three main parts: tower shell (1), distributor (2) and the suspended core inside (3) (Figure 1).[5] No agitating and dynamic packing surface is needed, which avoids the air leakage.

The tower shell consists of the top cover1–1, the main body 1–2, the bottom cover 1–3 and the jacket. The covers are connected to the core via flange. The function of the tower shell is to provide the temperature and pressure conditions which are demanded for final polycondensation. Both pre-polymer inlet A and vacuum-pumping nozzle C are on the top of the cover shell, and the polymer outlet B locates at the bottom of the cover shell which is upper connected with cone-shaped funnel 1-3-1 for holding polymer. The distributor (2) is set inside on the top, which distributes feeds on the first grid layer symmetrically.

The suspended core structure (3) with multi-layers grids is the main and key part of GFFT. The shape of this core is a square. The core is suspended inside the tower, which is easy to be assembled.

The multi-layers grids include transoms 3-2-1, up-oriented grids 3-2-2, down-oriented grids 3-2-3, and flow-guide combs 3-2-4. The transoms are riveted on the pillars, the grids and flow-guide combs are riveted on transoms. Both down-oriented grids and flow-guide combs compose a grating funnel. Grids are perpendicular between adjacent layers, ensuring film full renewal between two layers and uniformly flowing during whole reactor. From the top to the bottom, the width of grating slits of every layer, as well as the gap size among comb stick and the distance between layers, is adjustable to adapt to viscosity change.

Polymer melts flow through multi-layers grids from top to bottom to form falling film owing to gravity without agitation and shear, huge interfacial area for mass transfer is generated, which supported by comb. After flowing through the last layer, all melt fall down to the receiving funnel, and are pumped out subsequently. The volatile by-products generated by polycondensation reactions diffuse out of these film surfaces, go along the paths between adjacent films, gather in the embowed part between core and shell, then flow upward and draw out from outlet C finally.

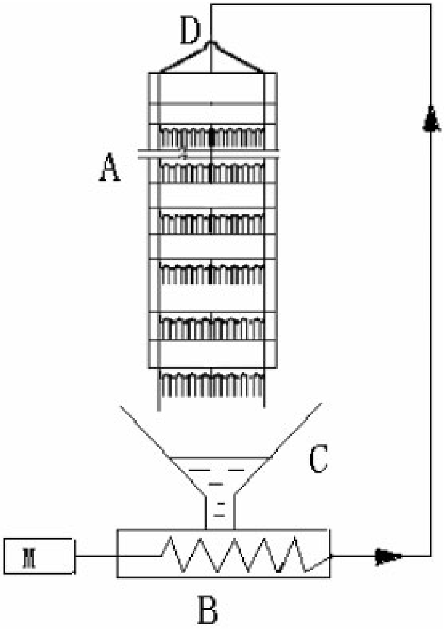


Figure 2.
Equipments for Mock-up experiment. A core of GFFT (160 × 160 mm); B screw pump; C cone-shaped tank; D distributor; M motor.

Experimental Apparatus and Procedures

The model equipments (Figure 2) were built to investigate the fluid flow, mixing, film forming and renewal in GFFT. The study of rheological behavior of molten PET had revealed that PET melt approached to Newtonian fluid at low shear rate (50–1000 s^{-1}).[6] The fluids used in the experiment were aqueous solutions of corn syrup with various concentrations (viscosity range from 1.5 Pa.s to 470 Pa.s), which were found to be Newtonian fluids in the range of viscosity from about 5 to 500 Pa.s.[7] The corn syrup solution with a certain viscosity was fed into the distributor by screw pump, then flowed through the whole model core and fell into the tank for cycling. The flowrate was regulated by the frequency of the motor of pump. The video technique was utilized to record the GFFT performance. The structural parameters of the core of GFFT can be modified to adapt to the corn sirup solution with different viscosity. The mock-up experiments were carried out at ambient temperature and pressure, and the viscosities of corn syrup were measured by NDJ-4 rotational viscometer (Brookfield-type, Shenzhen Sanuo Electronic Instrument Co., Ltd.).

The polyethylene terephthalate (PET) polycondensation process was performed in a pilot scale GFFT (Figure 3). The structural parameters of core in this GFFT along vertical direction are not same, varying according to expected polymer melt viscosity. The PET pre-polymers chips were molten and heated to desired temperature, and then fed into the distributor by the single screw extruder. The melt flew through multi-layers grids, and the product was got out of reactor by melt gear pump and sampled. The EG produced in polycondensation process could evaporate from film surface and be removed out from top outlet of reactor by the vacuum pumps. The average residence time was about 30 min.

The core under high vacuum state was actually in adiabatic state, the temperature of heating oil in jacket was the same as the temperature of inlet polymer melts. The vacuum of system was modulated by the

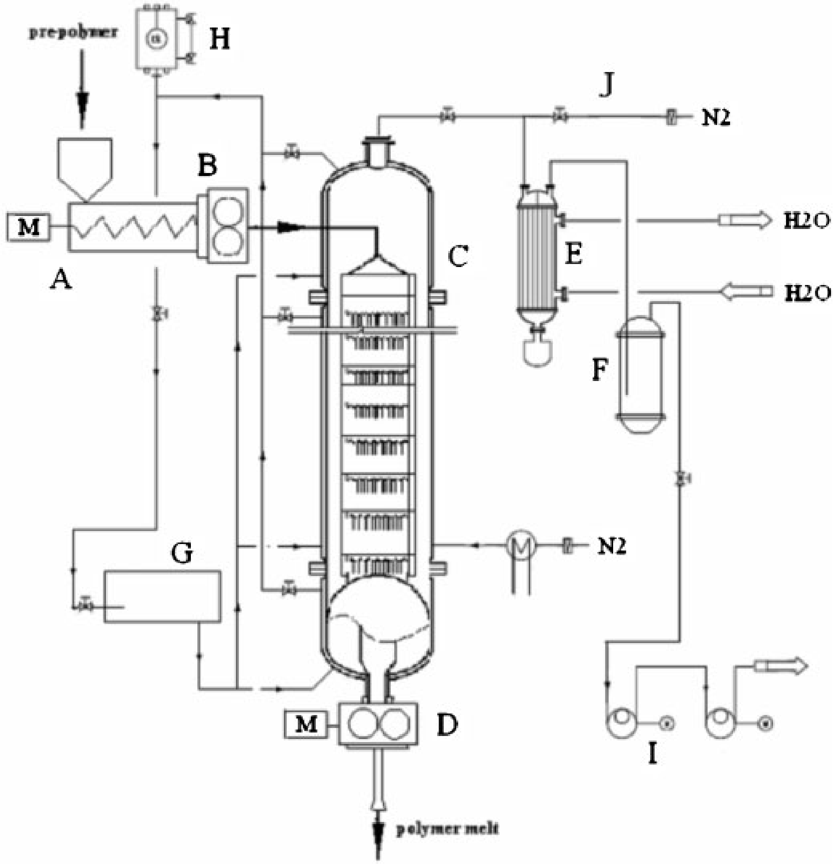


Figure 3.
Flow diagram of Pilot scale GFFT. A single screw extruder; B measuring pump; C GFFT (ϕ 300 mm); D gear pump; E condenser; F buffer vessel; G electrical heating furnace for oil; H heating oil expansion tank; I vacuum pump; J N_2 by-pass.

flowrate of by-pass N_2 and measured using vacuum gauge within the precision of 10 Pa.

The intrinsic viscosity (IV) $[\eta]$ was measured by solving in 60/40 (w/w) 1,1,2,2-tetrachloro-ethane/phenol mixture at 25 °C using an Ubbelohde viscometer. It could be converted into the molecular weight by means of the following relationship:

$$[\eta] = aM_n^b$$

where $a = 7.55 \times 10^{-4}$ dl/g, $b = 0.68$ and M_n was the number average molecular weight.[8]

While neglecting of the end groups, the degree of polymerization (DP) could calculated from M_n as follows:

$$M_n \approx 192.17 \times DP$$

The concentration of carboxyl end group [COOH] was analyzed according to standard analysis method GB/T17931-1999. The weighed 2 g PET sample was dissolved in 50 mL 70/30 (w/w) o-cresol/chloroform in the state of reflux, after dissolution, the cooled solution was potentiometric titrated by 0.05 mol/L alcoholic potash solution.

Results and Discussion

The Characteristics of Fluid Flow, Mixing, Film Forming and Renewal of GFFT

Due to the support of comb parts, thin falling film could be created stably in GFFT when the viscous fluid flowed through

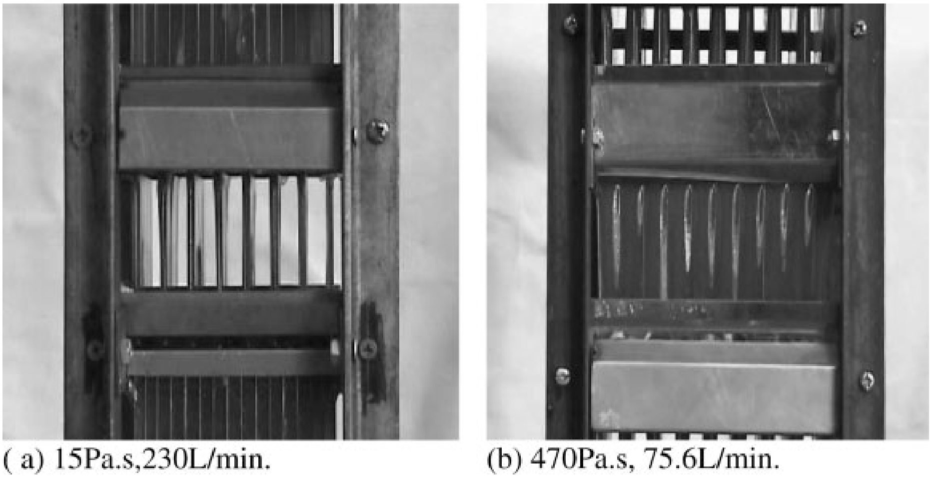

(a) 15Pa.s,230L/min. (b) 470Pa.s, 75.6L/min.

Figure 4.
Film-forming of different viscous fluids using different cores.

multi-layers grids by the gravity, the generating film was almost uniform, and the filming efficiency was near to 100% (Figure 4). The specific interfacial area of GFFT could reach over 200 m^2/m^3. Since the grids perpendicular between adjacent layers, films were re-generated after each layer to make film renewal sufficiently; fast free falling flow velocity was also benefit to improve film renewal. All melts were under the state of thin film, which avoided the negative effect of hydrostatic head on the mass transfer impetus. Furthermore, it was confirmed that GFFT could be applied in a wide viscosity range with different structural parameters. With the increase of viscosity from 1.5 Pas to 470 Pas, the size between up-oriented grids was changed about from 5 to 20 mm in height and 3 to 15 mm in width respectively, and the gap of combs was in the range of 5–18 mm. However, the core with same structural parameters was applicable in a certain viscosity range too (Figure 5).

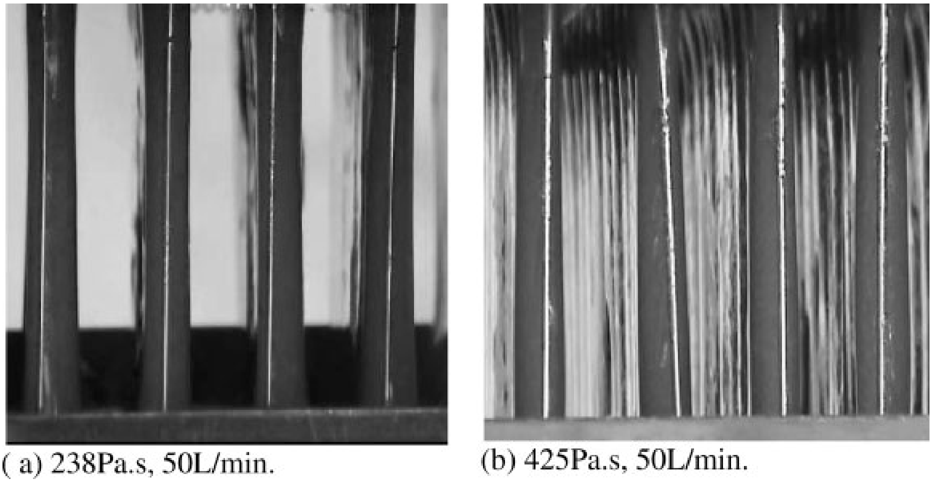

(a) 238Pa.s, 50L/min. (b) 425Pa.s, 50L/min.

Figure 5.
Film-forming of different viscous fluids using the same core.

A part from the height of tower, the residence time of fluid also could be tuned by the width of grating slits of layers and the numbers of layer.

Since the fluid re-mixed at every layer, and no back mixing and dead zones were discovered in GFFT, the fluid flow approached to plug flow.

The core with same structure parameters had wide operation flexibility, it was found that, the ratio of maximum flowrate to minimum flowrate could reach $5 \sim 8$ (Figure 6) for good performance, especially for film forming.

PET Polycondensation Process in GFFT

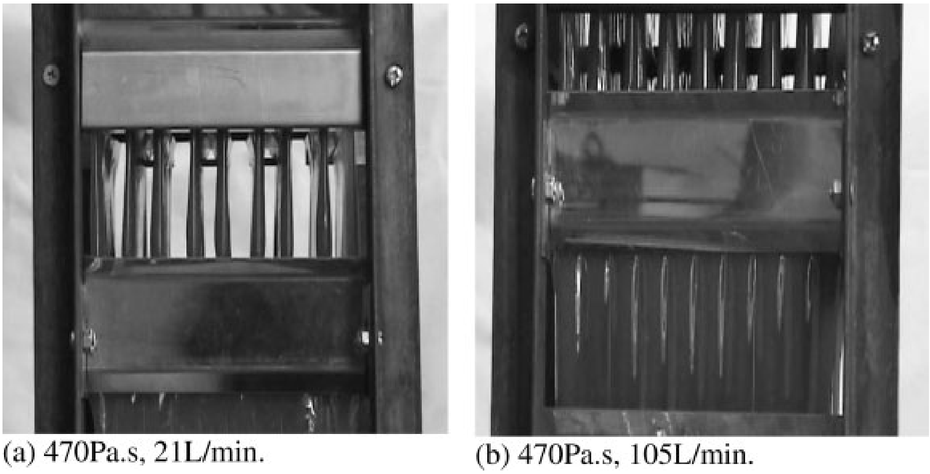
The polycondensation of polyester proceeds by the combination of two 2-hydroxyethyl end groups to form an internal ester group and an ethylene glycol molecule. The volatile ethylene glycol molecules must be continuously removed to produce PET with high molecular weight.

$$2(-\mathrm{COOC_2H_4OH}) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} -\mathrm{COOC_2H_4OOC}- + \mathrm{HOC_2H_4OH} \tag{1}$$

The appropriate structural parameters of the core along axial in GFFT, including the width of grafting slits, the gap size among comb stick and the distance between layers, must match the increasing of melt viscosity during polycondensation process, ensuring the right structure for good film forming of polymer melt. For PET polycondensation under thin film condition, the DP rose almost linearly with the reaction time.[9,10] So for this pilot-scale GFFT, the structure parameters of core were designed according to the change of viscosity which could be deduced by linear DP increase and reaction temperature. In consideration of the mock up experiments results that the core with same structure parameters has operation flexibility, the GFFT had been divided four sections; each section had different structure parameters and could be applicable to a certain viscosity range (see Table 1).

The conditions and results of the pilot experiment of PET polycondensation process in GFFT were displayed in Table 2. The intrinsic viscosity of PET increased from 0.45 dl/g to 0.8–0.9 dl/g successfully in GFFT, while the [COOH] decreased from 35.3 mol/t to 19.9–16.5 mol/t accordingly.

It was also observed that temperature gradients along axial direction less than 1 °C during experimental process, which mainly caused by reaction heat effect. The polymer melt in reactor can be easy to


(a) 470Pa.s, 21L/min.

(b) 470Pa.s, 105L/min.

Figure 6.
Fluid flow and film forming performance of GFFT at different flowrates.

Table 1.
Structure parameters of the core in pilot-scale GFFT.

Height of suspended core, mm	Section/number of layers	Width of grafting slits, mm	The gap size among comb stick, mm	The distance between layers, mm	Applicable viscosity range, Pa.s
4000 (120 × 120 mm in cross section)	1/16	7.5	10	60	25–120
	2/16	7.5	12.5	65	80–300
	3/15	8	15	69	160–420
	4/15	8	15	75	over 400

Table 2.
PET polycondensation process in pilot scale GFFT.

Capacity, kg. · hr^{-1}	10
Pressure, Pa	100–160
Temperature of inlet pre-polymer, °C	285
Residence time, min	~30
IV and [COOH] of inlet PET pre-polymer, dL · g^{-1}; mol/t	0.45; 35.3
DP of inlet PET pre-polymer	62
IV and [COOH] of outlet PET polymer, dL · g^{-1}; mol/t	0.8 ~ 0.9; 19.9 ~ 16.5
DP of outlet PET polymer	147 ~ 172

discharge completely during shutdown period, and little waste produces during re-startup period.

Though it has been testified that the GFFT was successful to perform PET melt polycondensation and obtain high molecular weight PET products, how the structure parameters of core can match the progressing of polycondensation reaction well is a challenging work, many experimental and simulation works need to be further done.

Apart from as the polycondensation reactor, the GFFT has been explored to some other devolatilization processes too, including the defoaming of nitrilon polymer solution and monomer of toluene diisocyanate (TDI) removal from polyurethane pre-polymers.

Conclusion

It is well known that the mass transfer interfacial area should be ensured to remove the volatile small molecules in most melt polycondensation process, especially during the last period, the viscosity of bulk melt usually increase so dramatically with the progress of polycondensation reaction that mass transfer have to be further intensified. Grid Falling Film Tower has been invented as a new apparatus for polycondensation reaction. This new reactor has over 200 m^2/m^3 specific interfacial area and good surface renewal, no back-mixing and dead zone. The success of the manufacture of PET with higher molecular weight in pilot scale GFFT has predicated that the GFFT is feasible and suitable for polycondesation processes involving high viscous melt. Owing to its excellent performances for mass transfer, the GFFT can also be expected as a satisfactory apparatus for many devolatilization processes.

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