



**HAL**  
open science

## Optimization and scale-up of twin-screw reactive extrusion: the case of EVA transesterification

Françoise Berzin, Chantal David, Bruno Vergnes

### ► To cite this version:

Françoise Berzin, Chantal David, Bruno Vergnes. Optimization and scale-up of twin-screw reactive extrusion: the case of EVA transesterification. *International Polymer Processing*, 2020, 35, pp.422-428. 10.3139/217.3958 . hal-04057838

**HAL Id: hal-04057838**

**<https://hal.science/hal-04057838>**

Submitted on 4 Apr 2023

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# International Polymer Processing

## Optimization and scale-up of twin-screw reactive extrusion: the case of EVA transesterification

--Manuscript Draft--

<b>Manuscript Number:</b>	IP3958R1
<b>Full Title:</b>	Optimization and scale-up of twin-screw reactive extrusion: the case of EVA transesterification
<b>Article Type:</b>	Regular Contributed Article
<b>Keywords:</b>	Optimization; Scale-up; Twin-screw; Reactive extrusion; Transesterification
<b>Corresponding Author:</b>	Bruno VERGNES Ecole des Mines de Paris Sophia Antipolis, FRANCE
<b>Corresponding Author Secondary Information:</b>	
<b>Corresponding Author's Institution:</b>	Ecole des Mines de Paris
<b>Corresponding Author's Secondary Institution:</b>	
<b>First Author:</b>	Françoise Berzin
<b>First Author Secondary Information:</b>	
<b>Order of Authors:</b>	Françoise Berzin
	Chantal David
	Bruno VERGNES
<b>Order of Authors Secondary Information:</b>	
<b>Manuscript Region of Origin:</b>	FRANCE
<b>Abstract:</b>	<p>Despite its complexity, reactive extrusion is continuously developing for the production of new and performing materials. Due to the strong coupling between flow, rheology and chemistry, optimizing this process for a given reaction remains a difficult task. Moreover, the scale-up from the laboratory to the production scale is another crucial question, which cannot be solved by conventional techniques. In this paper, we show how the use of numerical modeling may help answer these complex questions by providing realistic solutions, rapidly and without excessive costs. The example of a transesterification reaction was chosen because this reaction has been carefully characterized in previous studies. The reaction kinetics and the kinetic constants are well known and the modeling of this reactive extrusion process has proved to be realistic and accurate.</p>

## Answers to the reviewers

### Reviewer #1

In this paper the authors applied a "step-by-step" procedure to optimize the operating conditions and the screw configuration of a co-rotating twin-screw extruder for reactive extrusion. However, they must be aware that this optimization procedure is discrete, i.e., they were not able to explore the entire search space concerning both the operating conditions and screw configuration. Due to this reason there is a very strong possibility of not finding a good approximation to the optimum. Thus, I suggest that the authors point out that the optimization procedure adopted have these limitations.

*We agree. We have introduced these comments in the text.*

Also, they cannot say that "define optimal screw profile and processing conditions" with this certainty. Certainly, given that the search space was not really explored, there are other (much) better solutions.

*We agree for screw profile because the choice of possibilities is infinite. In contrast, when processing conditions are concerned (screw speed and feed rate), we are more confident as the search space does not exhibit local extrema. To account for the comment of the reviewer, we have replaced « optimal » by « optimized ».*

The authors referred to Pareto curves in figures: I think that will be better to say "approximate discrete Pareto curves", instead.

*We have introduced this change*

In page 10 authors said that they extrapolated the screw profiles. Please, explain how.

In fact, the methodology for scale-up was not well explained. Some effort must be made here.

*We have tried to be clearer and modified the text in consequence.*

### Reviewer #2

The paper is very interesting and practical/beneficial for polymer engineers and can be published after minor correction.

1) The abstract should be written more precisely to inform this research procedure and discussed results including the outline of the previous paper{IPP (1998)} published by the same authors.

*The abstract has been modified to explain the choice of the reaction.*

2) page 11: x is shown as scale-up power index)

*Sorry, but we do not understand this remark.*

3) The reason should be added why scale-up factor x shows more than 3.0.

Generally the screw design for a small laboratory TSE is restricted due to the limited screw torque to be transferred. Therefore the screw depth of the laboratory scale TSE is usually so shallower when

scaled down from larger TSE. This is one of the major reasons why the scale-up factor tends to show the discontinuity effect between a small TSE and production TSE. For example, from ZSE 27 to ZSE 75:  $x=3.4$ , from ZSE 27 to ZSE 135:  $x=3.1$ , but from ZSE 75 to ZSE 135  $x=2.7$ . In scale-up rule, the index value of more than 3.0 is impossible. Therefore I consider that the reason why the excessive large index value can be obtained should be discussed in this reactive extrusion.

*The scale-up rules based on the ratio of diameters to a  $x$  power are defined as function of undimensional numbers to keep constant during the operation. They cannot take into account the complexity of a reactive extrusion process, where the results depend on many coupled factors, such as the time-temperature history along the screw profile. When we speak about scale-up factor greater than 3, it just means that the classical rules evoked before cannot be applied in the conditions we studied.*

# Optimization and scale-up of twin-screw reactive extrusion: the case of EVA transesterification

Françoise Berzin<sup>1</sup>, Chantal David<sup>2</sup>, Bruno Vergnes<sup>3</sup>

<sup>1</sup> UMR FARE (Fractionnement des AgroRessources et Environnement), Université de Reims  
Champagne-Ardenne, INRAE, 2 esplanade Roland-Garros, 51686 Reims, France

<sup>2</sup> Sciences Computers Consultants, rue du Plateau des Glières, 42000, Saint Etienne, France

<sup>3</sup>MINES Paris Tech, PSL Research University, CEMEF, UMR CNRS 7635, CS 10207,  
06904 Sophia Antipolis, France

\* Correspondence: [bruno.vergnes@mines-paristech.fr](mailto:bruno.vergnes@mines-paristech.fr)

**Keywords:** optimization; scale-up; twin-screw; reactive extrusion; transesterification.

## Abstract

*Despite its complexity, reactive extrusion is continuously developing for the production of new and performing materials. Due to the strong coupling between flow, rheology and chemistry, optimizing this process for a given reaction remains a difficult task. Moreover, the scale-up from the laboratory to the production scale is another crucial question, which cannot be solved by conventional techniques. In this paper, we show how the use of numerical modeling may help answer these complex questions by providing realistic solutions, rapidly and without excessive costs. **The example of a transesterification reaction was chosen because this reaction has been carefully characterized in previous studies. The reaction kinetics and the kinetic constants are well known and the modeling of this reactive extrusion process has proved to be realistic and accurate.***

## 1 Introduction

Reactive extrusion consists in using an extruder as a continuous chemical reactor, for polymerization, grafting, controlled degradation or chemical modification of polymers (Xanthos, 1992; Janssen, 2004, Beyer and Hopmann, 2017). Due to its modularity and flexibility, co-rotating twin-screw extrusion is often preferred for these various applications. However, the control of the process is made difficult by the numerous interactions between the flow conditions (residence time, melt temperature, mixing conditions), the chemical reaction (reaction extent, endo- or exothermicity), and the polymer properties (viscosity). Therefore, by changing one parameter of the process (screw speed, feed rate, barrel temperature, screw profile), it is completely impossible to predict its effect on the quality of the final product. In these conditions, the optimization of a reactive extrusion process, and even more the scale-up from the laboratory to the production scale, remain very difficult tasks.

In the field of extrusion, in particular for the food extrusion, optimization is often carried out using the Response Surface Methodology (RSM). Initially introduced by Box and Wilson (1951), it consists in using a set of data (pressure, temperature, etc.) obtained from a design of experiments (factorial, central composite, etc.) to establish relationships with response variables (product quality), based on polynomial fitting (Myers et al., 2016). The method is easy to implement, but its accuracy depends on the number of data points and the quality of the regression model. In this approach, the set of data is generally obtained experimentally, but it can also be derived from numerical simulation. Optimization can also be conducted using specific algorithms, like Genetic Algorithms (GA). GA mimic the process of natural evolution through specific operations such as selection, crossover or mutation. Starting from an initial population, they allow to evolve towards the best individuals, the performances of which are characterized by an objective function (Gaspar-Cunha and Covas, 2011). GA were used for example by Gaspar-Cunha et al. (2002) to optimize the polymerization of  $\epsilon$ -caprolactone in a twin-screw extruder. RSM and GA can also be combined to improve the relevance of the results (Kowalski et al., 2018). Due to the complex nature of the reactive extrusion process, more sophisticated optimization techniques have been developed. Multi-Objective Evolutionary

Algorithms (MOEA) have allowed to define the best configuration of a twin-screw extruder to meet specific objectives, without (Gaspar-Cunha et al., 2005) and with chemical reaction (Teixeira et al., 2011). However, among the many solutions proposed by the optimization procedure, it is sometimes difficult to choose the best compromise. All of these techniques necessitate the use of a flow model to calculate the essential parameters of the reactive extrusion process. As many computations are necessary for the evolution of the population, the flow model must be very fast to avoid too long computing times. Therefore, models based on Finite Element Methods are often unappropriated for such applications and simplified 1D models are preferred. These models can also be used to perform optimization based on the design of experiments, both for the processing conditions and the screw design. Examples have been published on the starch transformation by Della Valle et al. (2011) and the starch cationization by Berzin et al. (2007).

Even for conventional extrusion, scale-up is a difficult problem. The first paper dealing with scale-up in single screw extrusion is probably by Carley and Mc Kelvey in 1953. Based on theoretical considerations, they proposed the following rules for geometrically similar extruders:

$$\frac{Q_1}{Q_2} = \left( \frac{D_1}{D_2} \right)^3 \quad (1)$$

$$\frac{W_1}{W_2} = \left( \frac{D_1}{D_2} \right)^3 \quad (2)$$

where subscripts 1 and 2 refer to the large and the small extruder, respectively.  $Q$  is the flow rate,  $D$  is the screw diameter, and  $W$  is the power consumption. In fact, almost all of the papers on scale-up have attempted to express the ratio of the quantities of interest (screw speed, pressure, temperature, shear rate, viscosity, residence time, etc.) as the ratio of the diameters at a certain power (Menges and Feistkorn, 1984; Ganzeveld and Janssen, 1990; Potente, 1991; Nakatani, 1998):

$$\frac{X_1}{X_2} = \left( \frac{D_1}{D_2} \right)^x \quad (3)$$

Estimates of these quantities by more or less accurate expressions allow to derive values for the exponents, and thus appropriate scale-up rules. However, these expressions are rough approximations



which cannot address the complexity of a highly non-isothermal process with evolutionary rheological behavior. Therefore, the use of numerical models to solve these complex issues is becoming more and more common (Markarian, 2005; Ortiz-Rodriguez and Tzoganakis, 2010; Pradel et al., 2014). They can simply be considered through a design of experiments, but the use of optimization methods, such as those presented previously (MOEA), have also been proposed for solving scale-up problems (Covas and Gaspar-Cunha, 2009; Gaspar-Cunha and Covas, 2014). In the following, we just want to show how a reactive extrusion model, previously experimentally validated, can be used in a simple way to help an engineer to optimize a process and to predict the performances of larger extruders from those of a smaller one.

## **2 Case study and methodology**

Similar approaches have been previously presented to optimize and extrapolate the starch transformation (Della Valle et al., 2011) and the starch cationization (Berzin et al., 2007). The present paper focuses on another case of reactive extrusion and concerns the chemical modification of a molten polymer realized in a twin-screw extruder.

### *2.1. EVA Transesterification*

The modification of an ethylene-vinyl acetate (EVA) copolymer with an aliphatic alcohol (octanol-1) is considered. Through a transesterification reaction, catalyzed by an organometallic compound (dibutyltin dilaurate, DBTDL), the vinyl acetate groups of the EVA are partially substituted by hydroxyl groups of the alcohol (Fig. 1). The reaction is equilibrated and a maximum conversion of 65% can be reached at equilibrium (Lambla et al., 1987). The kinetics was characterized by Bouilloux (1985). As the molecular structure of the EVA is not largely changed, the viscosity of the modified EVA (EVAL) does not depend on the conversion and a rheokinetic model is not necessary in the present case. These materials are principally used in food packaging because of their excellent barrier properties.

## 2.2. Modeling

The modeling of the transesterification reaction of EVA in twin-screw extrusion was proposed by Berzin and Vergnes (1998), based on the Ludovic<sup>®</sup> software (Vergnes et al., 1998).

### 2.2.1. Chemical reaction

The reaction scheme is presented in Fig. 1. The conversion percentage  $\chi$  is calculated from:

$$\chi (\%) = \frac{[A]_0 - [A]_t}{[A]_0} \times 100 \quad (4)$$

where  $[A]_t$  and  $[A]_0$  are the EVA concentrations at time  $t$  and  $t = 0$ , respectively.

The concentration of EVA as a function of time and temperature is given by:

$$[A]_t = \frac{(C_2 + C_3) \exp[-C_3 k_1 (1 - 1/K_e) t] + (C_3 - C_2) C_4}{2 C_4 - 2 \exp[-C_3 k_1 (1 - 1/K_e) t]} \quad (5)$$

$$\text{where } C_1 = -\frac{[A]_0^2 + [A]_0 [C]_0 + [A]_0 [D]_0 + [C]_0 [D]_0}{K_e - 1} \quad (6)$$

$$C_2 = \frac{K_e}{K_e - 1} \left( [B]_0 - [A]_0 + \frac{2 [A]_0 + [C]_0 + [D]_0}{K_e} \right) \quad (7)$$

$$C_3 = \sqrt{C_2^2 - 4 C_1} \quad (8)$$

$$C_4 = \frac{2 [A]_0 + C_2 + C_3}{2 [A]_0 + C_2 - C_3} \quad (9)$$

$[B]_0$ ,  $[C]_0$ ,  $[D]_0$ , are the initial concentrations of octanol, EVAL, and octyl acetate, respectively.  $k_1$  and  $k_2$  are the kinetic constants of the direct and reverse reactions, depending on the temperature through Arrhenius equations.  $K_e = k_1/k_2$  is the ratio of these constants. The values of the constants are taken from the previous paper by Berzin and Vergnes (1998).

### 2.2.2. Extrusion process

An experimental study was carried out on a pilot scale twin-screw extruder (Clextral BC45) to

validate the model (Berzin and Vergnes, 1998). However, for the purpose of the present paper, a laboratory scale twin-screw extruder has been selected (Leistritz ZSE 27 MAXX). It has a centerline distance of 23 mm, a screw diameter of 28.3 mm and a length of 990 mm ( $L/D = 35$ ). The screw profile, derived from the original one, is shown in Fig. 2. Beside screw conveying elements of various pitches, it includes two left-handed elements and a block of 12 kneading discs, staggered at  $60^\circ$ . 6 have a right-handed configuration, 6 a left-handed one. The EVA solid pellets are fed into the hopper (barrel element 1) and melted in the first left-handed element. Liquid reagents (a mix of alcohol and catalyst) are injected into the molten EVA after the melting zone (barrel element 4), and before the second left-handed element. For the modeling, the viscosity of the EVA is considered before the injection of the reagents and that of the EVA/EVAL/reagents mix thereafter. Indeed, at the stoichiometry (i.e. when the functional ratio  $r = [B]_0/[A]_0$  is equal to 1), 2.12 kg/h of alcohol and 0.3 kg/h of catalyst are injected for an EVA feed rate of 10 kg/h. This induces a dilution effect, which decreases the viscosity by around 41% (Berzin and Vergnes, 1998). The modeling of the process is carried out with the reactive version of the Ludovic<sup>®</sup> software. As an example, Fig. 3 shows the results obtained with the ZSE 27 extruder under the following conditions: screw speed  $N = 250$  rpm, EVA feed rate  $Q_{EVA} = 5$  kg/h, barrel temperature  $T_b = 170^\circ\text{C}$ . At each location along the screw profile, from the local values of the melt temperature and the residence time, the change in conversion is calculated by solving the Eqs. (4) to (9). The melt temperature along the screws remains around  $200^\circ\text{C}$ , with a maximum at  $208^\circ\text{C}$ . The development of the reaction closely follows the evolution of the residence time, which increases mainly in the filled sections, i.e. in the second left-handed element and in the block of kneading discs. These zones are also characterized by a local increase in temperature, due to viscous dissipation, which accelerates the reaction. The final conversion obtained at the die exit is

21%, far from the maximum of 65% at equilibrium.

### 3 Optimization

The objective of this section is to show how flow modeling may help improve the selected case of reactive extrusion. The goal is to reach the maximum conversion at the highest possible flow rate. This is conflictual because an increase in the flow rate induces a decrease in the residence time and thus a limited reaction extent. Moreover, some constraints are imposed: the maximum melt temperature must remain below 210°C to avoid evaporation of the alcohol and, for each screw, the maximum torque value is 145 N.m.

In a first step, the processing conditions will be optimized for the screw profile shown in Fig. 2. Then, this screw profile will also be optimized. **In fact, the optimization procedure is discrete, i.e. it does not explore the entire search space. Thus, it is possible not to find the real optimum, but just a local one. This is a risk in the case of screw optimization, as the possibilities are almost endless. However, for the processing conditions, the risk is limited because the search space is very regular.**

#### 3.1. Optimization of Processing Parameters

This first step will be achieved by applying a kind of Response Surface Methodology. The transesterification is calculated for different values of screw speed  $N$ , EVA feed rate  $Q_{EVA}$  and barrel temperature  $T_b$ . An example of result is shown in Fig. 4, where the conversion is plotted as a function of the EVA feed rate for various screw speeds. The processing window is quite narrow. Indeed, as soon as the screw speed is greater than 300 rpm, the melt temperature exceeds the maximum value of 210°C. The conversion increases slightly with the screw speed, but decreases rapidly with the feed rate, i.e. with a decrease of the residence time. At low screw speed, a second constraint, the maximum torque, limits the possible flow rate to 15 kg/h. The best extrusion conditions correspond to the limit imposed by the temperature. It provides what **can be called an approximate discrete Pareto curve**, i.e. the maximum conversion that can be attained for each flow rate, in accordance with the constraints

and whatever the processing conditions. It allows to select the best compromise, as function of the preferences and priorities: a high conversion at low flow rate (37.8% at 2 kg/h) or a lower conversion but at higher flow rate (6.9% at 25 kg/h). As shown in Fig. 5, the **discrete** Pareto curves depend on the barrel temperature. Increasing  $T_b$  increases the conversion, but at reduced speed to avoid inappropriate viscous dissipation. A reduced speed (75 rpm at  $T_b = 200^\circ\text{C}$ ) unfortunately limits the flow rate, due to the maximum torque constraint. Therefore, at  $195^\circ\text{C}$  and  $200^\circ\text{C}$ , it is impossible to reach flow rates above 10 and 20 kg/h, respectively. To summarize, if the flow rate is privileged, 25 kg/h with a conversion of 10,6% can be obtained at  $N = 150$  rpm and  $T_b = 190^\circ\text{C}$ . In contrast, if the conversion is privileged, 43.6% can be obtained at  $Q_{EVA} = 2$  kg/h and  $T_b = 200^\circ\text{C}$ . All intermediate combinations are possible, according to the data in Fig. 5.

### 3.2. Optimization of Screw Profile

**Optimizing a screw profile is much more difficult since a huge number of configurations are possible (Gaspar-Cunha et al., 2005; Teixeira et al., 2011). In the present case, as a discrete method is adopted, the optimal screw profile will probably not be obtained. But, if not completely optimal, an optimized one can be defined, capable of improving the previous results.** With the current screw profile (Profile 1), the conversion is limited. To increase this parameter, it is necessary to keep the temperature as high as possible, without reaching the maximum value, and to increase the residence time. For that, the number of restrictive sections can be increased. Therefore, we propose to test different profiles with an increasing number of kneading blocks, staggered at  $-60^\circ$ , and separated by screw conveying elements to regulate the melt temperature. Moreover, to increase the length of the reaction area, the first conveying zone is shortened and the injection point of the reagents is moved upstream. Fig. 6 shows the different profiles: on Profile 2, the second left-handed element was removed and five kneading blocks were introduced, the length of each being 30 mm. On Profile 3, three new blocks of kneading discs with the same configuration are implemented. On Profile 4, the number of blocks of kneading discs is reduced to six, but their length has increased from 30 to 60 mm. From Profile 1 to Profile 4, the severity progressively increases, with a respective length of restrictive elements

changing from 15 to 18, 27, and 39% of the total screw length. For each screw profile, the same methodology as that used in Section 3.1 is applied. Systematic calculations are performed, varying the screw speed and the feed rate, and selecting the optimal solution providing the highest conversion. The corresponding **approximate discrete** Pareto curves are shown in Fig. 7. Each improvement in the severity of the profile induces a higher conversion. However, for profile 4, flow rates higher than 15 kg/h cannot be reached, due to the limits in torque and maximum temperature. Nevertheless, this profile provides the highest conversion: 59.6 % at 140 rpm and 2 kg/h. If intermediate conditions are considered (15 kg/h), the changes in screw profiles have allowed to increase the conversion from 13.6% at 100 rpm to 15.5 at 200 rpm, 18.7% at 180 rpm and 22.5 at 160 rpm, i.e. a global increase of 65%.

To summarize, the use of a reactive extrusion model coupled with a design of experiments has allowed to define **optimized** screw profile and processing conditions, and, through the definition of **approximate discrete** Pareto curves, to provide decision support capable of helping the user to select optimal solutions corresponding to his priorities.

#### **4 Scale-up**

In this second step, the objective is to define the performance of industrial extruders, extrapolated from that of the laboratory scale machine. The Profile 3 is selected as it offers a larger processing window compared to Profile 4. On the laboratory scale machine, the conversion varies from 55.5% at 2 kg/h to 13.4% at 25 kg/h. The question is: which conversions and which flow rates can be expected on extruders with diameters of 77 mm (ZSE 75 MAXX) and 138.7 mm (ZSE 135 MAXX), respectively? The scale-up rules presented in Section 1 (Eq. (3)) can be applied for defining a first order of magnitude. The usual values of the scale-up parameter  $x$  supplied by the manufacturers are between 2.5 and 3. This leads to flow rates in the ranges of 24-500 kg/h and 107-2800 kg/h for the ZSE 75 and ZSE 135, respectively. To improve this preliminary guess, numerical modeling of the transesterification process is necessary.

In this section, the screw profiles of the large extruders are extrapolated from that of the laboratory scale. First, the  $L/D$  ratio is kept constant (here 35). Second, the number of restrictive elements (here, the blocks of kneading discs) is the same. Finally, the relative length (in terms of  $L/D$ ) and location of these elements along the screw profile are maintained. Of course, the screw pitches or the thickness of the kneading discs vary according to the size of the machine. For example, the pitches of the screw conveying elements are 20 and 30 mm for the ZSE 27, 48 and 72 mm for the ZSE 75, and 90 and 120 mm for the ZSE 135. The thicknesses of the kneading discs are respectively 5, 7.5, and 15 mm. However, the staggering angle is kept constant ( $-60^\circ$ ). The two profiles extrapolated from the ZSE 27 for the ZSE 75 and ZSE 135 are shown in Fig. 8. They appear very close, but their dimensions are very different: the lengths are 2.7 and 4.86 m, for screw diameters of 77 and 138.7 mm, respectively.

Another important issue in scale-up is the quantification of heat transfer. In the Ludovic<sup>®</sup> software, the screws are considered to be adiabatic (unless they are thermally regulated) and the heat flux at the barrel  $q$  is calculated as:

$$q = h_T (T_b - T_m) \quad (10)$$

where  $h_T$  is the heat transfer coefficient,  $T_b$  is the barrel temperature, and  $T_m$  is the melt temperature. The determination of the heat transfer coefficient is a delicate problem. In the literature, values between  $210 \text{ W}/^\circ\text{C}/\text{m}^2$  (Todd, 1988) and  $10.000 \text{ W}/^\circ\text{C}/\text{m}^2$  (Chen and White, 1992) can be found for twin screw extruders with a diameter of 30 mm. Based on our previous experience, a value of  $1000 \text{ W}/^\circ\text{C}/\text{m}^2$  was chosen for the simulations on the ZSE 27 extruder. But it is well known that the heat transfer is lower on a larger extruder as the surface/volume ratio decreases with the diameter (White et al., 2001). From the paper of Domschke and Justus (1993), it is possible to estimate the heat transfer coefficient at  $800$  and  $500 \text{ W}/^\circ\text{C}/\text{m}^2$  for the ZSE 75 and ZSE 135, respectively.

For each extruder, simulations of the transesterification process are carried out, for different values of feed rate and screw speed. The barrel temperature is kept constant and equal to  $190^\circ\text{C}$ , what appeared to be an optimal value for the lab scale extruder.

For the ZSE 75 and ZSE 135 extruders, the control of the temperature is more crucial, because heat transfer is less efficient. Therefore, to respect the maximum value of 210°C, low screw speeds are required. But a low screw speed will restrict the maximum flow rate, due to limits in feeding and maximum torque. Therefore, the highest value obtained by the simulation is 250 kg/h at 90 rpm for the ZSE 75, and 1700 kg/h at 85 rpm for the ZSE 135. The **approximate discrete** Pareto curves of the three extruders are illustrated in Fig. 9. Flow rates are presented on a log-scale to make the changes between 2 and 2000 kg/h more clear. For each extruder, the conversion varies from 20 to 60%, according to the flow conditions. If the same conversion of 50% is considered, it is reached at 2.7 kg/h for the ZSE 27 (at 150 rpm), 78 kg/h for the ZSE 75 (at 70 rpm) and 380 kg/h for the ZSE 135 (at 45 rpm). When applying this data to Eq. (3), values of  $x$  equal to 3.4, 2.7 and 3.1 are obtained for the extrapolations ZSE 27→ZSE 75, ZSE 75→ZSE 135 and ZSE 27→ZSE 135, respectively. **All these values are close to 3, but sometimes higher than 3. This unexpected result only proves that the simple theoretical rules** of scale-up cannot be applied in the complex case of reactive extrusion. Table 1 compares the flow conditions leading to this conversion of 50%. When the size of the extruder increases, the screw speed decreases a lot, leading to a decrease in the specific mechanical energy (SME). SME cannot thus be considered as a good criterion for this type of scale-up. However, the final temperatures and the residence times are very close. Nevertheless, the development of the reaction along the screws is different for the various extruders, as shown in Fig. 10. It is more linear for the largest extruder.

## 5 Conclusions

Due to the numerous interactions between parameters it is quite impossible without a model to optimize and extrapolate a reactive extrusion process. Using the transesterification reaction of an EVA as an example, it was shown in this paper how a flow model based on continuum mechanics coupled with a kinetic module allows one to define the best processing conditions for a selected screw profile, and then to test the ability of various profiles to provide **optimized** solutions in terms of level



of reaction and flow rate. Then, a scale-up procedure was proposed, to define the optimal conditions for a pilot-scale and an industrial-scale extruder. The results show that the usual scale-up rules based on the ratios of diameters to a certain power are ineffective as soon as complex phenomena, like the development of a chemical reaction, are involved in the extrusion process.

## References

- Berzin, F., and Vergnes, B., “Transesterification of ethylene acetate copolymer in a twin-screw extruder”, *Intern. Polym. Proc.*, **13**, 13-22 (1998).
- Berzin, F., Tara, A., and Vergnes, B., “Optimization and scale-up of starch cationization in a twin-screw extruder”, *Polym. Eng. Sci.*, **47**, 814-823 (2007).
- Beyer, G., and Hopmann, C., “*Reactive Extrusion – Principles and Applications*”, Wiley, Hoboken (NJ) (2017).
- Bouilloux, A., « *Etude de la transestérification à l'état fondu des copolymères d'éthylène et d'acétate de vinyle* », PhD dissertation, Université Louis Pasteur, Strasbourg (1985).
- Box, G.E.P., and Wilson, K.B., “On the experimental attainment of optimum conditions”, *J. Royal Stat.Soc. Series*, **B13**, 1-45 (1951).
- Carley, J.F., McKelvey, J.M., “Extruder scale-up theory and experiments”, *Ind. Eng. Chem.*, 989-992 (1953).
- Chen, Z., and White, J.L., “Simulation of non-isothermal flow in modular co-rotating twin screw extrusion”, *SPE ANTEC Tech. Papers*, 1332-1335 (1992).
- Covas, J.A., and Gaspar-Cunha, A., “Extrusion scale-up: An optimization-based methodology”, *Intern. Polym. Proc.*, **24**, 67-82 (2009).
- Della Valle, G., Berzin, F., and Vergnes, B., “Modelling of twin screw extrusion process for food products design and process optimization”, in: *Advances in Food Extrusion Technology*, M. Maskan, A. Altan Eds., CRC Press, Boca Raton (FL), 327-354 (2011).
- Domschke, T., and Justus, C., “Heat transfer in single and twin screw extruders”, *Intern. Polym. Proc.*, **8**, 294-307 (1993).
- Ganzeveld, K.J., and Janssen, L.P.B.M., “Scale-up of counter-rotating closely intermeshing twin screw extruders without and with reactions”, *Polym. Eng. Sci.*, **30**, 1529-1536 (1990).
- Gaspar-Cunha, A., Poulesquen, A., Vergnes, B., and Covas, J.A., “Optimization of processing conditions for polymer twin-screw extrusion”, *Intern. Polym. Proc.*, **17**, 201-213 (2002).

- Gaspar-Cunha, A., Covas, J.A., and Vergnes, B., “Defining the configuration of co-rotating twin-screw extruders with multiobjective evolutionary algorithms”, *Polym. Eng. Sci.*, **45**, 1159-1173 (2005).
- Gaspar-Cunha, A., and Covas, J. A., “Optimization in Polymer Processing”, Nova Science Publishers, Hauppauge (NY) (2011).
- Gaspar-Cunha, A., and Covas, J. A., “An engineering scale-up approach using multi-objective optimization”, *Intern. J. Nat. Comp. Res.*, **4**, 17-30 (2014).
- Janssen, L.P.B.M., “*Reactive Extrusion Systems*”, CRC Press, Boca Raton (FL) (2004).
- Kowalski R.J., Li, C., and Ganjyal G.M., “Optimizing twin-screw food extrusion processing through regression modeling and genetic algorithms”, *J. Food Eng.*, **234**, 50-56 (2018).
- Lambla, M., Druz, J., and Bouilloux, A., “Transesterification reactions in molten polymers”, *Polym. Eng. Sci.*, **27**, 1221-1228 (1987).
- Markarian, J., “Compounders look to simulation software for savings in time and costs”, *Plast. Add. Compound.*, **7**, 34-37 (2005).
- Menges, G., and Feistkorn, W., “Scale-up of twin screw extruders. Application and verification with the example of PVC”, *Adv. Polym. Tech.*, **4**, 123-129 (1984).
- Myers, R.H., Montgomery, D.C., and Anderson-Cook, C.M., “*Response Surface Methodology – Process and Product Optimization Using Designed Experiments*”, Wiley, Hoboken (NJ) (2016).
- Nakatani, M., “Scale-up theory for twin-screw extruder, keeping the resin temperature unchanged”, *Adv. Polym. Tech.*, **17**, 19-22 (1998).
- Ortiz-Rodriguez, E., and Tzoganakis, C., “Scaling-up a reactive extrusion operation: A one-dimensional simulation analysis”. *Intern. Polym. Proc.*, **25**, 242-250 (2010).
- Potente, H., “Existing scale-up rules for single-screw plasticating extruders”, *Intern. Polym. Proc.*, **6**, 267-278 (1991).

- Pradel J.L., David, C., Quinebeche, S. and Blondel, P., “Scale up tools in reactive extrusion and compounding processes. Could 1D-computer modeling be helpful?”, AIP Conf. Proc., **1593**, 530-533 (2014).
- Teixeira, C., Covas, J.A., Berzin, F., Vergnes, B., and Gaspar-Cunha, A., “Application of evolutionary algorithms to the definition of the optimal twin-screw extruder configuration for starch cationization”, Polym. Eng. Sci., **51**, 330-340 (2011).
- Todd, D., “Heat transfer in twin screw extruders”, SPE ANTEC Tech. Papers, 54-58 (1988).
- Vergnes, B., Della Valle, G., and Delamare, L., “A global computer software for polymer flows in corotating twin screw extruders”, Polym. Eng. Sci., **38**, 1781-1792 (1998).
- White, J.L., Kim, E.K., Keum, J.M., Jung, H.C., and Bang, D.S., “Modeling heat transfer in screw extrusion with special application to modular self-wiping co-rotating twin-screw extrusion”, Polym. Eng. Sci., **41**, 1448-1455 (2001).
- Xanthos, M., “*Reactive Extrusion – Principles and Practice*”, Hanser, Munich (1992).

## Figure captions

Figure 1: Transesterification reaction of EVA copolymer.

Figure 2: Screw profile of the laboratory-scale extruder.

Figure 3: Example of results for the laboratory-scale extruder ( $N = 250$  rpm,  $Q_{EVA} = 5$  kg/h,  $T_b = 170^\circ\text{C}$ ).

Figure 4: Conversion as function of EVA flow rate for the laboratory-scale extruder ( $T_b = 170^\circ\text{C}$ ), at different screw speeds (●: 100 rpm, ○: 200 rpm, ■: 300 rpm).

Figure 5: Pareto curves for the laboratory-scale extruder, at different barrel temperatures (●:  $170^\circ\text{C}$ , ○:  $190^\circ\text{C}$ , ■:  $195^\circ\text{C}$ , □:  $200^\circ\text{C}$ ).

Figure 6: Screw profiles used for the optimization of the laboratory-scale extruder.

Figure 7: Pareto curves for the different profiles of the laboratory-scale extruder, at  $T_b = 190^\circ\text{C}$  (●: Profile 1, ○: Profile 2, ■: Profile 3, □: Profile 4).

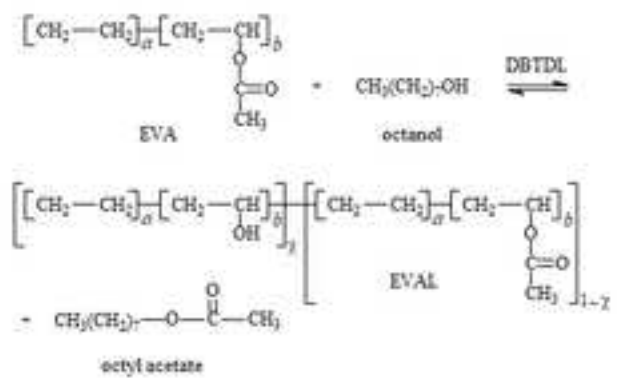
Figure 8: Screw profiles used for the scale-up of the laboratory-scale extruder (Profile 3).

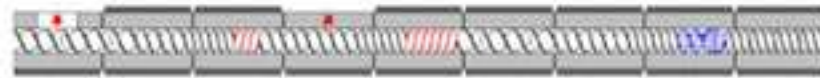
Figure 9: Pareto curves for the different extruders, at  $T_b = 190^\circ\text{C}$  (●: ZSE 27, ○: ZSE 75, ■: ZSE 135).

Figure 10: Change in conversion along the screw profile for the different extruders, for a final conversion of 50% (□: ZSE 27, ∙∙: ZSE 75, ---: ZSE 135).

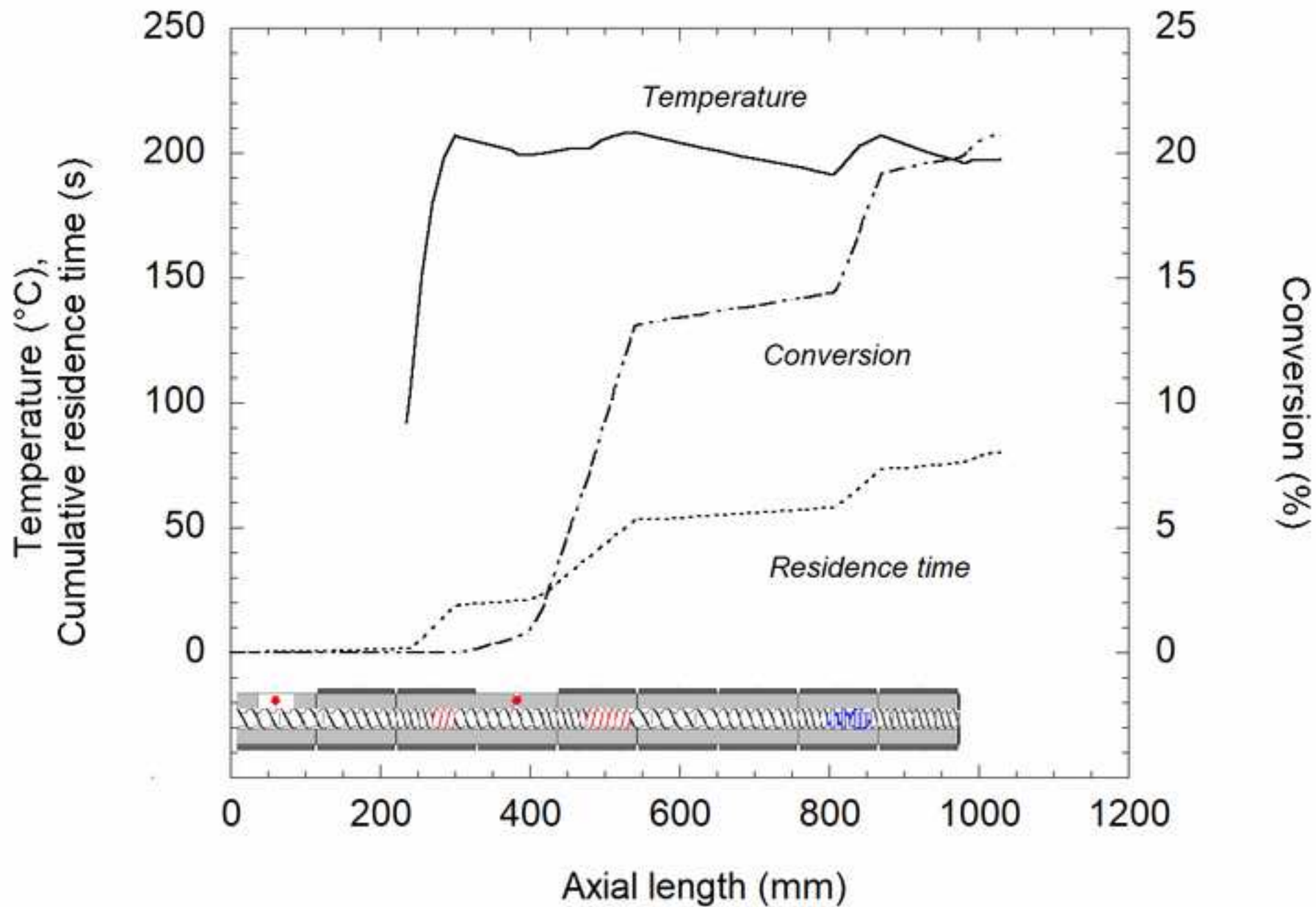
Table 1. Flow conditions to reach 50% conversion.

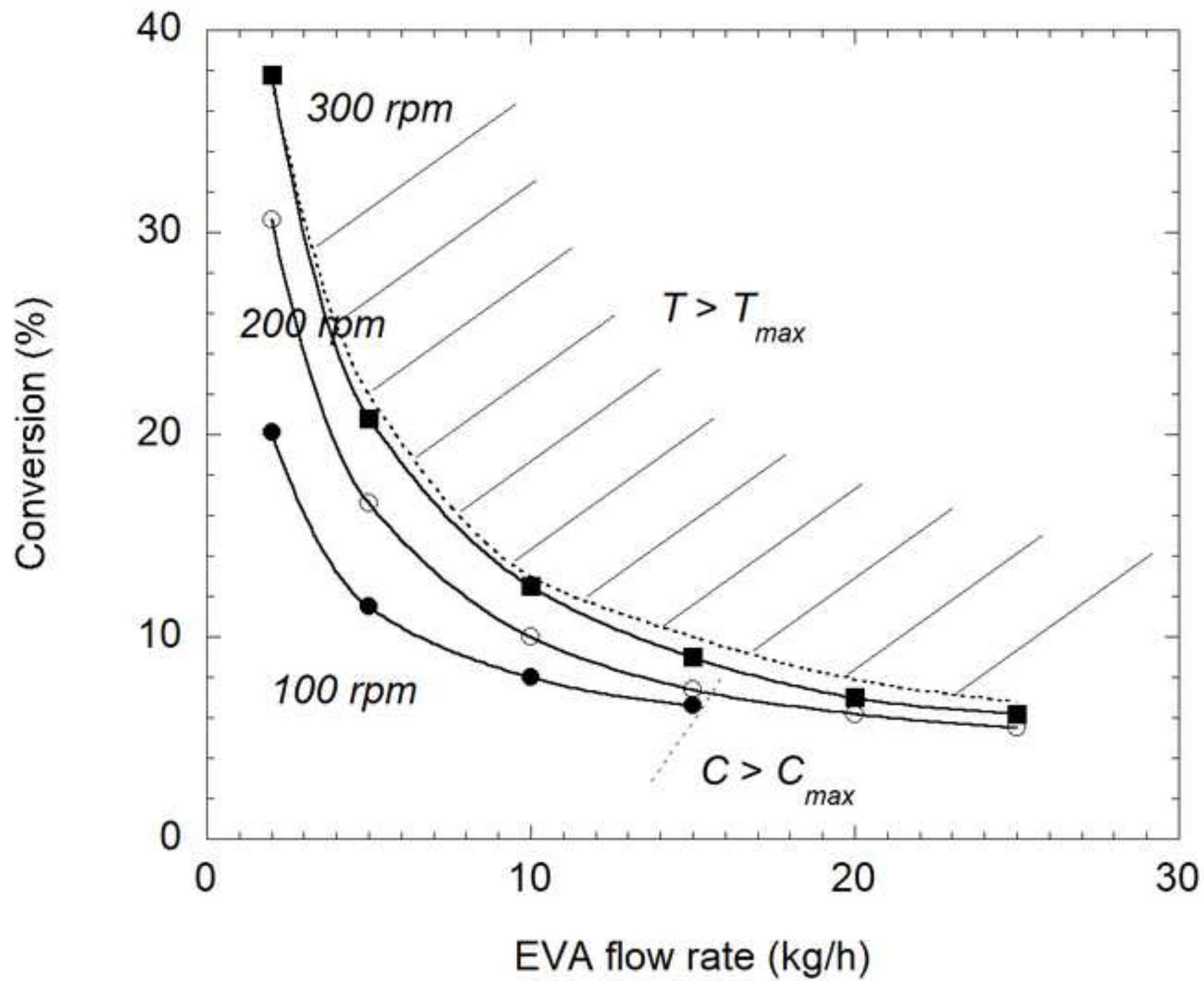
Extruder	EVA feed rate (kg/h)	Screw speed (rpm)	Final temperature (°C)	Average residence time (s)	Specific energy (kWh/t)
ZSE 27	2.7	150	204	256	393
ZSE 75	78	70	207	269	157
ZSE 135	380	45	210	297	105

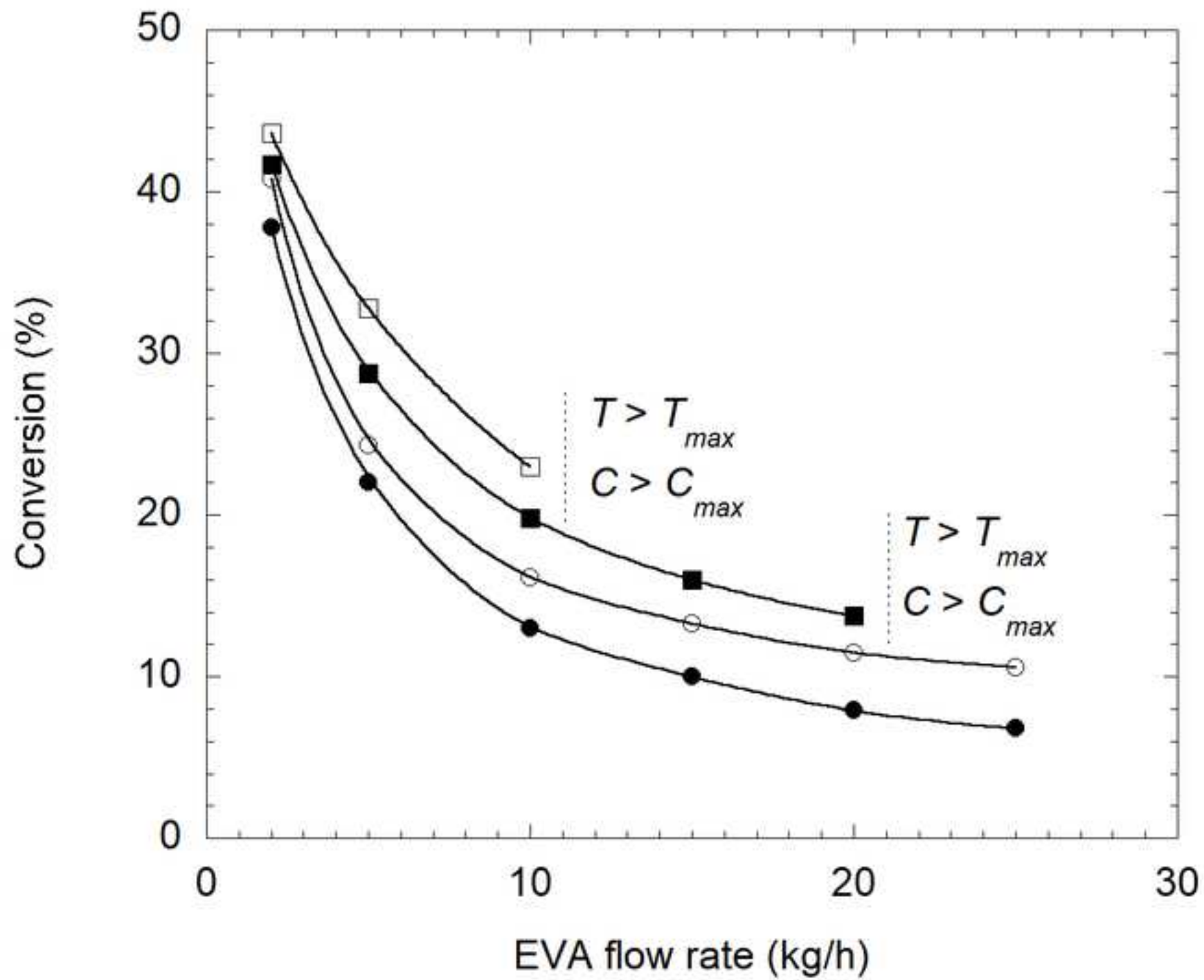


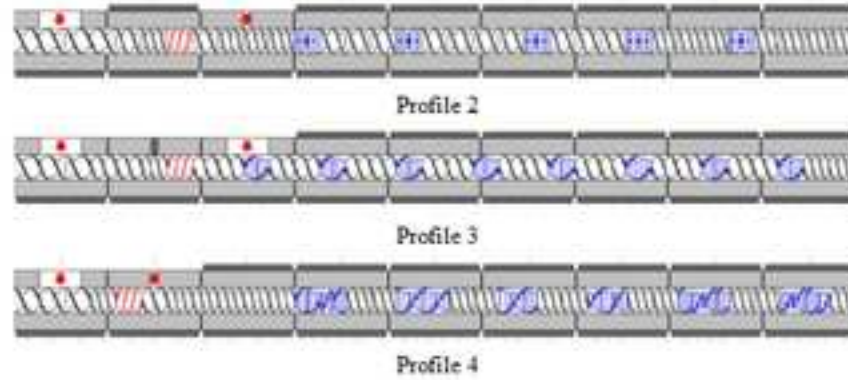


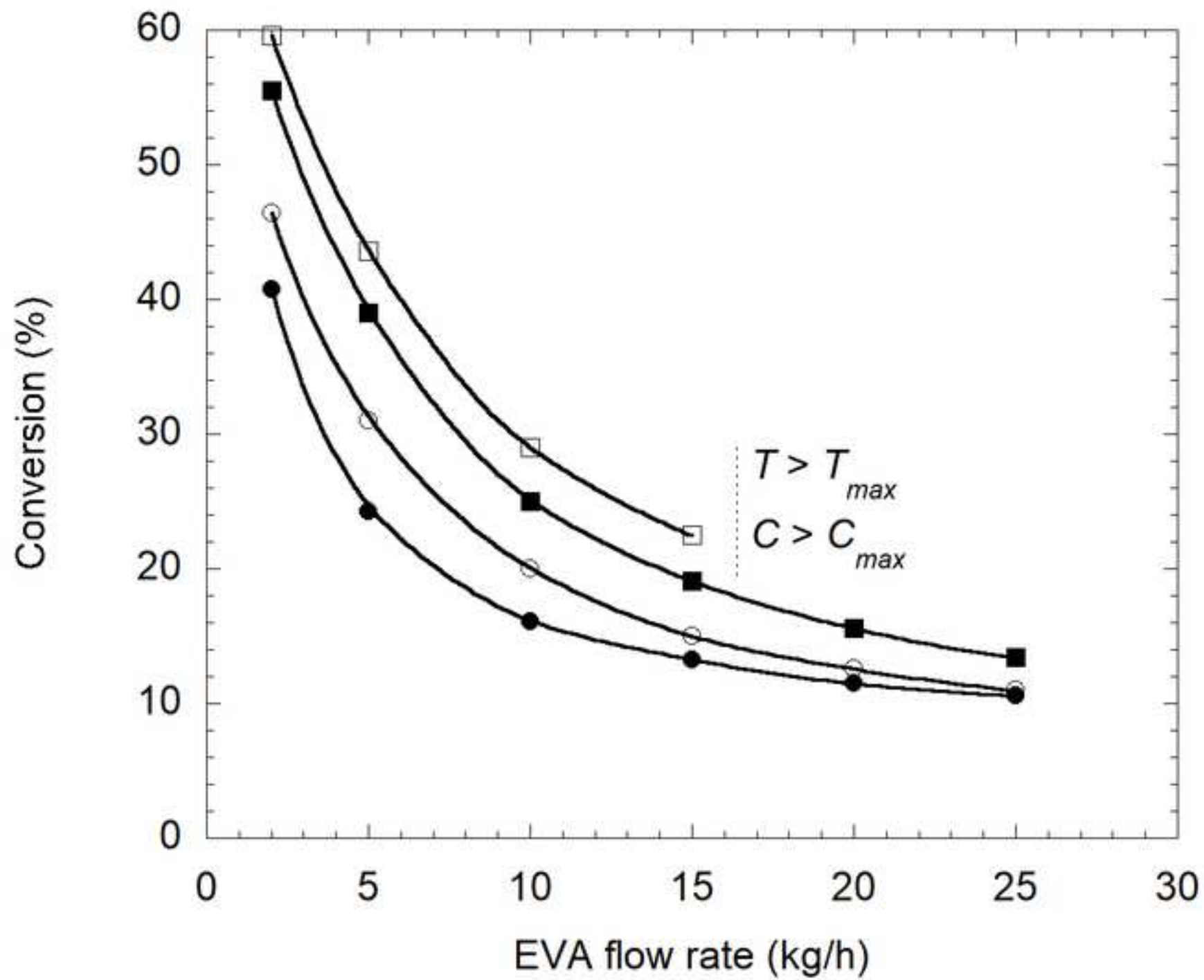














ZSE 75



ZSE 135

