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CFD analysis of the depolymerization of a dilute solution of two polymers using twin-screw extrusion

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 Integration Project

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Abstract

Polymer processing, more particularly polymer extrusion, is one of the fundamental aspects in the downstream industry. Understanding how extrusion works, being able to predict the fluid's behavior during the process, and optimizing the process parameters to minimize energy consumption is of the utmost importance. This thesis constitutes one of the first attempts at modeling depolymerization reactions with CFD while linking the fluid dynamics, heat transfer, and chemical reaction phenomena to one another. This is done, on one hand, by using a complex viscosity model for shear-thinning/-thickening inelastic non-Newtonian fluids dependent on temperature, shear rate, and species concentrations. On the other hand, a linearly-combined exponential kinetic model is used to include both thermal- and mechanical- induced chain scission. For the sake of completeness, a polymerization reaction of the depolymerized oligomers is also investigated via injection of a cross-linking agent from a secondary inlet to the extruder. The results show that coupling of all physical phenomena is imperative, solving them separately offsets greatly the practicality of the solution. Also, it is crucial to simulate accurately the transient startup phase of the extruder to ensure that the desired product quality is achieved.

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As a very special group of people constantly reminds me:

" Work Hard, Have Fun, Make History."

Introduction

In industry, polymers are some of the most widely used molecular classes and they make up many of the every day products. Reason for this is that polymers serve effectively as substitutes to heavier and more expensive materials. Moreover, polymer formulation allows polymer product to span their material properties over a wide range of applications. Polymer processing is therefore a fundamental field that, directly and indirectly, supports almost every industry. One of such processes is twin-screw extrusion. Nowadays, twin-screw extrusion is a upstream process intended to mix and shape thermoplastic polymers at high shear rates, temperatures, and pressure gradients to produce finished or semi-finished products [1]. After this process, the extrudate usually receives secondary processing. More recently, extrusion has also been studied for its opportunity to depolymerize polymer chains and offer a viable recycling method of monomer units [2] [3] [4]. The problem with mechanical depolymerization is that the material partly loses its original properties compared to the virgin material [5] [6]. Moreover, previous studies have not focused on developing and advanced 3D model but they rather conducted experiments which were followed up by simple computational models [7] [4]. Therefore, there is still little understanding of how the variables within the extruder system are linked to the physical phenomena and the process conditions [8]. In principle, the complexity lays in the fact that the degradation of one, or more, polymers introduces new species into the fluid mixture. This, in turn, affects the fluid's concentration which reflects on the kinetics of the chemistry involved and the rheological properties. Thus far, the relationship between the kinetics and the fluid's internal stresses and the one between the fluid's concentration and its viscosity are both unknown.

This work offers new insights in the modeling of chain scissions in a 3D twin-screw extrusion process. The focus of the thesis is that of creating a working model of closely intermeshing co-rotating screws and to implement advanced kinetic and rheological models that can account for the process conditions and the fluid's evolution. Furthermore, the impact of the rotational velocity on the system will be analyzed. The result of this work

will provide engineers and researchers with a benchmark model for polymer degradation that they can build upon and tune for different materials. One such model is necessary to better predict the fluid’s behavior, the materials’ degradation extent and properties, and so to optimize the extrudate quality and energy consumption.

Literature Review

CFD of Twin-screw Extrusion and Depolymerization

While there are abundant studies on extrusion, be that single-screw or twin-screw, not so many consider polymer degradation from a CFD perspective [9]. Besides, challenges still stand due to the complex interactions between non-Newtonian fluids behavior, mixing, and heat transfer phenomena [10]. Some of the few examples of depolymerization in screw extrusion come Farahanchi et al. [11] [12]. In their work, they explored ultrahigh rotational speeds to study the mixing efficiency and molecular weight reduction [11] [12]. Despite the affinity of their work with this thesis, ultrahigh rotational speeds are too extreme to appreciate the interplay of processing conditions, fluid properties, and chemical reactions.

Rheology

In the literature, there are extremely few examples of concentration-dependent viscosity models [13]. Researchers have rather investigated the role played by particle and nanoparticle sizes and shapes towards the viscous behavior of the polymer solutions [14][15]. Generally, they make use of simple Power-Law [16], Carreau, or Cross models as the fitting parameters for these are easily available and obtainable through experiments. These studies then vary concentration and extrapolate the fitting parameters for each [13]. Even less explored in the literature are rheological models that explicitly include concentration as a variable upon which viscosity depends on. In one study this was attempted; but the focus of the researcher was on supercritical fluids [17]. Parisi et al. used the Huggins and Kraemer methods to measure the viscosity of diluted PVA at different concentrations [18]. The models,

$$\frac{\eta_{sp}}{c} = [\eta] + k_H [\eta]^2 c \quad (1)$$

and

$$\frac{\ln(\eta_{sp})}{c} = [\eta] + \left(k_H - \frac{1}{2}\right) [\eta]^2 c, \quad (2)$$

use the specific viscosity $\eta_{sp} = \eta_r - 1$, the relative viscosity η_r , the intrinsic viscosity $[\eta]$, the polymer concentration c , and the Huggins coefficient k_H . Both account for concentration with a second-degree polynomial but neither is complete of the thermal and mechanical effects. Besides, they do not provide flexibility in terms of the complexity of the fluid’s composition. Modarress et al. instead derived a Eyring-type model from the reaction rate theory [19]. This model is able to capture well the effect of a complex composition and the influence of temperature,

$$\eta(T, x_i) = \sqrt{2\pi RT} \prod_i^c \left(\frac{M_i}{V_i^2}\right)^{\frac{x_i}{2}} \exp\left(\frac{x_i E_{ai}}{RT}\right) \quad (3)$$

R is the universal gas constant, T is the temperature and M_i , V_i , x_i , E_{ai} are respectively the molecular mass, liquid molecular volume, molecular fraction, and activation energy of species i .

More recently, Kousemaker used a complex model combining Carreau-Yasuda and the Unified Viscosity Model (see Equation 4) [20]. There, Ap_1 , Ap_2 , Ap_3 , β_1 , β_2 , n , AP_{11} , AP_{22} , τ_0 , τ_1 , and n_2 are parameters to be fitted. Instead, μ_s is the solvent viscosity, μ_p^0 is the zero-shear viscosity, μ_{max} is the maximum viscosity, $\dot{\gamma}$ is the shear rate, and C_p is the polymer concentration. The model is able to represent well the non-Newtonian behavior of the polymer fluid and it was used to include shear-thickening effects and non-linearity. However, also this combined equation is limited. Thermal effects are not considered and the fluid is assumed dependent on only one species, p .

$$\mu(\dot{\gamma}, C_p) = \mu_s + (\mu_p^0 - \mu_s) \left[1 + (\lambda\dot{\gamma})^2\right]^{\frac{n-1}{2}} + \mu_{max} \left[1 - \exp\left(-(\lambda_2\tau_r\dot{\gamma})^{n_2-1}\right)\right] \quad (4)$$

$$\mu_p^0 = \mu_s \left[1 + Ap_1C_p + Ap_2C_p^2 + Ap_3C_p^3\right] \quad (5)$$

$$\lambda = \beta_1 \exp(\beta_2 C_p) \quad (6)$$

$$\mu_{max} = \mu_s (AP_{11} + AP_{22} \ln C_p) \quad (7)$$

$$\tau_r = \tau_0 + \tau_1 C_p \quad (8)$$

Degradation Kinetics

When polymer chains are exposed to thermal or mechanical effects, the molecule receives energy. If this energy exceeds the strength of the intramolecular bonds, the chain will depolymerize into oligomers [21]. In the context of an extruder, high temperature and shear rate exposition occurs. While the thermal effects are commonly included in kinetic models by an Arrhenius-like term, there is not as much clarity on how to relate shear rate to the kinetic constant.

$$k_T = A \exp\left(\frac{-E_a}{RT}\right) \quad (9)$$

Before diving into the literature for a kinetic model of shear rate, it must be determined the reaction order. With this regard, multiple studies reported a first-order degradation reaction of PVA and bPAM and mechanical depolymerization reactions overall [22] [23] [24]. Instead, Figure 1 provides a good overview of the plausible behavior of the kinetic rate with respect to shear rate. In the image, NL denotes the non-linear relationships. Meanwhile, by T is meant a threshold-like behavior and by J a jump-like behavior.

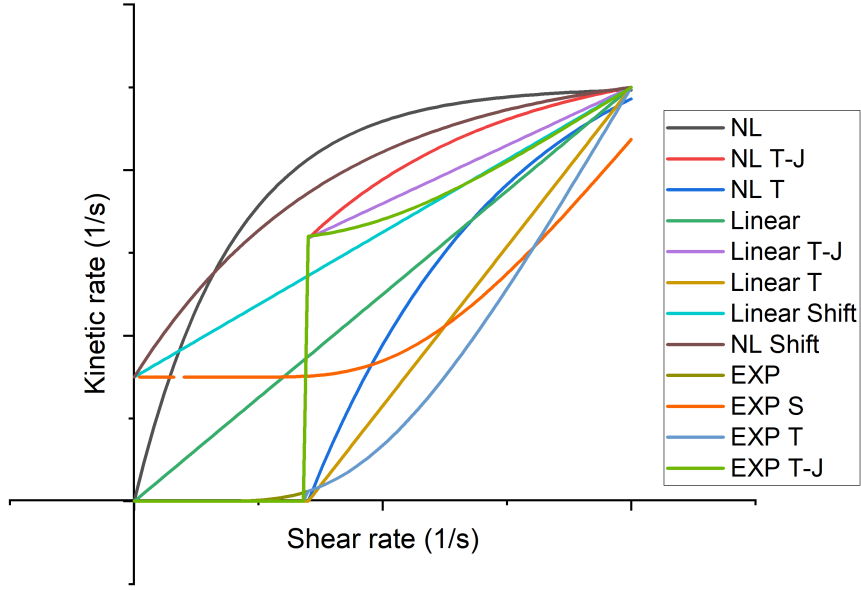


Figure 1: Different relationships between shear rate and kinetic constant for polymer chain scission.

From the literature, Rognin et al. [24], Liu et al. [25], Zheng et al. [26], and Nghe et al. [27] all concluded that there is a threshold shear rate before the chains are broken. Rognin et al. did so at the atomic level, using the Brownian dynamics the rupture of linear polymer chains [24]. Nghe et al. further observed a decreasing critical deformation rate, the threshold, for an increasing molecular weight and concentration which they explained as a compensation effect of the friction between polymer chains for the mechanical stress [27]. Moreover, many papers reported non-linear degrading behavior. Radtke et al. tested entangled polymer chains and observed that the cleavage rate follows an exponential decay and begins with a jump [28]. The same exponential decay trend was observed by Melik [29], Basedow et al. [23], Mansour[30], and Elbing et al.[31]. The latter also mentions a steady-state molecular rate or in other words, an asymptote the kinetic rate does not exceed, regardless of any further increase in shear-rate.

In the literature, the following kinetic models have been used, so far, to introduce the mechanical degradation effects. Farahanchi et al. combined the thermal and shear-induced terms by multiplication while maintaining the shear-induced contribution linear and implementing a screw-geometry-dependent parameter C , see Equation 12 [11].

$$k_d = k_T \cdot k_S = A \exp\left(\frac{-E_a}{RT}\right) \cdot \dot{\gamma} e^{-1/C} \quad (10)$$

Instead, Zheng et al. modeled starch degradation by linearly combining the thermal term and shear-induced term; where each term is defined exponentially [26]. In Equation 39, $k_{T,0}$ is the pre-exponential parameter of the thermal degradation, $k_{S,0}$ is the pre-exponential parameter of the mechanical degradation, τ is the shear stress, and ν is the molar volume.

$$\begin{aligned}
k_d &= k_T + k_S + \sqrt{k_T \cdot k_S} \\
&= k_{T,0} \exp\left(\frac{-E_T}{RT}\right) + k_{S,0} \exp\left(\frac{-E_S}{\tau\nu}\right) + \sqrt{k_{T,0} \cdot k_{S,0} \exp\left(\frac{-E_T}{RT} \cdot \frac{-E_S}{\tau\nu}\right)} \quad (11)
\end{aligned}$$

Similar to the previous model is Cai et al.'s work. This time, though, the exponential is simplified to reduce the fitting parameters so that E_a becomes the activation energy in a shearless environment, V_0 is the activation volume, and G is a geometry parameter depending on the screw configuration [32] [33].

$$k_d = k_0 \exp\left(\frac{-(E_a - V_0 G^{0.51} \tau)}{RT}\right) \quad (12)$$

Methodology

Physical Model

Extruder Geometry

Screw extruders are well-known units among the polymer processing industry. Their design varies according to the requirements of the operation to be performed and the material to be processed. However, the general configuration of a screw extruder consists of: the chamber, the hopper(s) inlet(s), the screw(s), the exit die, the heating and/or cooling units, and the motor. Figure 2 provides a clear overview of a typical screw extruder. The motor generates the electric power that is transmitted to the gear box and converted to mechanical power. Meanwhile, as the screws rotate in the barrel, the feed is injected from the hopper. Then, as the screws convey the fluid along the barrel, heaters and coolers are used to regulate the internal temperature. Finally, the fluid reaches the die, where it is extruded.

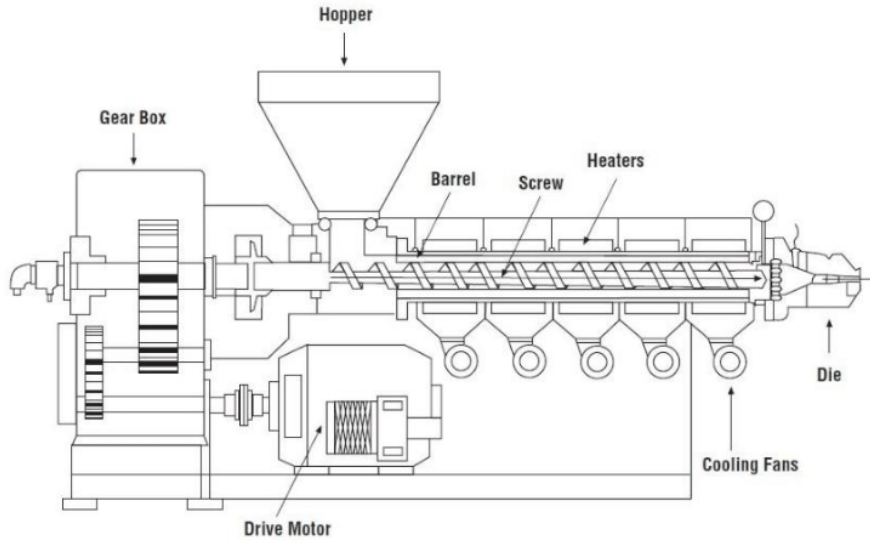


Figure 2: Scheme of the main elements in a screw extruder [34].

Screw extruders like the ones discussed in this project are referred to as twin-screw extruders. For these, the joint effect of each screw contributes to the conveying movement

and shear stresses the fluid is subject to. Depending on the setup chosen, co-rotation or counter-rotation, and the degree of intermeshing, fully to non-intermeshed, the same screw geometry can lead to significantly different results. Figure 3 provides a summary of all main design possibilities. For instance, counter-rotating screws have been determined to provide lower shear rates and a single-screw-like flow pattern compared to the counter-rotating setup [35]. Moreover, the extent of intermeshing is also known to affect the fluid flow and the shear stresses. Namely, fully intermeshing screws are crosswise closed, meaning the fluid does not move perpendicularly to the orientation of the extruder, but could be lengthwise open or closed depending on whether the screws are co-rotating or counter-rotating, respectively. Instead, partially and non-intermeshing screws are both lengthwise and crosswise open [36]. Regarding shear stresses, their relationship with intermeshing is directly proportional as closeness between the screws improves friction in their interstitial areas and renders higher shear rates; ideal for mixing and compounding [37][38].

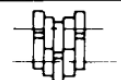
SCREW ENGAGEMENT		SYSTEM	COUNTER-ROTATING	CO-ROTATING
INTERMESHING	FULLY INTERMESHING	LENGTHWISE AND CROSSWISE CLOSED	1 	2 THEORETICALLY NOT POSSIBLE
		LENGTHWISE OPEN AND CROSSWISE CLOSED	3 THEORETICALLY NOT POSSIBLE	SCREWS 4 
		LENGTHWISE AND CROSSWISE OPEN	5 THEORETICALLY POSSIBLE BUT PRACTICALLY NOT REALIZED	KNEADING DISCS 6 
	PARTIALLY INTERMESHING	LENGTHWISE OPEN AND CROSSWISE CLOSED	7 	8 THEORETICALLY NOT POSSIBLE
		LENGTHWISE AND CROSSWISE OPEN	9A 	10A 
			9B 	10B 
	NOT INTERMESHING	LENGTHWISE AND CROSSWISE OPEN	11 	12 

Figure 3: Summary of twin-screw extruders setup options [36].

Screw and Kneading Element Geometries

Selecting a proper geometry for the screw and kneading elements is fundamental as these greatly influence the fluid's experience in the extruder. For instance, an angled flight leads, while keeping all other screw parameters constant, to a higher pressure growth rate and so to increased shear stresses on the fluid [39]. Screws are generally differentiated between conical and parallel. Conical screws are usually used to extrude polyvinyl chloride [40] [41], to process heat-sensitive materials [42] [41], and to produce foams [43]. In fact, depending on the conical geometry chosen, pressure, shear, and mixing can be

moderated naturally. Instead, parallel screws are more traditional and more widely used. They offer a larger available volume and uniform mixing and shear. For this reasons they are typically chosen to extrude thermoplastic materials and in recycling operations [4] [5] [6]. Besides the choice of screw shape, other screw elements affect the extrusion process. Figure 4 provides an overview of all these. The outer screw diameter, the root diameter, and the channel depth are responsible for the available free volume and torque in the barrel [44]. The pitch, which includes the axial channel width and the axial flight width, is particularly important as the residence time of the fluid in the extruder heavily depends on it; typically, a longer pitch corresponds to faster conveyance [44]. The same consideration applies to the helix angle.

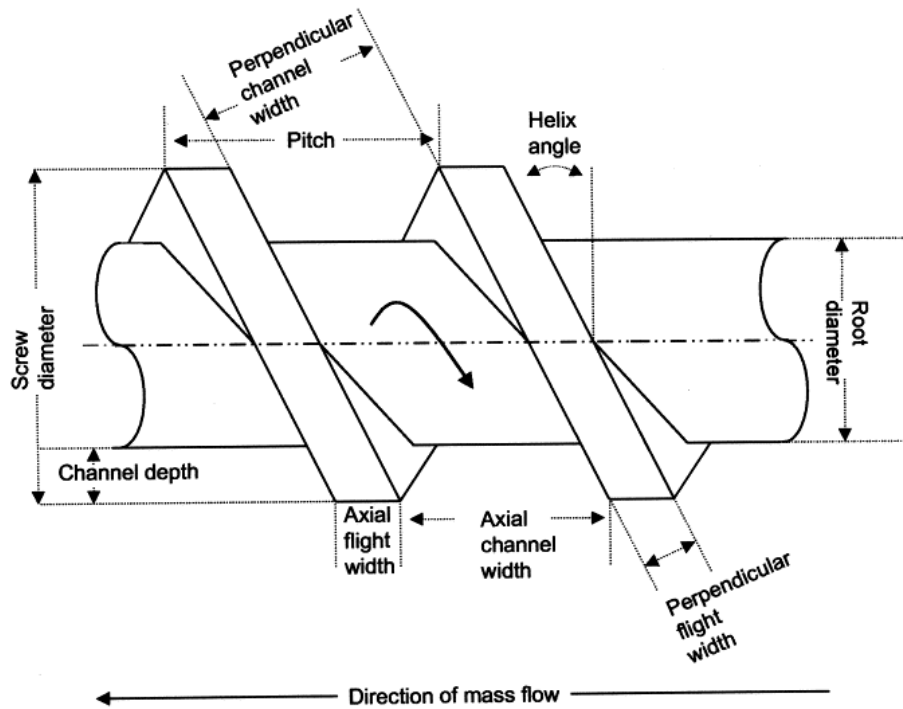


Figure 4: Extrusion screw scheme complete of all its parameters [45].

Regarding kneading blocks, these are the most common examples of mixing elements in screw extrusion. By imposing planar shear to the fluid they promote distributive mixing, this is especially true for thinner kneading disks [44] [46], and increase the residence time [47]. Another design choice that affects the system as to do with the stagger angle of the disks. Kneading disks are normally staggered with respect to one another to control the mixing and conveying extent of the element. A 90-degree stagger angle has no effect on the conveying and it is therefore referred to as neutral [46]. In this study, one such configuration is used [48] [20]. Below, in Figure 5 is an overview of different K-type kneading elements.

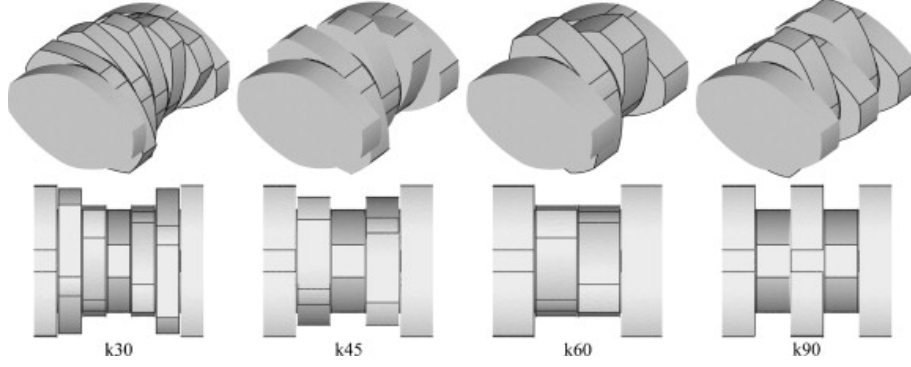


Figure 5: Kneading blocks at 30°, 45°, 60°, and 90° [49].

Non-Newtonian Fluids

Fluids, particularly polymer melts, are particularly fascinating for their rheological properties. Gels and emulsions, to name a few, deform non-linearly with respect to shear rate, time, or polymer structure and concentration. Depending on the intermolecular forces and architecture, polymers show two main behaviors: shear thinning and shear thickening. The simplest model in this sense is the Power-Law model [13]. For $n < 1$, the fluid shear thins; for $n > 1$ it shear thickens [13]. However, one of the main drawbacks of one such model is that at low and high shears the viscosity is free to take infinite values. So, more complete models, such as the ones discussed earlier in the theoretical background, have been devised to better capture the entire curve of polymeric solutions. For instance, the Carreau-Yasuda model is one of the best at estimating the shear thinning behavior by implementing the molecule's relaxation time [50]. Instead, Delshad proposed an equivalent model for shear thickening fluids [51]. The model is similar to the approach taken by Carreau-Yasuda in the sense that viscosity is related to the molecule's relaxation time, shear rate, and a plateau value. This leads back to Kousemaker and his combined viscosity model where the fluid is expected to present shear thinning behavior at low shear rates and shear thickening behavior at high shear rates[20]. In Figure 6 is presented an approximation of the resulting rheological curve.

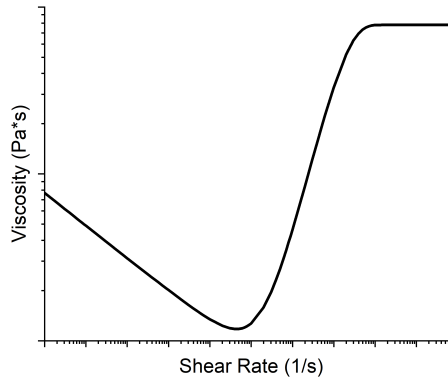


Figure 6: Approximate viscosity curve of the combination of Carreau-Yasuda and the Unified Viscosity Model on the log-log scale.

Mathematical Model

The project was carried out using COMSOL Multiphysics®(version 6.2) as the mathematical tool [52]. As its name suggests, one of the main strengths of this tool, which is also the reason it was selected to be used for this project, is its ability in coupling different physical and chemical phenomena. Thanks to the user-friendly interface, COMSOL has pre-built functions for most of the possible designer’s choices. As a result, the researcher can build a model by simply defining the necessary parameters and properties such as the materials’ dynamic and thermal properties, sources, and possible constraints. To solve the governing equations, COMSOL relies on the finite element method (FEM) and provides the designer with different solver options to achieve the desired balance between accuracy, convergence, and computational time [53].

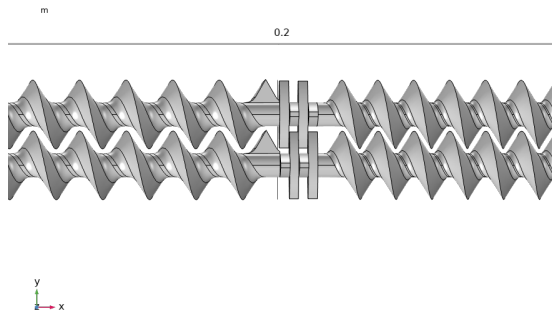
Prior to COMSOL, the screws were constructed in SolidWorks before being imported into COMSOL and assembled with the barrels, the exit nozzles, and the hopper feeds [54]. Table 1 and Table 2 can be referenced for all relevant parameters. To mention is that in Table 1 the anti-helix angle represents the angle opposite to the flight angle (compare Figure 4 and Figure 7a for a visual representation).

Table 1: Parameters used to build the screw geometrical elements.

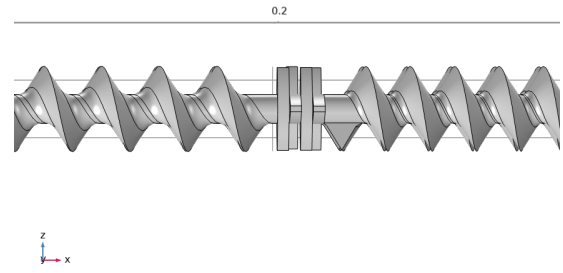
Parameter	Symbol	Value	Unit	Ref.
Root diameter	D_{root}	5	mm	[55]
Channel depth	$l_{ch,depth}$	4.26	mm	[56]
Screw diameter	D_{screw}	9.26	mm	[57]
Screw length	L_{screw}	300	m	[58] [57]
Centerline distance	C_L	10.8	mm	[55]
Base axial flight width	$W_{flight,b}$	4.26	mm	[59]
Axial channel width	$W_{channel}$	4.63	mm	[55]
Pitch	L_{pitch}	8.9	mm	[20]
Helix angle	θ	$\frac{\pi}{3}$	rad	[60] [61]
Anti-helix angle	ϕ	$\frac{\pi}{3}$	rad	[60] [61]
Kneading disk thickness	l_{disk}	2	mm	[62]
Kneading disk width	W_{disk}	1	mm	[62]
Kneading disk face curvature	κ_{disk}	75	m ⁻¹	[48]

Table 2: Parameters used to build the chamber elements, all values are expressed in millimeters [mm].

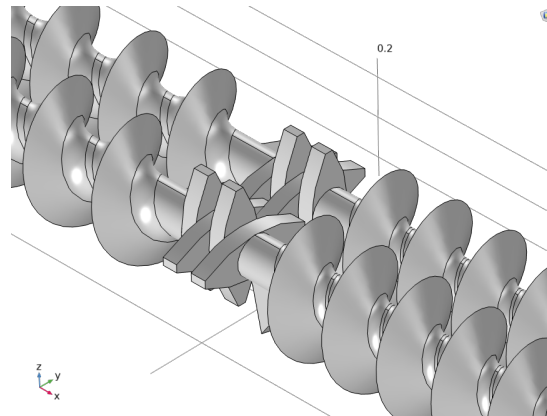
Parameter	Symbol	Value	Parameter	Symbol	Value	Ref.
Barrel length	L_{barrel}	400	Barrel diameter	D_{barrel}	15.3	[45]
Main hopper height	$H_{onlet,1}$	1.5	Main hopper radius	$R_{inlet,1}$	5	[63]
Secondary hopper height	$H_{inlet,2}$	1.5	Secondary hopper radius	$R_{inlet,2}$	1	[63]
Nozzle cone length	L_{cone}	5	Nozzle cone bottom radius	$R_{cone,b}$	2	[45]



(a) View from the xy plane.



(b) View from the xz plane.



(c) View from an angle.

Figure 7: Schematic of the screw geometry from three different points of view zoomed about the kneading block.

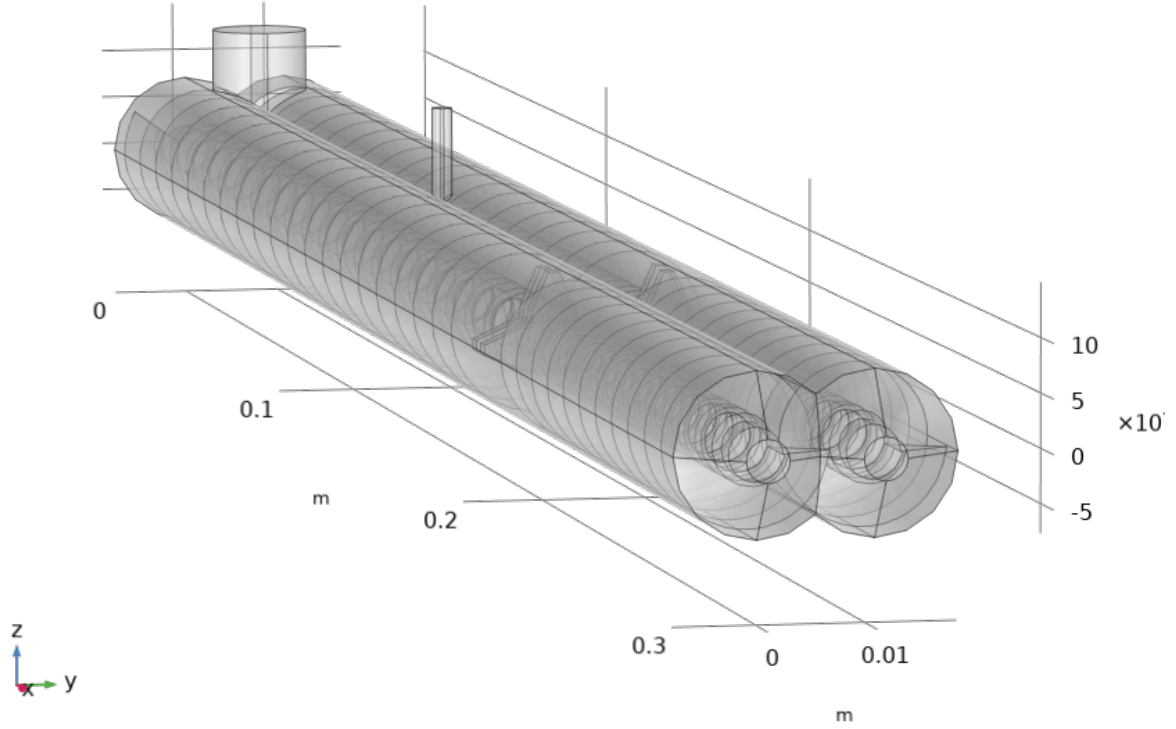


Figure 8: Representation of the twin-screw extruder with main and secondary inlet hoppers.

Rotating Boundary and Fluid Domain

Although COMSOL is equipped with a frozen rotor study option which would perfectly match the dynamics of the system, it was concluded that such approach would lead to a larger computational effort than by manually specifying the rotation of the screw elements. Because the screws are intermeshing and due to the fact that COMSOL takes the rotating boundary as the volume occupied by the screws, rather than the screw surface itself, the software would struggle to find a solution at the intersection. Instead, using a stationary study approach allows COMSOL to apply centrifugal and Coriolis forces by considering the defined angular velocity [20].

Therefore, the screws' angular velocity is represented by

$$\omega = \omega \hat{i} \rightarrow \mathbf{v} = \omega \times \mathbf{r} \begin{bmatrix} 0 \\ -\omega z \\ \omega y \end{bmatrix} \quad (13)$$

Meanwhile, the volume forces the fluid will respond according to are:

$$\rho \hat{a} = \rho (\omega \times \omega \times \mathbf{r} + 2\omega \times \mathbf{v}_{ref}) \quad (14)$$

$$\rightarrow \rho \hat{a} = \rho \left(\begin{bmatrix} 0 \\ -\omega^2 y \\ -\omega^2 z \end{bmatrix} + 2 \begin{bmatrix} 0 \\ -\omega \mathbf{v}_{ref,z} \\ \omega \mathbf{v}_{ref,y} \end{bmatrix} \right) \quad (15)$$

To notice is that Equation 13 and Equation 14 are only valid for one rotational frame. When, like in a twin-screw extruder, there are two axis of rotation, it must be modified the equation by introducing the screw axis distance as an offset term of the axis displacement. For the rotational velocity of the screws' faces, this fix can be implemented easily in COMSOL. The screws exist as independent boundaries and so each can be assigned the proper rotation. Laying the left screw on the y-axis zero coordinate (see Figure 8), Equation 13 remains valid. Instead, the rotational velocity of the right screw is

$$\omega = \omega \hat{i} \rightarrow \mathbf{v} = \omega \times \mathbf{r} \begin{bmatrix} 0 \\ -\omega z \\ \omega (y - d_{axis}) \end{bmatrix} \quad (16)$$

In a similar fashion is modified Equation 14 for the fluid domain. The way to do so is, however, less intuitive. Since the fluid domain is inevitably created as one unified volume composed of two sides of the extrusion chamber, it is resorted to "if" conditions to write a single equation that holds for the entire domain. That is:

$$\begin{aligned} \rho \hat{a} = & \begin{bmatrix} 0 \\ -\omega^2 y \\ -\omega^2 z \end{bmatrix} + 2 \begin{bmatrix} 0 \\ -\omega \mathbf{v}_{ref,z} \\ \omega \mathbf{v}_{ref,y} \end{bmatrix} - \left(\begin{bmatrix} 0 \\ -\omega^2 y \\ -\omega^2 z \end{bmatrix} + 2 \begin{bmatrix} 0 \\ -\omega \mathbf{v}_{ref,z} \\ \omega \mathbf{v}_{ref,y} \end{bmatrix} \right) \left(y > \frac{d_{axis}}{2} \right) \\ & + \left(\begin{bmatrix} 0 \\ -\omega^2 (y - d_{axis}) \\ -\omega^2 z \end{bmatrix} + 2 \begin{bmatrix} 0 \\ -\omega \mathbf{v}_{ref,z} \\ \omega \mathbf{v}_{ref,y} \end{bmatrix} \right) \left(y > \frac{d_{axis}}{2} \right) \end{aligned} \quad (17)$$

Creeping Flow

To model the fluid dynamics in the system, the creeping flow interface is used. This is suitable since a reacting single-phase ideal flow inside an extruder can be considered creeping or laminar [20]. The creeping flow interface takes care of solving the mass continuity and Navier-Stokes equations, see Equation 18 and Equation 19. While the fluid's density and viscosity are specified in this interface, information on temperature is pulled from the "Heat Transfer in Fluids" interface. During the mesh sensitivity analysis a Newtonian fluid with viscosity $1 \text{ Pa} \cdot \text{s}$ is used for simplicity. Instead, the simulation of the extruding process is done with a complex non-Newtonian model. The latter still uses a fictional viscosity for water of $1 \text{ Pa} \cdot \text{s}$ to better analyze the behavior of the solution.

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \quad (18)$$

$$\frac{\partial (\rho \mathbf{v})}{\partial t} + \nabla \cdot (\rho \mathbf{v} \otimes \mathbf{v}) = -\nabla p + \nabla \cdot \boldsymbol{\tau} + \rho \mathbf{g} \quad (19)$$

From the various rheological models discussed earlier, Kousemaker's is by far the most complete. Although it does not include thermal effects, an Arrhenius-like term can be added to adjust the shear and concentration dependent viscosity. Then, just like in Kousemaker's model, the zero-shear viscosity μ_p^0 , the relaxation time λ , the maximum viscosity μ_{max} , and the polymer relaxation time τ_r are expressed in terms of concentration. An addition to the previous model is that also the fluid index constants n and n_2 are dependent on concentration and that a weighted linear approach is taken to account for the many species present in the solution. These are six; respectively: the linear polymer,

the branched polymer, the linear and the branched depolymerized oligomers, the cross-linking agent, and the cross-linked polymer. More on the chemistry is discussed in the following sections.

$$\mu(\dot{\gamma}, C_p, T) = \exp\left(\frac{E_a}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right) [\mu_s + (\mu_p^0 - \mu_s) [1 + (\lambda\dot{\gamma})^2]^{\frac{n-1}{2}} + \mu_{max} [1 - \exp(-(\lambda_2\tau_r\dot{\gamma})^{n_2-1})]] \quad (20)$$

$$\mu_p^0 = \mu_s \left[1 + \sum_i^6 (Ap_{1,i}C_{pol,i} + Ap_{2,i}C_{pol,i}^2 + Ap_{3,i}C_{pol,i}^3) \right] \quad (21)$$

$$\lambda = \beta_1 \exp\left(\sum_i^6 \beta_i C_{pol,i}\right) \quad (22)$$

$$\mu_{max} = \mu_s \left(AP_0 + \sum_i^6 AP_{ii} \ln C_{pol,i} \right) \quad (23)$$

$$\tau_r = \tau_0 + \sum_i^6 \tau_i C_{pol,i} \quad (24)$$

$$n = \sum_i^6 N_{1,i} C_{pol,i} \quad (25)$$

$$n_2 = \sum_i^6 N_{2,i} C_{pol,i} \quad (26)$$

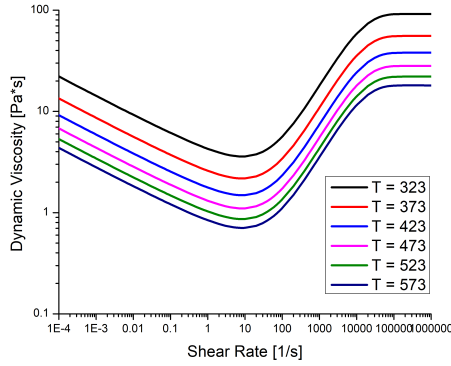
However, [Equation 20](#) can be simplified. Since the solution is diluted, the cross linker, which is fed at very low concentrations, can be omitted. Similarly, the oligomer species do not influence viscosity significantly. From polymer rheological theory is known that viscosity is strongly dependent on molecular weight [\[64\]](#). Given that the broken polymer chains have a much lower molecular weight than the original chains and the cross-linked polymer, their contribution is ignored. [Equation 20](#) thus simplify to [Equation 27](#).

$$\begin{aligned} \mu(\dot{\gamma}, C_p, T) = & \mu_s \exp\left(\frac{E_a}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right) \left[1 + \left(\sum_i^3 (Ap_{1,i}C_{pol,i} + Ap_{2,i}C_{pol,i}^2 + Ap_{3,i}C_{pol,i}^3) \right)^{\frac{\sum_i^3 N_{1,i} C_{pol,i} - 1}{2}} \right. \\ & \cdot \left(1 + \left(\beta \exp\left(\sum_i^3 \beta_i C_{pol,i}\right) \dot{\gamma} \right)^2 \right)^{\frac{\sum_i^3 N_{1,i} C_{pol,i} - 1}{2}} + \left(AP_0 + \sum_i^3 AP_{ii} \ln C_{pol,i} \right) \\ & \cdot \left. \left(1 - \exp\left(-(\lambda_2 \left(\tau_0 + \sum_i^3 \tau_i C_{pol,i} \right) \dot{\gamma})^{\sum_i^3 N_{2,i} C_{pol,i} - 1}\right) \right) \right] \end{aligned} \quad (27)$$

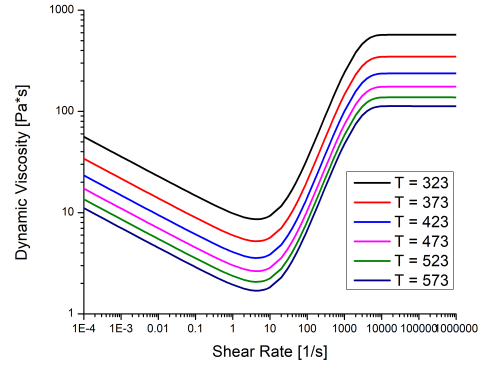
The input parameters and relevant data for the rheological model are presented in [Table 3](#). The resulting curves, for a inlet-/outlet-like solution composition, are instead presented in [Figure 9](#) over a wide shear rate range and largely different temperatures. The outlet curves, richer in the polymerized species, reflects well the sharper thickening response.

Table 3: Input parameters for the rheological model.

Parameter	Value [unit]	Parameter	Value [unit]
ω	60,100,150 [rpm]	ρ_s	1000 [kg/s]
η_s	1 [Pa · s]	E_a	10 [kJ/mol]
T_{ref}	298 [K]	λ_2	0.0005
R	8.314 [J/mol · K]	τ_0	0.008905 [s]
$\tau_{(1,2,3)}$	0.005, 0.02, 0.05 [s]	$Ap_{1,(1,2,3)}$	4, 6, 8 [m ³ /mol]
$Ap_{2,(1,2,3)}$	0.4, 0.6, 0.8 [$\cdot 10^{-2} m^6/mol^2$]	$Ap_{3,(1,2,3)}$	0.4, 0.6, 0.8 [$\cdot 10^{-6} m^9/mol^3$]
AP_0	3	$AP_{(11,22,33)}$	1.5, 6, 100
β	0.02 [s]	$\beta_{(1,2,3)}$	0.06, 0.1, 0.015 [m ³ /mol]
$N_{1,(1,2,3)}$	0.004, 0.002, 0.0001	$N_{2,(1,2,3)}$	0.1, 0.5, 1 [$\cdot 10^{-3} m^3/mol$]



(a) Inlet-like composition: 1000 mol/m³ *pol1*, 1000 mol/m³ *pol2*, 2 mol/m³ *pol_{cl}*.



(b) Outlet-like composition: 10 mol/m³ *pol1*, 10 mol/m³ *pol2*, 2000 mol/m³ *pol_{cl}*.

Figure 9: Contribution of each kinetic term from Zheng et al.'s model.

Boundary and Initial Conditions

In creeping flow, the walls are imposed the no-slip condition,

$$\mathbf{v} = \mathbf{v}_{wall} \quad (28)$$

Equation 28 applies to the screw faces as well as the barrels' internal surface. With respect to the initial conditions in the creeping flow interface, first it is set a mass flow rate of $\phi_m = 0.005$ kg/s for the main hopper. Then, the secondary inlet is given a normal inflow velocity of 5 m/s. Meanwhile the fluid in the chamber is static and with pressure $p = 0$ bar. At the outlet, the pressure is also static and equal to $p_0 = 0$ bar and the backflow is suppressed. This way air is stopped from entering the extruder.

$$[-p\mathbf{I} + \mu(\nabla\mathbf{v} + \nabla\mathbf{v}^T)]\mathbf{n} = -\hat{p}_0\mathbf{n} \quad (29)$$

$$\hat{p}_0 \leq p_0, \quad (30)$$

Heat Transfer in Fluids

The heat transfer in fluids is assessed in its own interface. Here COMSOL solves the energy equation for conduction, convection, radiation, and the heat of reaction.

The basic energy conservation law is

$$\frac{\partial (\rho e)}{\partial t} + \nabla \cdot (\rho \mathbf{v} e) = \nabla \cdot \mathbf{q} - p \nabla \cdot \mathbf{v} + \tau : \nabla \mathbf{v} + \mathbf{Q} \quad (31)$$

of which $\mathbf{q}$ is Fourier's law of heat conduction

$$\mathbf{q} = -\mathbf{k} \nabla T, \quad (32)$$

Between Equation 31 and Equation 32 the variables include: the internal energy e , the density ρ , the thermal conductivity $\mathbf{k}$, the viscous stress tensor τ , the velocity vector $\mathbf{v}$, the temperature T , the pressure p , and the energy production per volume $\mathbf{Q}$.

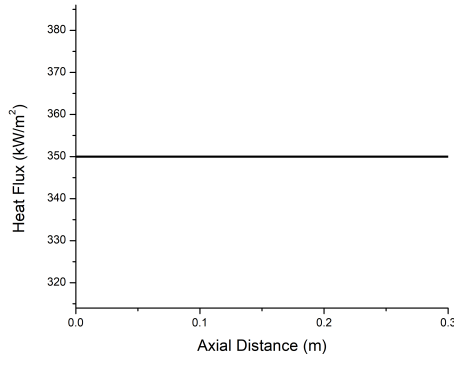
Since the screws play a major role towards the heat transfer phenomena, heat transfer in fluids and solids is considered [20]. Two materials are added to the global environment: water and 17-4PH stainless steel. For the first, the thermal conductivity, heat capacity and ratio of specific heats are available in the material database. 17-4PH stainless steel is instead chosen for its wide applications in the chemical, petrochemical, and food industry and suitable physico-chemical properties [65]. Below, Table 4 summarizes the properties used in the heat transfer module.

Table 4: Physical properties of the materials.

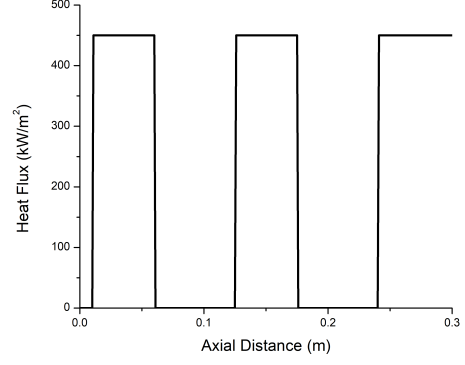
Parameter	Value [unit]	Parameter	Value [unit]
<i>Water</i>		<i>17-4PH Stainless steel</i>	
$c_{p,w}$	4181 [J/kg · K]	$c_{p,s}$	460 [J/kg · K]
ρ_w	1000 [kg/m ³]	ρ_s	7780 [kg/m ³]
k_w	0.6 [W/m · K]	k_s	17.9 [W/m · K]

Boundary and Initial Conditions

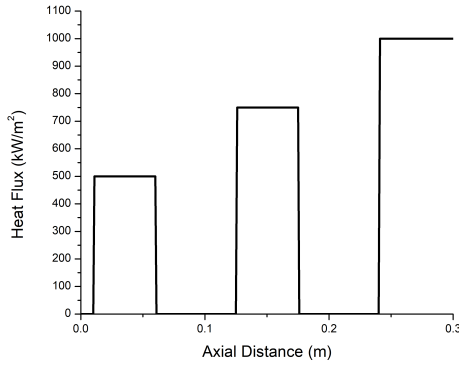
In heat transfer in fluids, the solution is fed in the extruder at the ambient temperature of 298 K. Same is the initial temperature of both the screws and the fluid. From the barrels' surface, heat flux is applied. The heat flux distribution is assumed constant, 350 kW/m², in the first part of the stationary study. In the second part is instead studied the heat phenomena with three configurations of three heating elements situated along the barrel's length. The configurations are presented in Figure 10 along with the uniform heat flux used in the first part of the stationary study and can be classified as: constant (450 kW/m²), increasing (500,750,1000 kW/m²), and decreasing (550,450,300 kW/m²) heating element power.



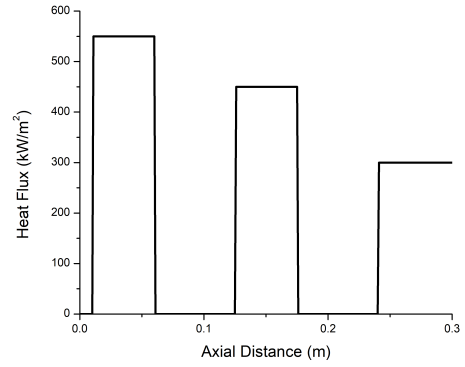
(a) Uniform.



(b) Constant.



(c) Increasing.



(d) Decreasing.

Figure 10

While the study focuses on the heat transport phenomena in the chamber, considering both solid and liquid elements, the hoppers and the nozzles are ignored. Therefore, these surfaces are thermally insulated and do not contribute to the heat phenomena so that the solution does not cool down excessively via convection. Furthermore, the net heat generation due to the energy demand of the depolymerization reaction is accounted for by a enthalpy of reaction term. Finally, at the outlet convection is forced by preventing conduction (see Equation 32) with the boundary condition

$$-\mathbf{n} \cdot \mathbf{q} = 0 \quad (33)$$

Transport of Diluted Species

The mass transfer of the diluted polymer species within the fluid is described by Fick's law. The general equation is,

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (-D_i \nabla c_i) + \mathbf{u} \cdot \nabla c_i = R_i, \quad (34)$$

where c_i , D_i , R_i represent, respectively, the concentration, the diffusion coefficient, and the reaction rate of species i . The diluted solution contains six species. Namely, the linear polymer $pol1$, the branched polymer $pol2$, their respective oligomers $pol1_{bd}$ and $pol2_{bd}$, the cross-linking agent $cross_{link}$, and the newly cross-linked polymer pol_{cl} . Their

diffusion coefficient is dependent on their molecular weight. Lower molecular weights are associated with a faster diffusion in water. On the contrary, longer polymer chains tend to diffuse slower [66]. For this reason, fictitious values of diffusion that respect this relationship are reported in Table 5. It is important to mention that diffusion in water is several orders of magnitude lower than the one used. However, the computational time and COMSOL proved very sensitive to these parameters; therefore, given the purpose of the preliminary nature of this thesis, it is opted for fictitious values. Notice that $pol1_{bd}$ and $pol2_{bd}$ diffuse faster than $pol1$ and $pol2$ since they have lower molecular weight. $cross_{link}$ also has a higher diffusion coefficient because the cross-linking agent is assumed to be a smaller molecule than the original polymers. Lastly, pol_{cl} diffuses slowly since it resembles a complex polymer with branching and high molecular weight.

Table 5: Diffusion coefficients of the diluted species.

Parameter	Value [unit]	Parameter	Value [unit]
D_{pol1}	$5 \cdot 10^{-4} [m^2/s]$	$D_{pol1,bd}$	$1 \cdot 10^{-4} [m^2/s]$
D_{pol2}	$1 \cdot 10^{-4} [m^2/s]$	$D_{pol2,bd}$	$5 \cdot 10^{-4} [m^2/s]$
$D_{cross,link}$	$5 \cdot 10^{-4} [m^2/s]$	$D_{pol,cl}$	$1 \cdot 10^{-4} [m^2/s]$

Boundary and Initial Conditions

Through the main hopper, $pol1$ and $pol2$ are fed at a maximum inlet concentration of 1000 mol/m^3 according to their respective injection patterns (see Figure 11). This is done to investigate the startup phase of the extruder for a batch process. Instead, 500 mol/m^3 of $cross_{link}$ is constantly introduced from the secondary hopper. Next, the initial concentration of all species in the fluid domain is set to zero and a no-flux boundary condition is imposed on the extruder and screws domain as these are solid elements where the solutions does not flow.

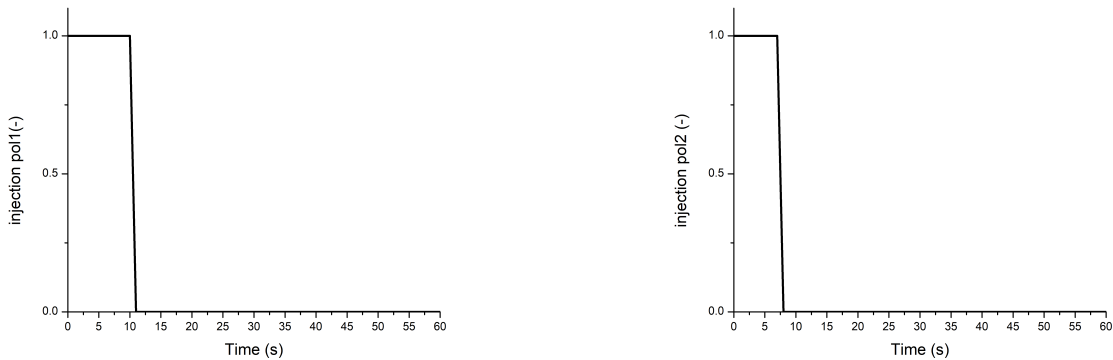


Figure 11: Injections patterns of $pol1$, on the left, and $pol2$, on the right.

Chemistry

This thesis explores the depolymerization of a linear and a branched polymer and the polymerization of a new species via the introduction of a cross-linking agent. Chemical species $pol1$, $pol2$, $pol1_{bd}$, $pol2_{bd}$, $cross_{link}$, and pol_{cl} are therefore considered and they

are treated as bulk species. In the solution, three reactions take place. The two polymer degradations are first-order as discussed in the theoretical background.



with the reaction rates

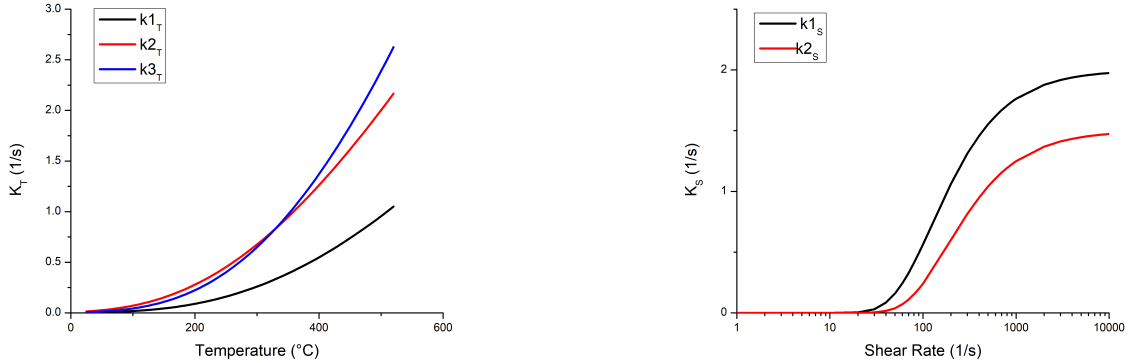
$$R_{pol1} = -k_1 C_{pol1} \quad (37)$$

$$R_{pol2} = -k_2 C_{pol2} \quad (38)$$

The reaction rate constant is defined using the model proposed by Zheng et al that was previously discussed.

$$k_d = k_{T,0} e^{\frac{-E_T}{RT}} + k_{S,0} e^{\frac{-E_S}{\tau\nu}} + (k_{T,0} e^{\frac{-E_T}{RT}} \cdot k_{S,0} e^{\frac{-E_S}{\tau\nu}})^{1/2} \quad (39)$$

The profile obtained resembles the one presented in Figure 12. The kinetic curves are tuned so to represent the different degradation behavior between the linear *pol1* and the branched *pol2*. From a thermal standpoint, the compactness and stackability of a linear polymer allows to better withstand this depolymerization pathway. On the other hand, when it comes to mechanical degradation the branched polymer performs better as it is able to distribute stress on its various branches rather than overloading the main chain.



(a) Thermal-induced kinetic constant k_T .

(b) Shear-induced kinetic constant k_S .

Figure 12: Contribution of each kinetic term from Zheng et al.'s model. On the left is also included the polymerization reaction's kinetic rate.

Instead, the polymerization reaction is assumed stoichiometric and thus third order.



$$R_{pol,cl} = k_3 C_{pol1,bd} C_{pol2,bd} C_{cross,link} \quad (41)$$

This reaction is not shear-induced and so its kinetic constant is strictly thermal-induced and represented by the Arrhenius expression

$$k = A \exp\left(\frac{-E_a}{RT}\right) \quad (42)$$

Table 6 bears the parameter values used in each kinetic model, which were either taken from the literature or fitted to render a plausible curve [33]. For the depolymerization reactions, the enthalpy of reaction is chosen to simulate an endothermic behavior and its value is 350 kJ/mol [67]. This is consistent with the average enthalpy needed to break C-C bonds, which are assumed to constitute the backbone of both *pol1* and *pol2*. Instead, polymerization reactions are typically exothermic and their enthalpy of formation, which is used in this thesis, is commonly around -60 kJ/mol.

Table 6: Input parameters for the kinetic model.

Parameter	Value [unit]	Parameter	Value [unit]
$k1_{T,0}$	40 [s^{-1}]	$k1_{S,0}$	2 [s^{-1}]
$k2_{T,0}$	45 [s^{-1}]	$k2_{S,0}$	1.5 [s^{-1}]
A	100 [$m^6/mol^2 \cdot s^1$]	E_a	24,000 [J/mol]
$E1_T$	24,000 [J/mol]	$E1_S$	0.009 [J/mol]
$E2_T$	20,000 [J/mol]	$E2_S$	0.75 [J/mol]
ν_1	$0.079 \cdot 10^{-3}$ [m^3/mol]	ν_2	$4.55 \cdot 10^{-3}$ [m^3/mol]

Results and Discussion

The results discussed in this section pertain to the following strategy. A first study is conducted for simplified conditions that is composed of two parts, in both the system is at steady-state and so there is no influence of the polymers on the fluid's behavior. This is done to isolate the fluid dynamics, observed in the first part at 60, 100, and 150 RPM, and heat transfer phenomena, observed for three heating elements configurations. The second study builds on the previous one. It isolates the mass transport of the species and the reactions in the start-up phase of the extruder. Lastly, it is coupled all multiphysics checked for differences with the decoupled solutions.

Note that this thesis focuses mostly on the first and second studies. It is left to future research to investigate thoroughly the fully coupled study, other than improving on the level of fidelity of the rheological and kinetic models with real materials.

Mesh Sensitivity Analysis

In order to deem the numerical results accurate a mesh sensitivity analysis of the 3D system has to be conducted. Since testing the mesh does not require for the entire multiphysics, the analysis is run for the creeping flow module only of a Newtonian fluid; doing so will speed up the computation of the results. In Table 7 is presented the results of the mesh sensitivity. In order to evaluate the quality of the mesh, it is calculated the element size average. This is an indicator of the resolution of the finite elements the mesh is composed of. Moreover, to capture the quality of the results, the inlet and outlet pressures are also extrapolated as surface average pressures at the respective boundaries. With both these it is possible to calculate the pressure drop across the extruder. Finally, the computational time is reported so that the choice of the mesh can be optimal. Finer meshes increase exponentially the computational demands and so it is important to find a balance between accuracy and time-consumption. This is also the reason why in Table 7 the normal mesh is the finest resolution investigated. Higher quality meshes would require too much computational time and they are therefore not included in the analysis.

Table 7: Parameters used to build the screw geometrical elements.

Mesh	N. Elements	h	P_{in}	P_{out}	ΔP	Time
	-	$\cdot 10^{-3}$ m	$\cdot 10^6$ Pa	$\cdot 10^6$ Pa	$\cdot 10^6$ Pa	s
Extremely Coarse	155,556	2.9788	1.4299	0.0026136	1.4273	309
Extra Coarse	392,916	2.3255	1.5717	0.0022601	1.5694	906
Coarser	376,435	2.3885	1.6934	0.0028989	1.6905	855
Coarse	914,007	1.7591	1.7715	0.0017911	1.7697	3,545
Normal	910,590	1.6402	1.7534	0.0019193	1.7515	7,049

As it can be seen in Figure 13, a rather clear trend emerges for the computational time. Expect for the results from the Extra coarse and Coarser mesh, where the second actually requires 51 s less to compute, the time increases exponentially with the refining of the mesh. Meanwhile, the reciprocal element size does not always increase. It appears that the element size increases between the Extra Coarse and Coarser mesh. This can be explained by looking at Table 7. Because the number of elements generated in the entire geometry decreases between the Extra Coarse and Coarser mesh, the average element size is inevitably larger to compensate for the fewer elements, and vice versa.

After reviewing the mesh sensitivity results, it is concluded that a Coarser mesh is the best choice for this study. Including all the physics involved and the non-Newtonian fluid behavior would, in fact, lead to time-expensive computations. In Figure 14 the built mesh is shown for two relevant perspectives and over the entire system. Instead, Figure 15 corroborates the choice for the Coarser mesh as the quality of the mesh proves good overall with lower qualities only at the intersection of the inlets with the chamber and at the intersection of the barrels.

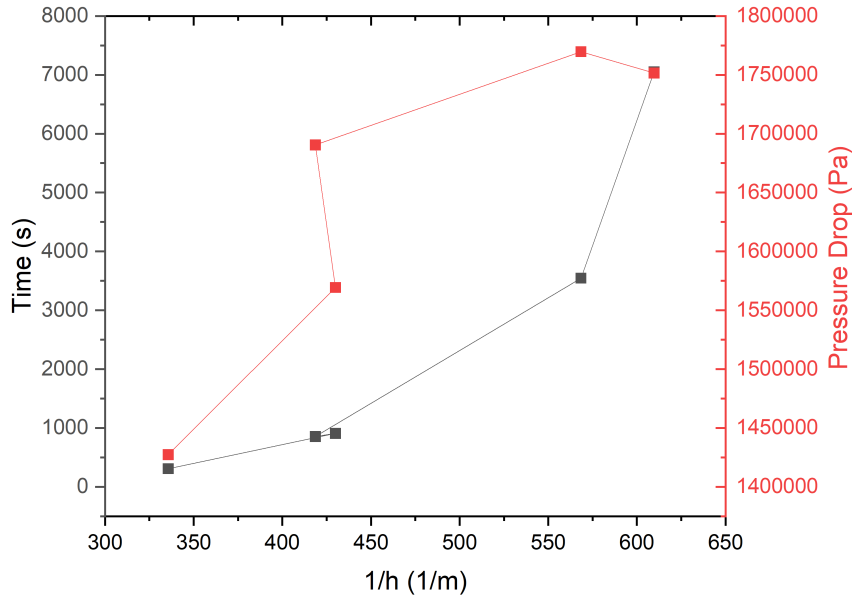
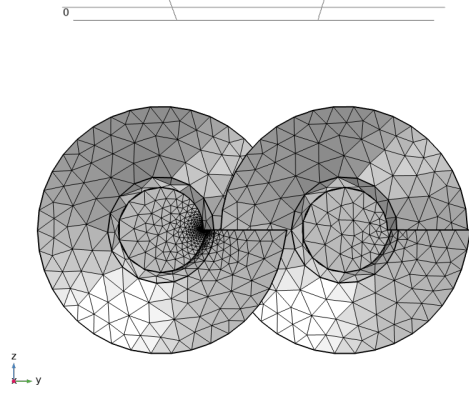
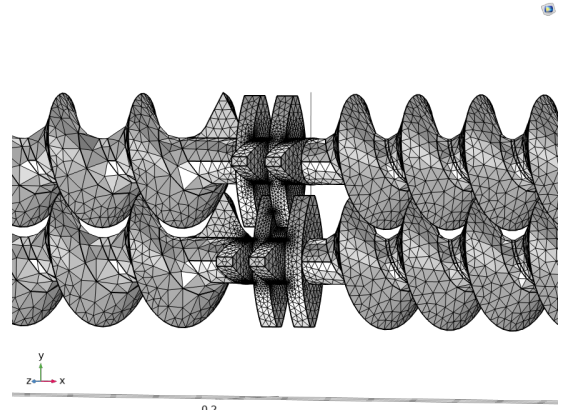


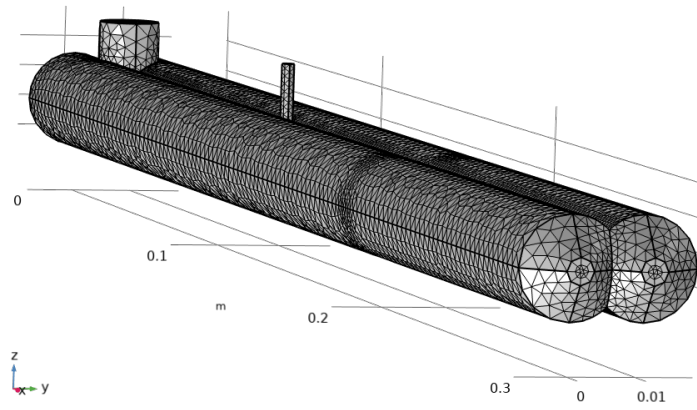
Figure 13: Computational time and pressure drop trends with respect to the reciprocal element size.



(a) View of the screws from the yz plane.

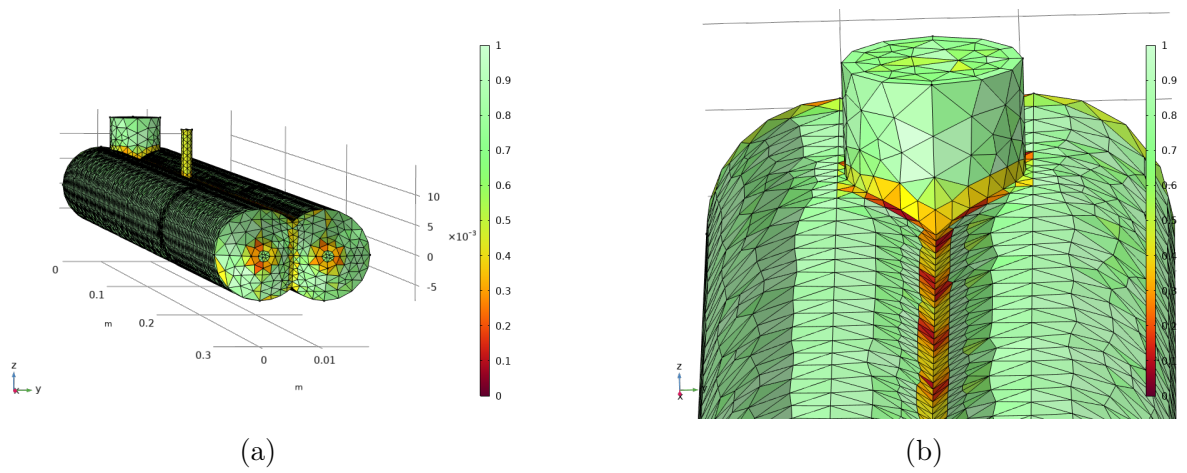


(b) View of the kneading block.



(c) Mesh of the system.

Figure 14: Schematic of the meshing from three different points of view.



(a)

(b)

Figure 15: Mesh quality.

Steady-State, Non-Isothermal Flow

Varying RPMs

These first results are meant to achieve an understanding, for the non-isothermal flow at steady-state, that can be later used when assessing the full process. For this reason, since polymers are not being added, the rheological model loses its dependency on mixture composition.

Figure 16, showing the overall velocity profile across the extruder, presents the velocity magnitude with different qualities. The slices provide a good sense of the development of the velocity profile along the barrel. The streamlines rather give the sense of rotation.

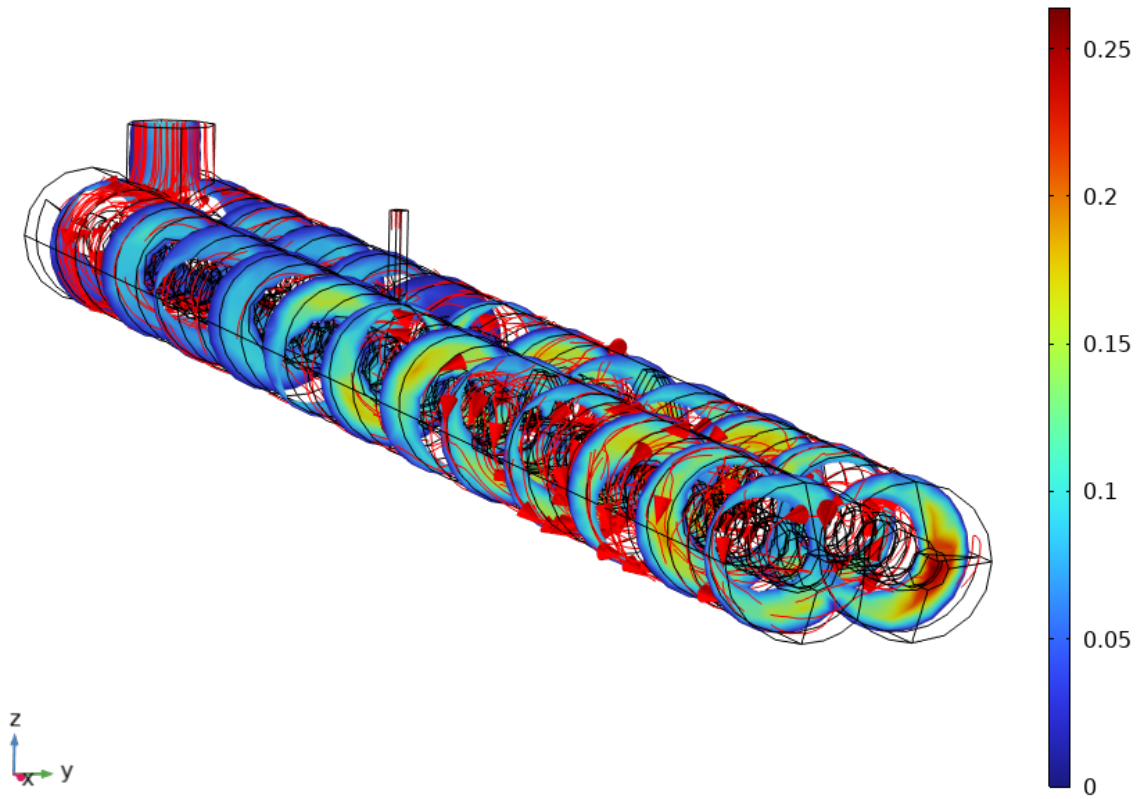


Figure 16: Velocity magnitude over the entire domain at 100 RPM.

To assess these qualities better it is turned to Figure 17, where the results for 60 and 150 RPM are compared about the primary hopper. As it can be seen, in neither view there is relevant qualitative difference between the two speeds. This is in line with the expectation of the fluid behaving the same regardless of the screw speed; the only difference is quantitative and has to do with the higher velocities observed at 150 RPM. This is coherent with the abundant examples in the literature. Setting comparisons to the side, what is worth mentioning is that the corotation of the screws is well captured in the bottom plots of Figure 17, thus corroborating the frozen rotor approach taken with Equation 13. More importantly, the entering fluid seems to prevent the one in the barrel section preceding the hopper from flowing, Figure 17c and Figure 17d expose this. The fact that

a portion of the fluid is blocked represents a problem. Not only is the solution not processed thoroughly but also the fluid there causes a buildup of heat, since the back of the extruder and the barrel feed it constant uniform heat. Later in this section is assessed the temperature buildup. An important consideration is therefore formulated. The position of the hopper, its shape, and the entrance speed of the fluid are parameters to be taken into consideration when designing the extrusion process. However, this work does not focus on the injection stage per se and so in-depth analysis is postponed to future studies.

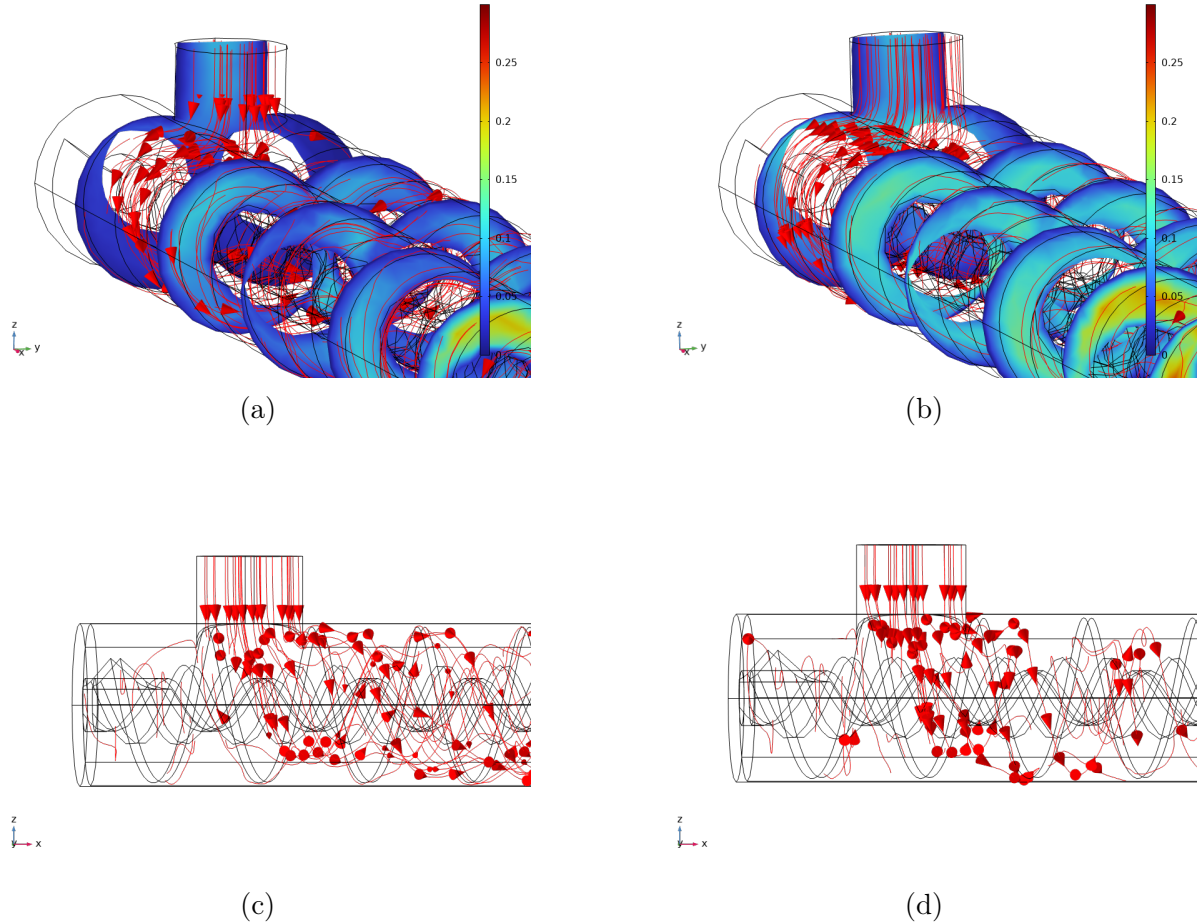


Figure 17: Velocity magnitude comparison at 60 (on the left) and 150 (on the right) RPM about the primary inlet.

The assessment of velocity is completed in [Figure 18](#), where it is plotted, respectively, the velocity as a function of the dimensionless distance between the screw tip and the barrel and the one between the screw root and the barrel. For the sake of avoiding to show redundant results, only the plots at 100 RPM are reported. The profile is consistent with a Couette flow and with previous results on extrusion [\[20\]](#).

The pressure profile corresponds to previous results. Pressure, in [Figure 19](#), drops across the extruder as a result of temperature rising and velocity increasing. The difference between 60 and 150 RPM proves this. As higher velocities, previously discussed, are induced by the screw rotation speed, the pressure inferred to the fluid also grows. The pressure drop is also consistent with the well-known circumstances for fluid to flow, stating that flow occurs from a high to a low pressure region.

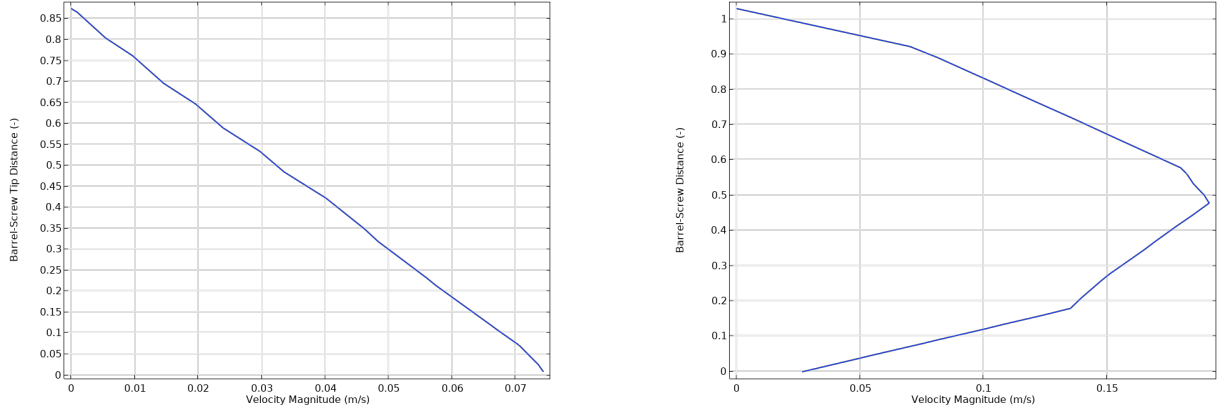


Figure 18: Velocity in the interstitial area between the barrel and the (a) screw tip (b) screw root.

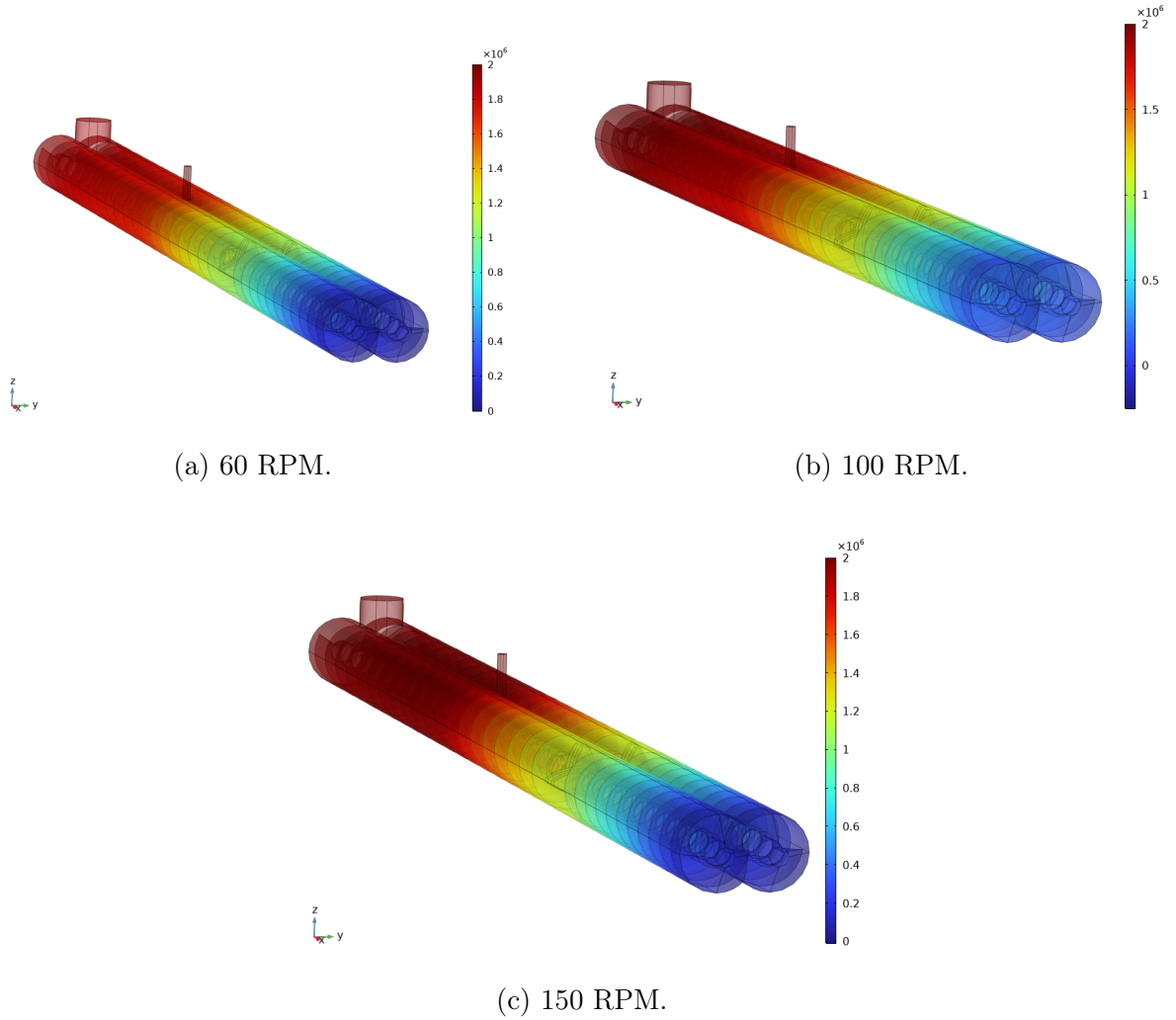


Figure 19: Pressure profile for the stationary non-Newtonian study.

From the non-isothermal flow at steady-state simulations are also analyzed the temperature and the viscosity. Later, in the next section, it will be expanded on these. The temperature profiles also agree with expectations. It is important to remember that in

the stationary study the contribution of the chemical reactions is excluded. Thus, the heat phenomena are based on viscous dissipation and the heat flux applied on the barrels, see [Figure 10](#) for reference. The results show a negative correlation between the rotation speed and temperature. This suggests that while the viscous dissipation, directly correlated to the RPMs, is higher at increased speeds, the residence time is more dominant. With less exposure to the heating of the barrel, the fluid leaves the extruder before heat can be given to it [\[7\]](#) [\[20\]](#). Thus, a consideration is drawn that when designing an extrusion process it is crucial to both account for the heat flux necessary to achieve the processing condition of the melt and the optimal residence time to deliver the calculated heat flux in full.

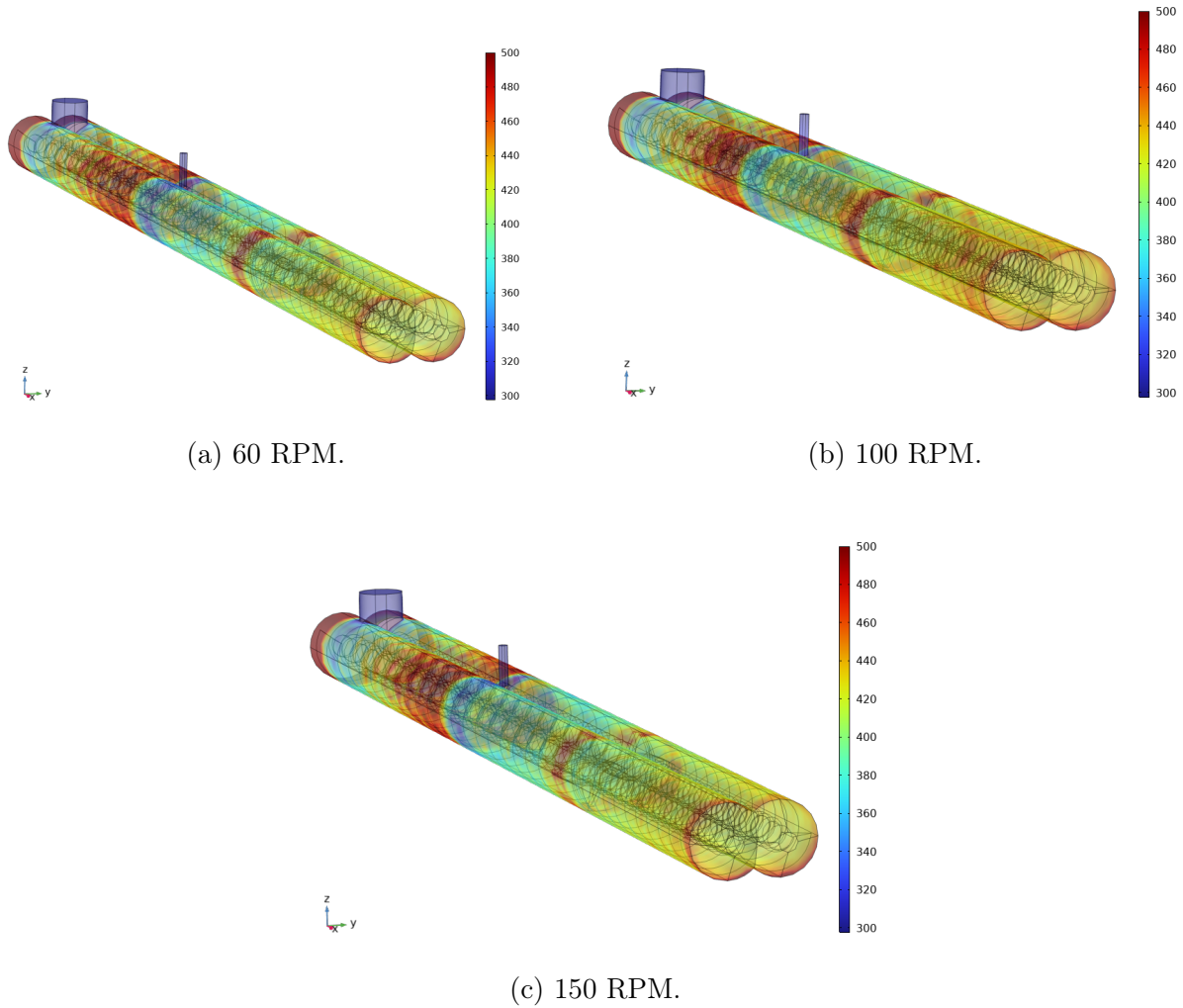


Figure 20: Temperature profile for the stationary non-Newtonian study.

Moreover, [Figure 21](#) shows the oscillation in temperature at the top and bottom of the barrel. These are not entirely in line to the results obtained in previous studies [\[20\]](#). Reason for this has to be attributed to the relatively large distance between the screw tip and the barrel and to the short axial flight width. The first is 3.02 mm, from [Table 1](#) and [Table 2](#), which is much larger than the average 0.1 – 0.3 mm used in industry [\[68\]](#) [\[69\]](#). The second is knife-edged and so there is not large enough portion of the screw in contact with the barrel. While it is expected to see a clear oscillation that would reflect the alternation of solid and fluid, the flight clearance and axial flight width are such that there

is a rather continuous liquid phase instead of an alternation of solid and liquid. Figure 22 shows how the fluid is not only conveyed by the screw but also is able to escape through the clearances with the barrel. For the future is therefore strongly suggested that the geometry is adjusted to ensure screw conveying is the only transport mode. Furthermore, in Figure 21 can be contextualized the temperature profile with the physical domain. As previously mentioned, there is flow blockage at the main hopper that inevitably leads to a temperature buildup, here displayed. At $x = 0.015$ m the temperature drops rapidly, this is explained by the entering of the cold feed. Since heating is applied uniformly in this case, the temperature rises as expected until the secondary inlet. Here, again, cold feed is injected, which results in a second temperature drop. At $x = 0.2$ m temperature peaks. To understand this behavior, it is looked again to Figure 22 and it is revealed that when the fluid reaches the mixing elements it is slowed down almost entirely. This is in agreement with the theory on kneading blocks. The fluid's residence time is increased and as a result its absorption of heat is prolonged.

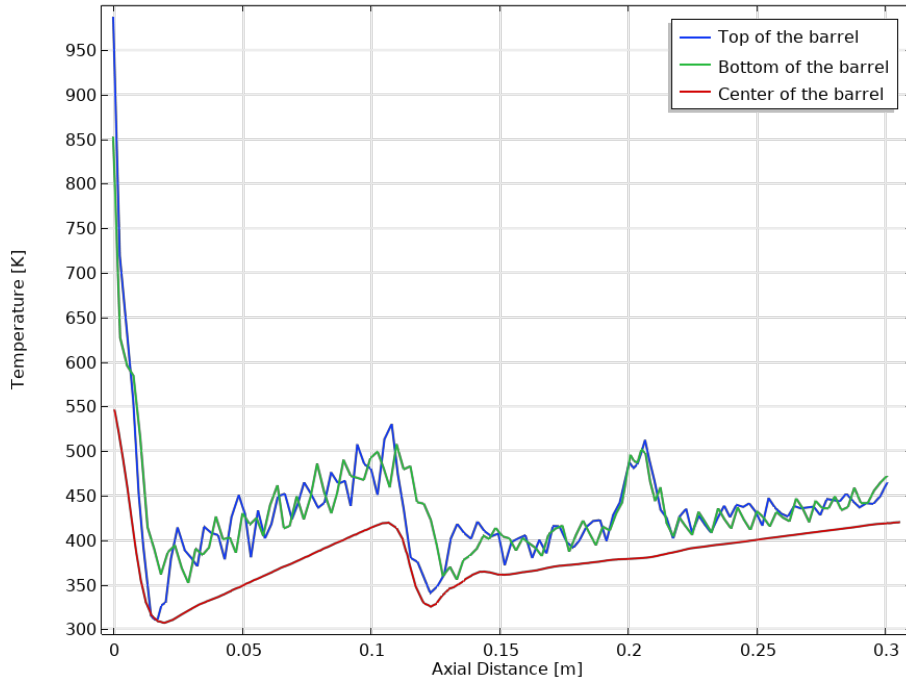


Figure 21: Temperature evaluated in different areas of the extruder with respect to the axial dimension.

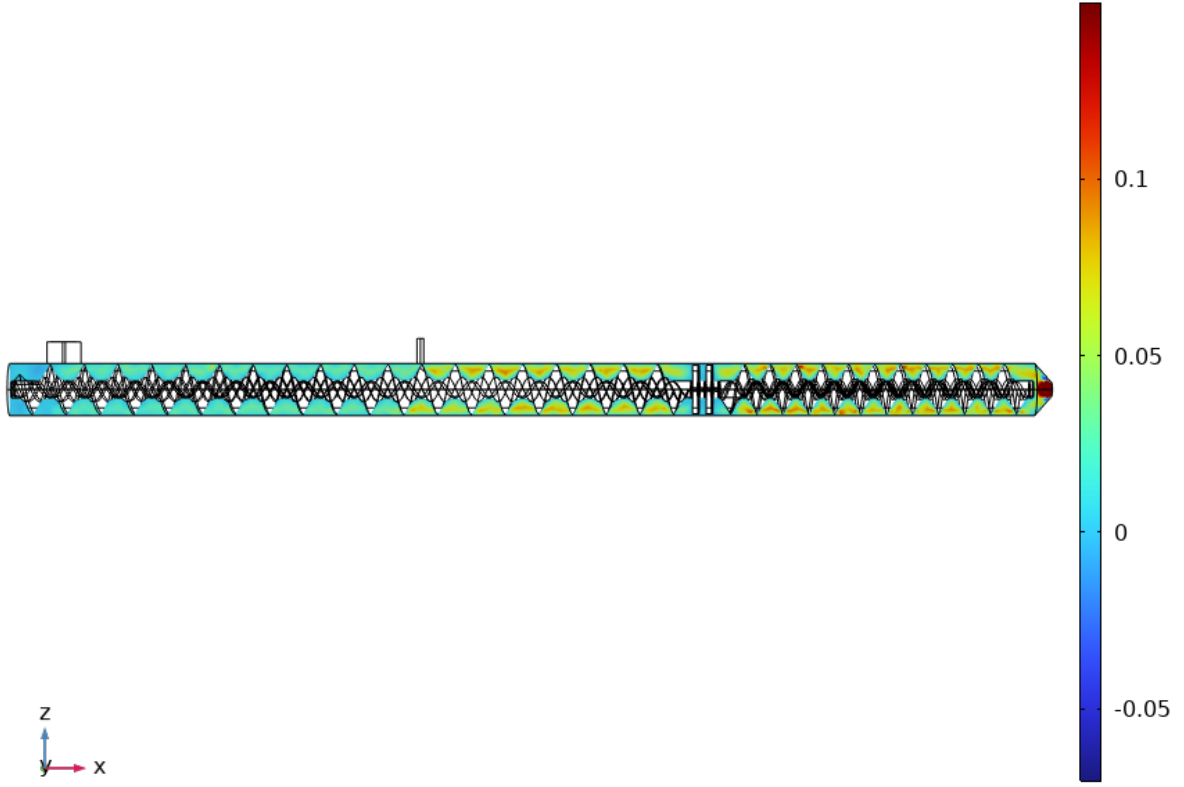


Figure 22: Axial velocity at the outlet.

Lastly, viscosity is checked. From [Figure 23](#) it is observed a distinction between shear-dominant and temperature-dominant regions. Generally speaking, the viscosity is highest in the fluid's interface with the screw blades. The large shear gradients induce the elastic term of [Equation 20](#) to take over the model. That is,

$$\mu_{el} \gg \mu_{Carreau} \quad (43)$$

Regardless, in temperature-dominated regions, shear dependency not relevant. An example of a shear-dominated region is about the inlets. Following injection, the cold fluid shear-thickens around the blades. Meanwhile, it can be noticed how the heating up reduces the shear-thickening to the point where the fluid approaches the solvent's viscosity of $1 \text{ Pa} \cdot \text{s}$. The pattern repeats after the second inlet. About the kneading block the fluid suddenly shear-thins. This is normal given that kneading blocks, as earlier discussed, are meant to increase the residence time in the extruder. An extended exposure to heating causes the peak in temperature and so to form a temperature-dominant shear-thinning region where,

$$\mu_T \gg (\mu_{el} + \mu_{Carreau}) \quad (44)$$

Such behavior respects the concept of polymer melting, where a polymer fluid will suddenly shear-thin past its melting temperature, T_m [\[64\]](#).

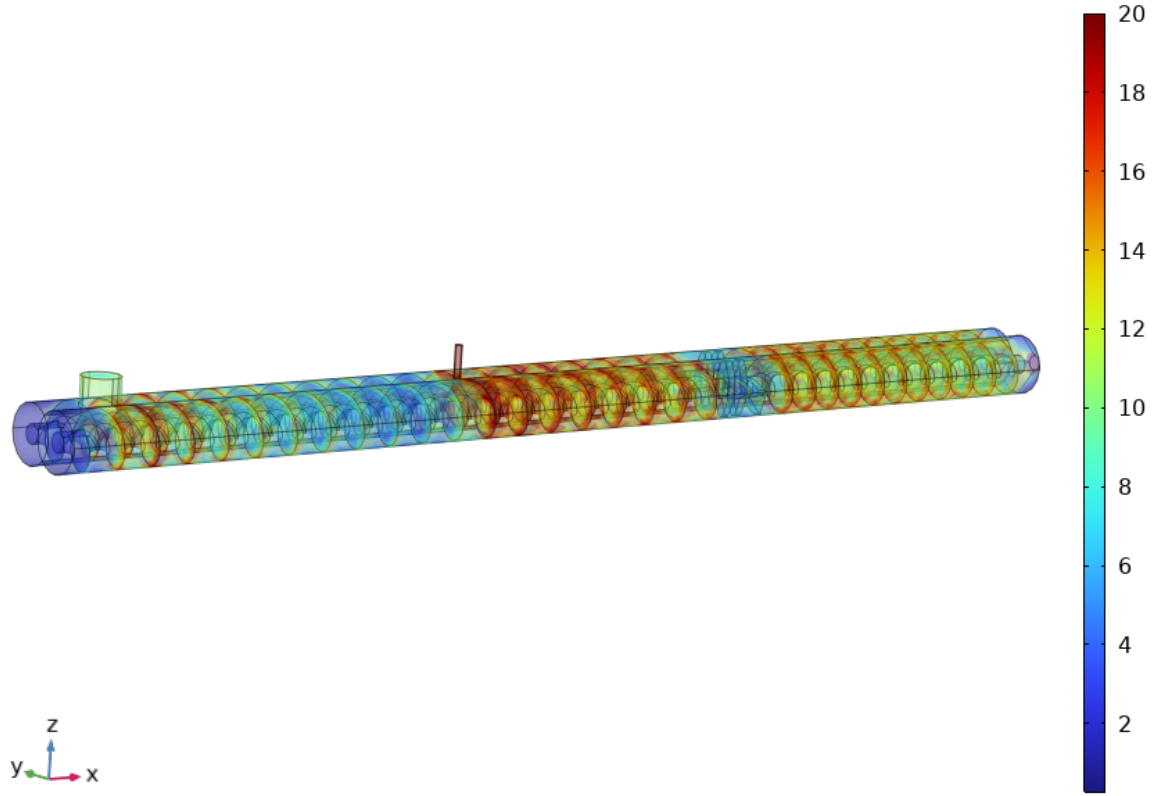


Figure 23: Viscosity profiles throughout the extruder for the stationary study.

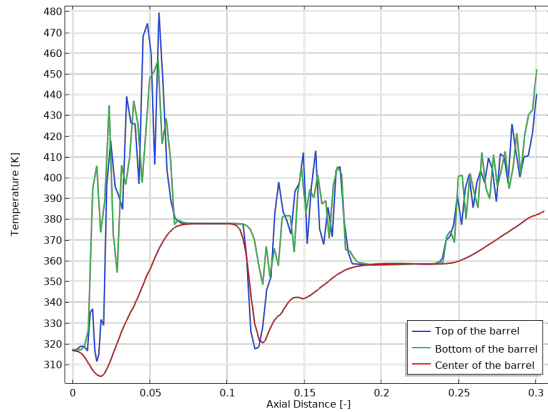
Varying Heating Configurations

In this section it is investigated the thermal and rheological behaviors for different heating element configurations, see [Figure 10](#). For better contextualization, the model simulates the heaters to be placed, respectively, about the first inlet, the second inlet, and the outlet. The reference angular speed in these simulations is 100 RPM.

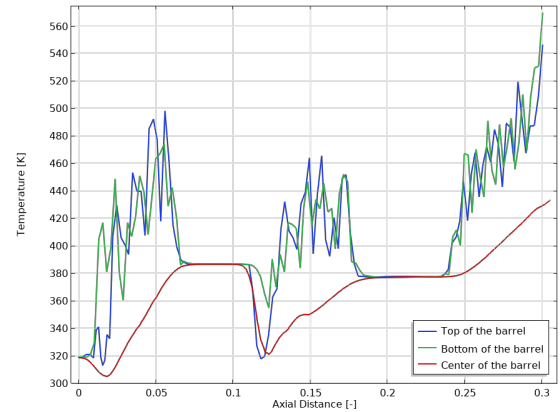
During an extrusion process, heating must be properly managed to ensure the fluid is processed at the desired temperatures and locations. At the same time, it is generally undesirable to expose the material to temperature swings. Variations of this kind affect the fluid's viscosity and can lead to compromised physical properties of the final product. On the other hand, more complex processes where endothermic and exothermic reactions are involved may require specific thermal patterns. Engineers must therefore make careful use of heaters to ensure proper process conditions are achieved throughout the extruder while preventing material degradation and safety hazards.

Like for [Figure 21](#), the thermal profile is studied by evaluating the temperature at three coordinates with respect to the axial distance. In [Figure 24](#), the position of each heater is clearly proved by the top and bottom barrel temperatures and by the similar underlying trend common to all heating configurations. It is also noticed how in [Figure 24](#) no buildup appears. This is consistent with the fact that, while the fluid is still blocked by the feed, heating now occurs further down the barrel, where the fluid will not indefinitely

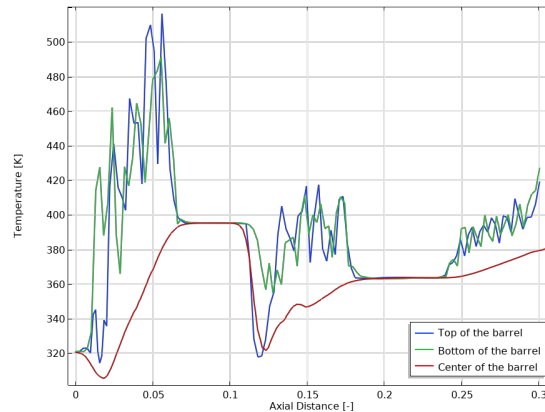
accumulate energy. Thus, proper functioning of the heat transfer module can be asserted. While the top and bottom barrel temperatures are rather boundary values, the center of the barrel is the profile that concerns the fluid the most. From polymer science is determined that the melting temperature of the polymer solution is in the range of 120-250 °C, or 393-523 K [64]. If that is the the case, then none of the current configurations is powerful enough to achieve operating conditions. Trial and error can be implemented to resolve this. Among the three configurations, the decreasing heating trend seems the most appropriate for the system of reactions that will later be studied. Since the endothermic reactions take place in the first section of the extruder, most of the heat needs to be applied here. Only after the cross-linking agent is injected can the exothermic polymerization reaction occur. In the second half of the extruder heat must therefore be managed carefully to avoid overheating of the system. This is why an increasing and a constant heating trend are not fit. One design option largely adopted in industry is that of heat coupling. Heat is harvested from the exothermic region and used back in the endothermic one [70] [71]. With it, the energy demand of the process can, at least partly, be reduced. To be remembered is that the current study is stationary. Later, when time dependency is introduced, heat recirculation by the metal screws will play a major role in the heat phenomena as demonstrated before [20]. Hence, accurate estimation of the heat effects is crucial.



(a) Constant heating trend.



(b) Increasing heating trend.



(c) Decreasing heating trend.

Figure 24: Temperature profiles of three heater configurations for the stationary non-isothermal flow.

Despite the heating configurations change, it is not expected to see a clear distinction in the other fluid properties. In fact, the intensity of the heaters is such that similar temperatures are achieved at respective axial distances. To better frame the significance of Figure 24 it is thus looked more closely to the viscosity and shear rate at the main elements of the physical domain: the primary inlet, the secondary inlet, the kneading block, and the outlet. Figure 25 provides an overview of shear rate throughout the extruder. Shear rate is calculated independent of temperature and so the plots presented are valid for all three heating trends. Contextualizing the temperature profiles with the shear rate helps understand Figure 26, Figure 27, Figure 28, and Figure 29.

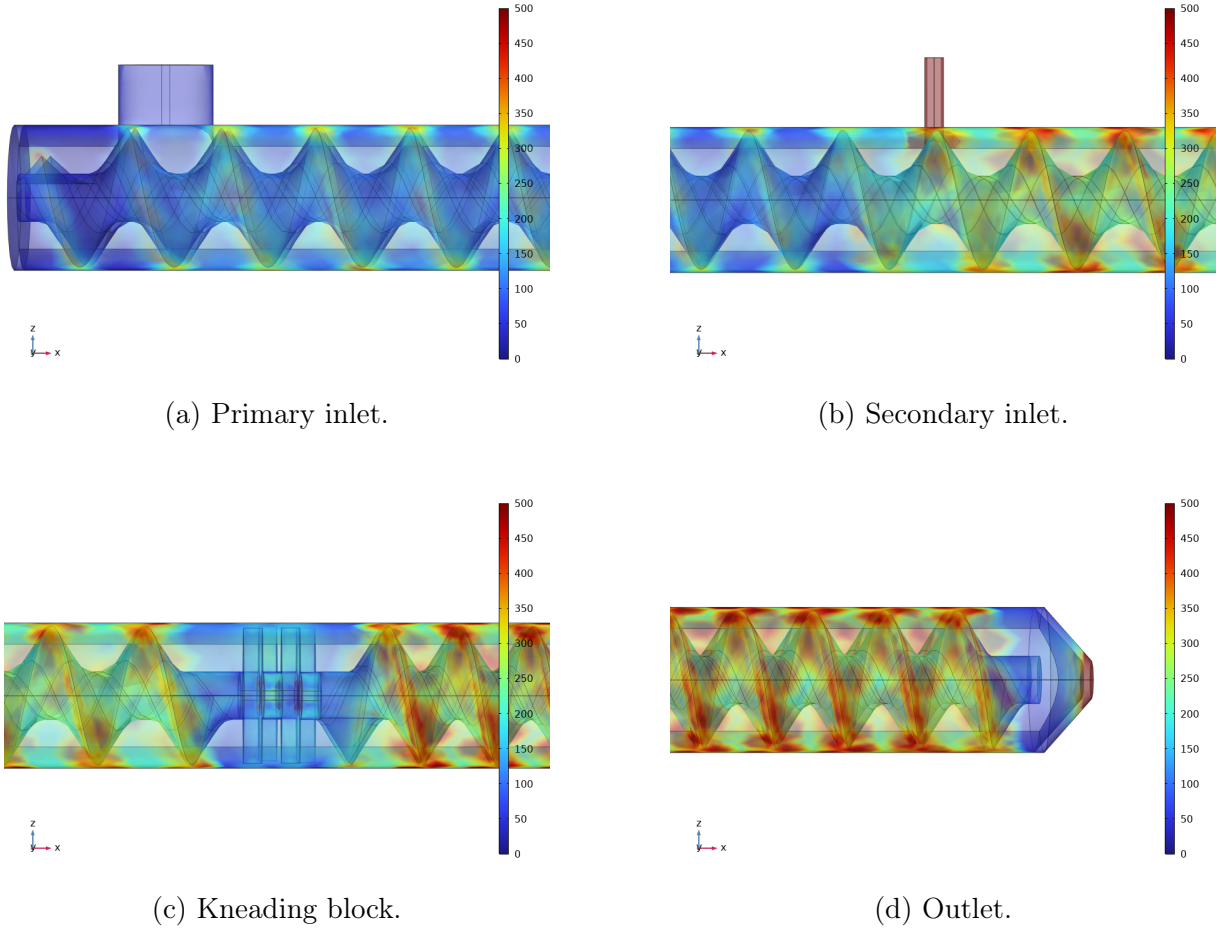


Figure 25: Shear rate throughout the extruder at 100 RPM.

As previously anticipated, the results are overall equivalent. No significant difference can be appreciated in Figure 26, Figure 27, and Figure 28. Figure 29 is an exception but only because in the increasing trend the last heater, 1000 kW/m^2 , generates a high enough temperature to shear-thin the solution. While not much is to be said in terms of the heating configuration's influence, something important can be noticed by reassessing an earlier argument. Once again it can be explained the viscosity profile from the perspective of shear- and temperature- dominated regions. Clearly, the current heating configurations are insufficient to induce a thermally-driven viscosity profile. About the primary inlet, the fluid is initially too cold to thin. However, also the shear rate is low. Thus, viscosity is closer to the zero-shear viscosity. Only further down the barrel does the fluid heat up sufficiently to start showing thinning tendencies. Despite this, the secondary inlet, in

Figure 27 feeds new cold fluid into the barrel. The fluid again thickens until the kneading block. Around the kneading block, shear rate drops. When taken into consideration both with Figure 24 and Figure 28 it is inferred that at constant temperature and concentrations, viscosity depends only on shear rate. Thus, the drop in shear rate reflects in a shear-thinning response on the viscosity. Such cannot really be thought of as a thermally-dominated region as temperature is constant. Finally, about the outlet, Figure 29, a similar condition as for the kneading block takes place. Shear rate is minimal because the fluid is freed from the screw meanwhile temperature, for all configurations, rises. A key takeaway is that regardless of which configuration is chosen and the intensity of the heaters, a major role is played by the interplay of mechanical and thermal components. Based on these results, it is concluded that for the fluid modeled in this study, viscosity does not show thermal-dominance unless shear rates are below 150 s^{-1} and temperatures exceed 360 K .

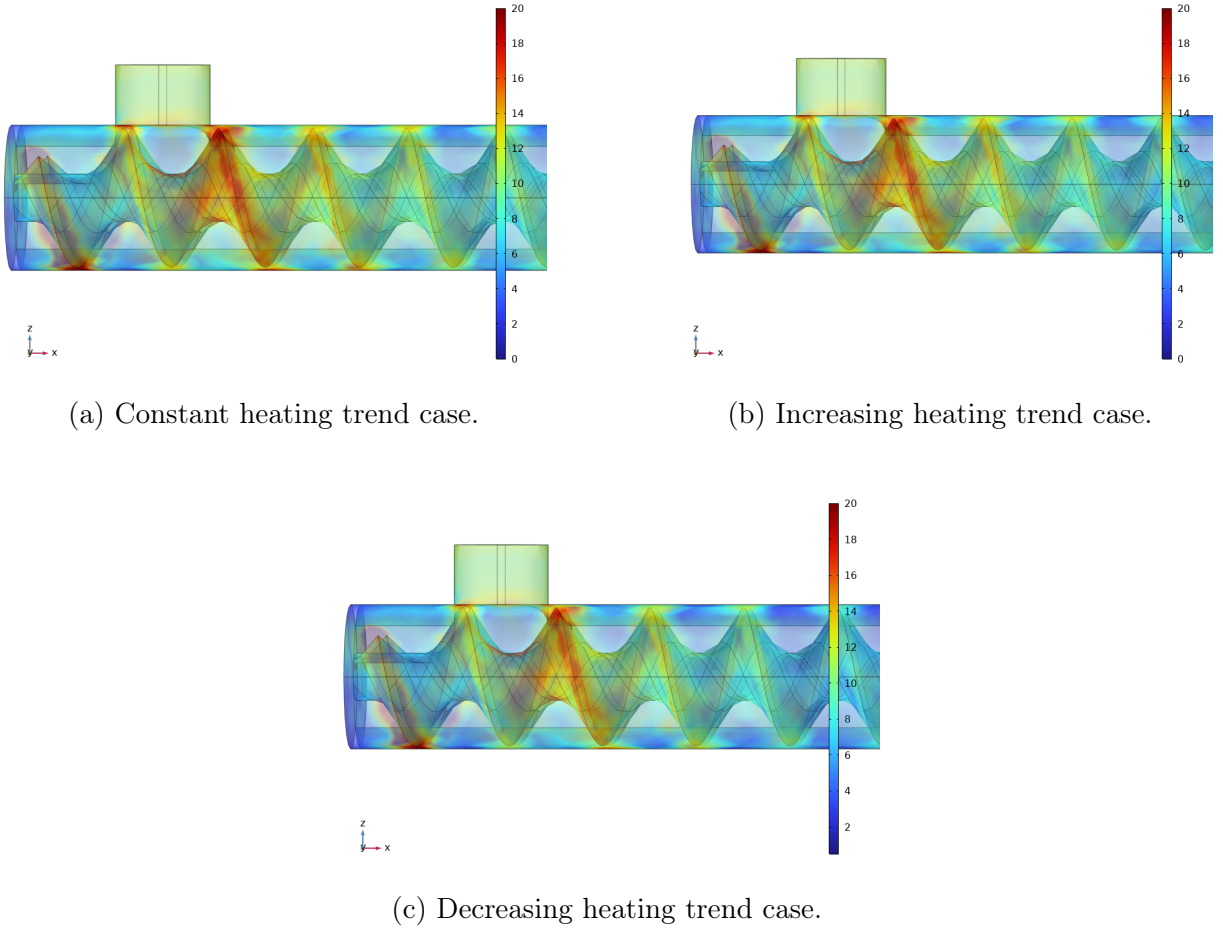
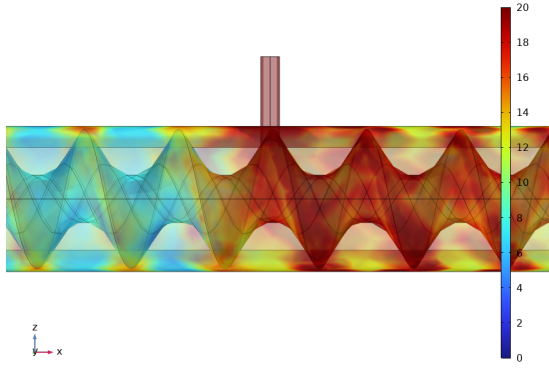
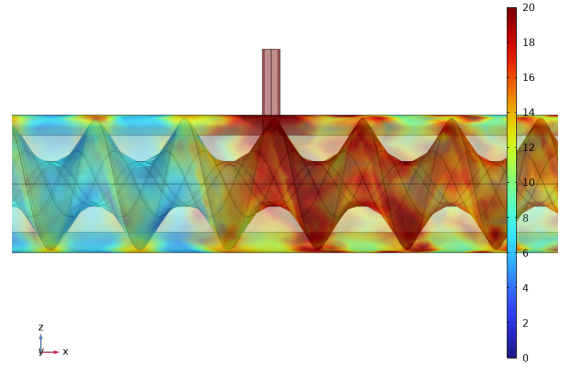


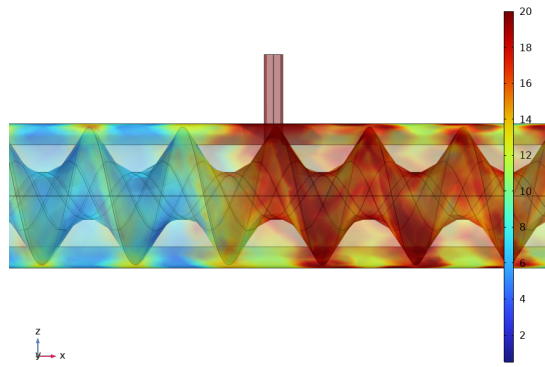
Figure 26: Dynamic viscosity about the primary inlet.



(a) Constant heating trend case.

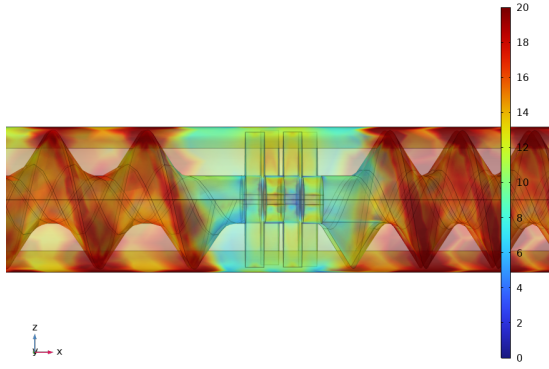


(b) Increasing heating trend case.

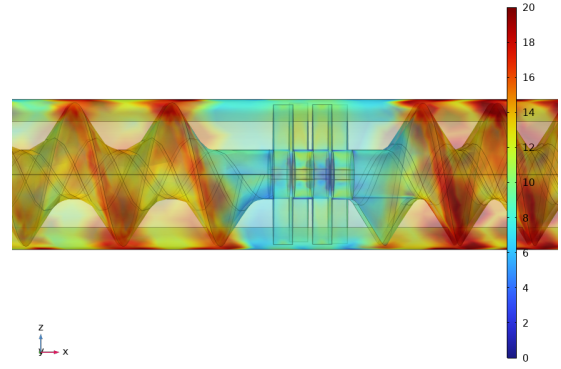


(c) Decreasing heating trend case.

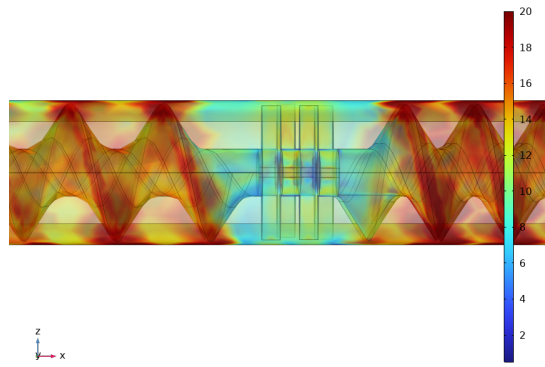
Figure 27: Dynamic viscosity about the secondary inlet.



(a) Constant heating trend case.



(b) Increasing heating trend case.



(c) Decreasing heating trend case.

Figure 28: Dynamic viscosity about the kneading block.

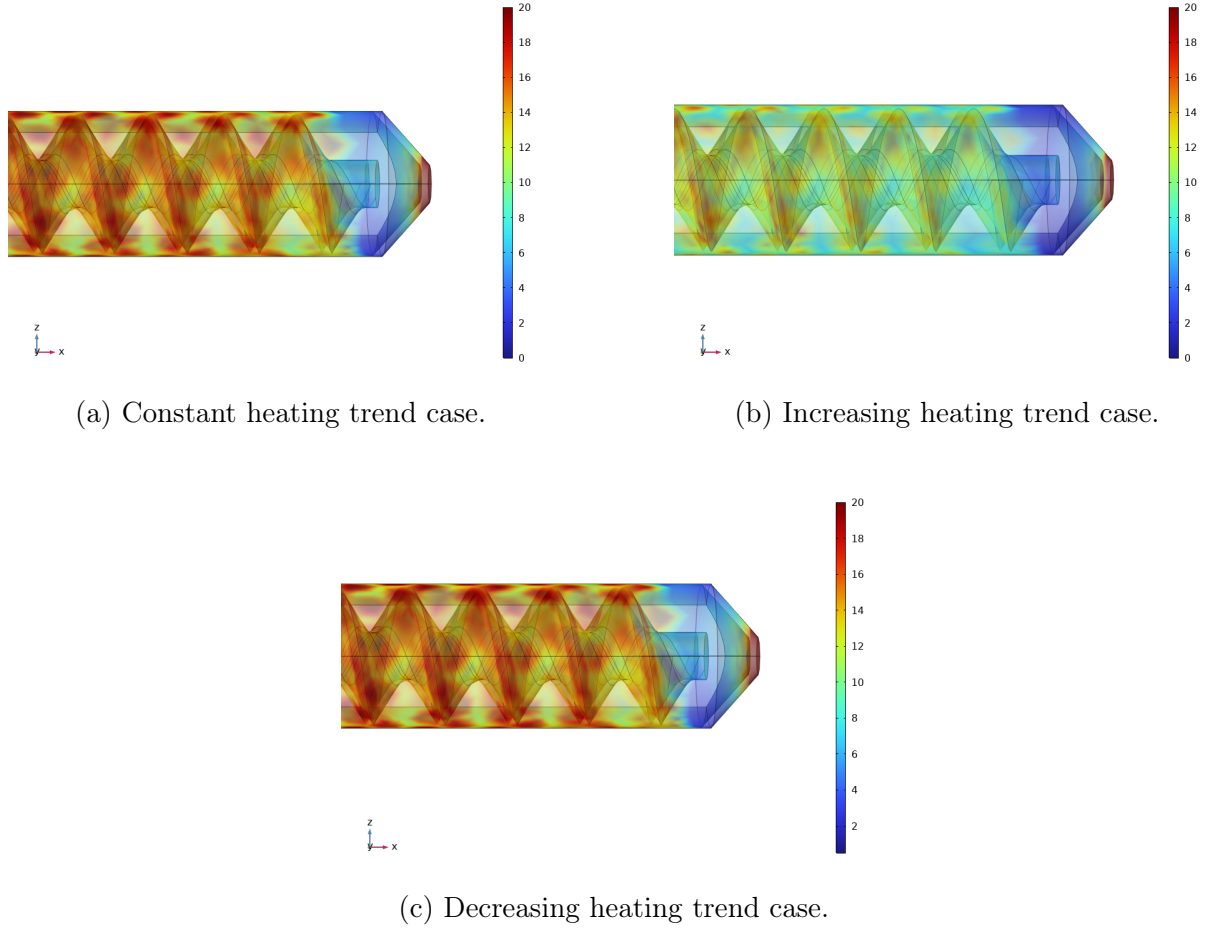


Figure 29: Dynamic viscosity about the outlet.

Time-dependent, Reacting Flow

The second set of results regards the mass transport of diluted species and the chemical reactions that take place in the fluid domain. The variables involved within the reacting flow module are not involved neither in the heat transfer nor the fluid properties. Once again, the analysis is split. In the first part the mass transport is compared for 60,100,150 RPM, in the second part it is rather looked at the effect the selected heating configurations have on the process, refer to [Figure 10](#). In both investigations, the focus of the study is to look into the residence time of the chemicals and the system of reactions. The outcome of this section is to provide a fundamental understanding of the mass transport and reaction module that can be built upon in the fully coupled study. The reactants being injected in the dilute solution follow the patterns previously presented in [Figure 11](#).

Varying RPMs

In [Figure 30](#), the outlet concentrations of the chemicals is used to evaluate the residence time at 100 RPM. From the graph can be made several observations. First, the residence time of *pol1* is virtually infinite or, better put, *pol1* is consumed entirely; thus it goes undetected at the outlet. Instead, *pol2* has a residence time of approximately 7.5 seconds. *cross_{link}* takes about 2 seconds to exit the extruder from the secondary inlet. The products

have a similar residence time, 5 seconds for $pol1_{bd}$ and pol_{cl} and 9 seconds for $pol2_{bd}$.

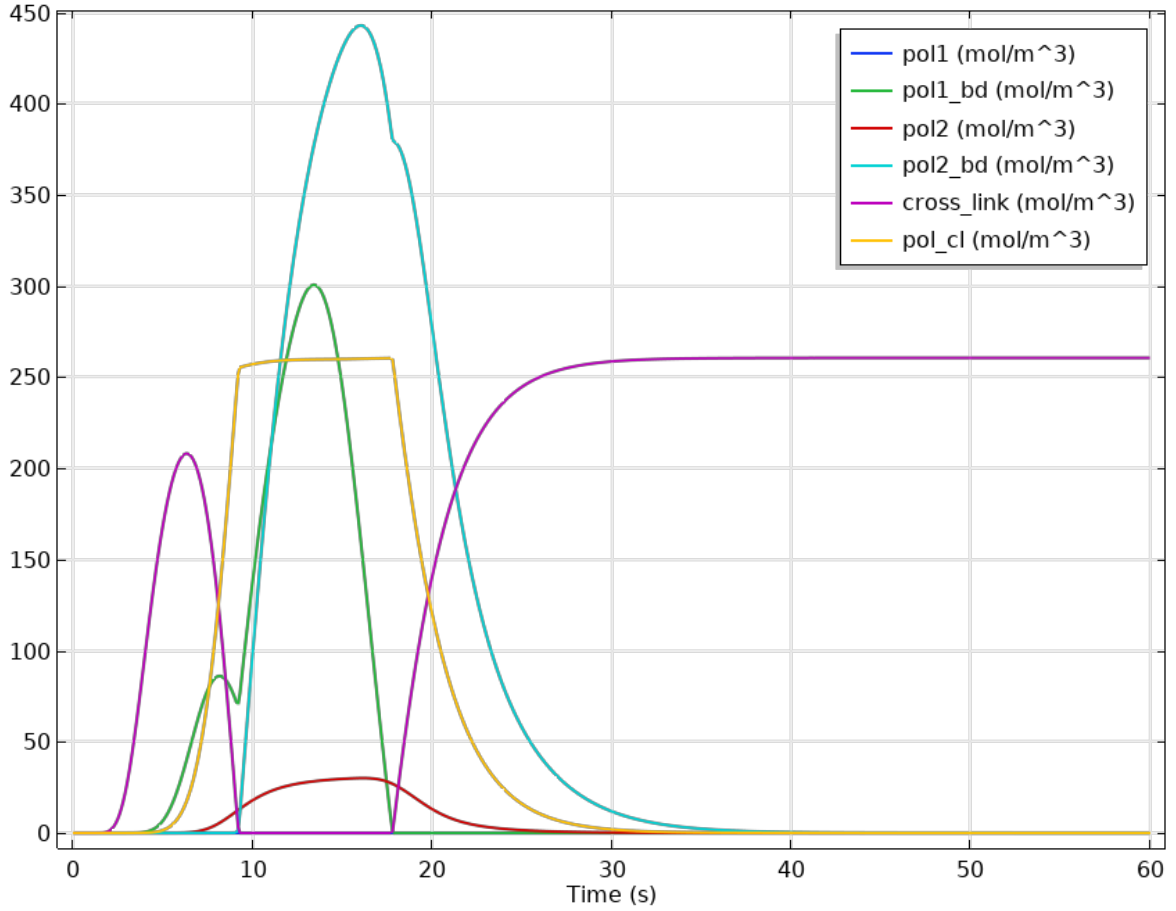


Figure 30: Average concentration at the outlet surfaces over the simulation time.

To quantify the extent to which the transport phenomena is susceptible to the rotation speed, complementary outlet concentration graphs at 60 and 150 RPM are presented in Figure 31. From comparing the two graphs, it is concluded that the screw speed does not play a role towards the residence time of the chemicals. What appears is rather an influence on the production/consumption of the polymers. Namely, $pol2$ is visibly more consumed at 150 RPM. Moreover, it is noticed an earlier onset in the maximum production of pol_{cl} . At 150 RPM pol_{cl} 's maximum production is sustained for approximately 10 seconds compared to the 8 seconds at 60 RPM. However, in the latter case the peak production itself is able to reach up to 260 mol/m³ instead of the 250 mol/m³ at the higher speed. This can be related back to $cross_{link}$. The cross-linking agent is transported faster out of the extruder at higher rotations. As it can be seen from the graph, because $cross_{link}$ acts as a limiting reactant, at lower RPMs its residence time is higher and so it is more available to participate in the polymerization reaction.

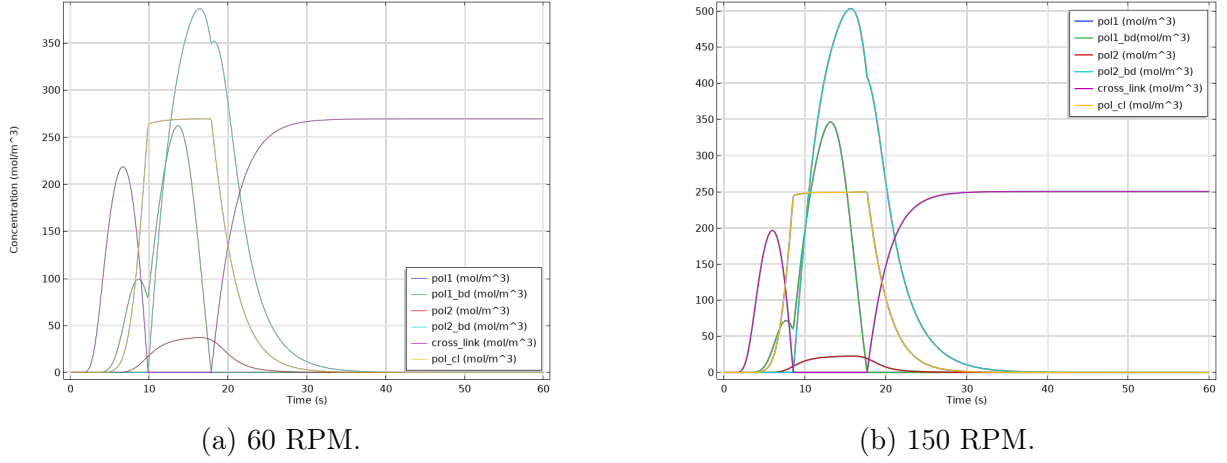


Figure 31: Comparison of surface average outlet concentrations at 60 and 150 RPM.

A way to complement the previous figures is that of visually appreciating the 3D concentration fields of the chemicals. Since in Figure 30 it was observed that the extruder is flushed of all species by $t = 40$ seconds, it is chosen to look into three time steps: 5, 20, and 40 seconds.

pol1 and *pol2* are limited by the rectangular injection functions to the first 10 seconds of simulation. This can be seen in Figure 32 and Figure 33, respectively. Both reactants appear more diluted at 150 RPM than 60 RPM. The effect is caused by the joint effect played by the increased shear stresses, which enhance the mechanical degradation, and the increased velocity field, which pushes the diffusion of the reactants and thus reduces the local concentration for each volume cell of the mesh. Since the reactants have identical diffusion coefficients, the instantaneous consumption of *pol1* has to be related to the difference in the extent of reactions.

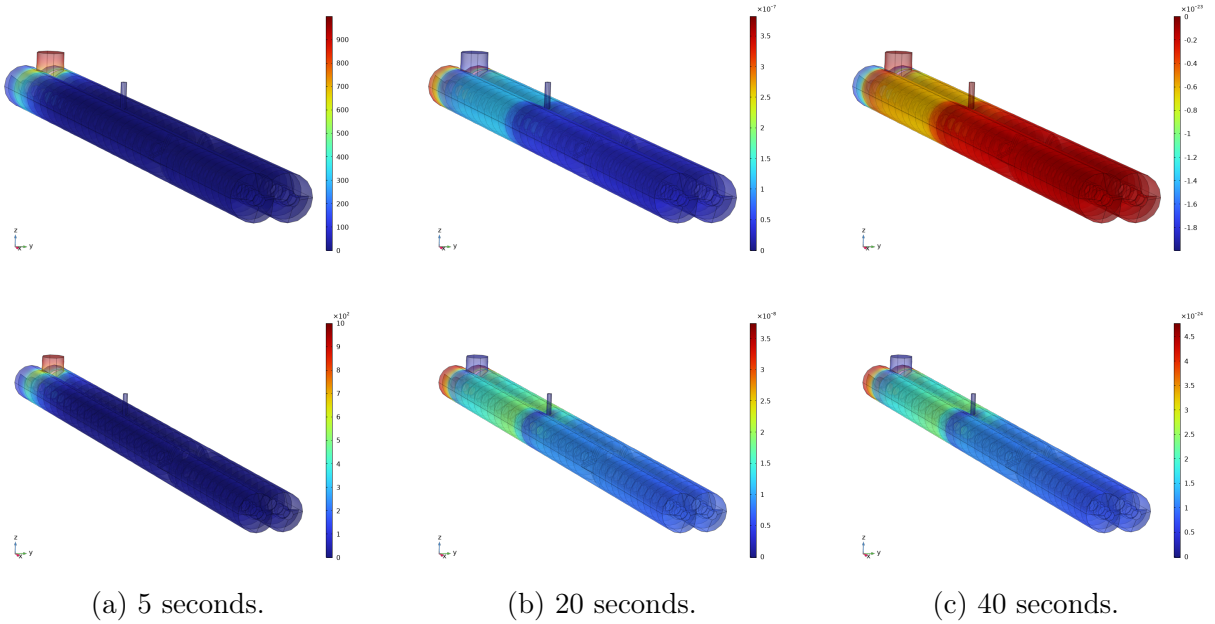


Figure 32: Concentration profile of *pol1* at 60 RPM (top) and 150 RPM (bottom).

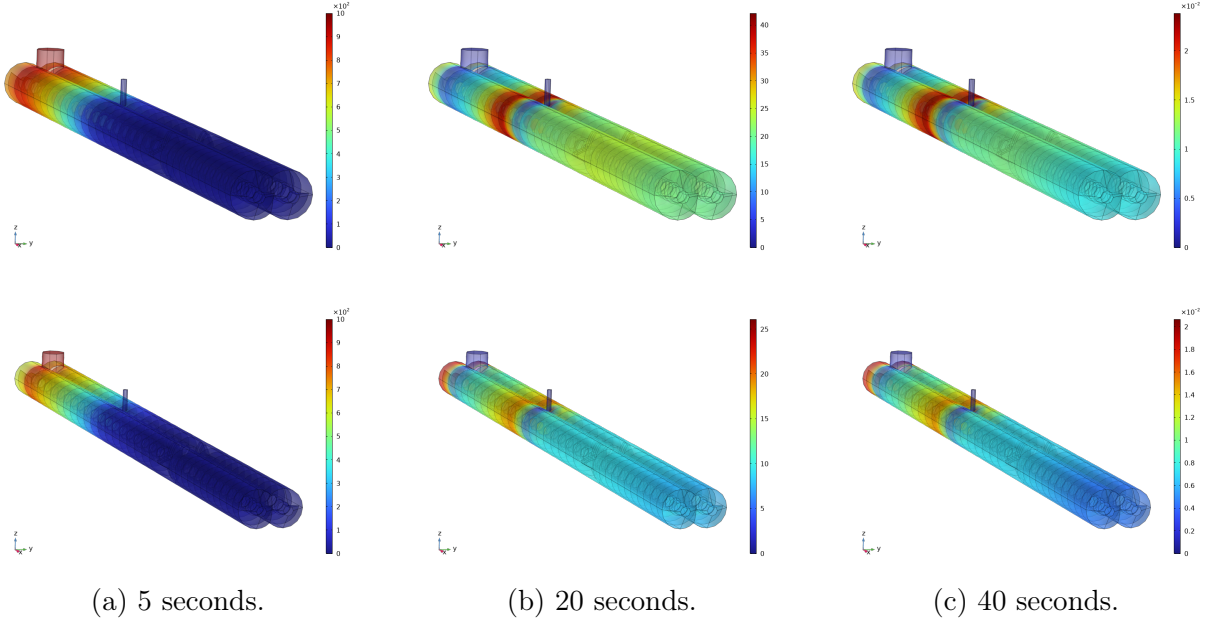


Figure 33: Concentration profile of pol_2 at 60 RPM (top) and 150 RPM (bottom).

Looking at $cross_{link}$, it appears diffusion occurs contrary to the general direction of flow. This ultimately leads to the production of pol_{cl} before the secondary inlet. Such behavior must be closely monitored in an industrial setting. The formation of the product in a non-designated area could lead to the degradation of the product. Because each section of an extruder is designed to operate at specific conditions, among which temperature and mixing efficiency, pol_{cl} could undergo unintended processing if the reaction would begin moving upstream.

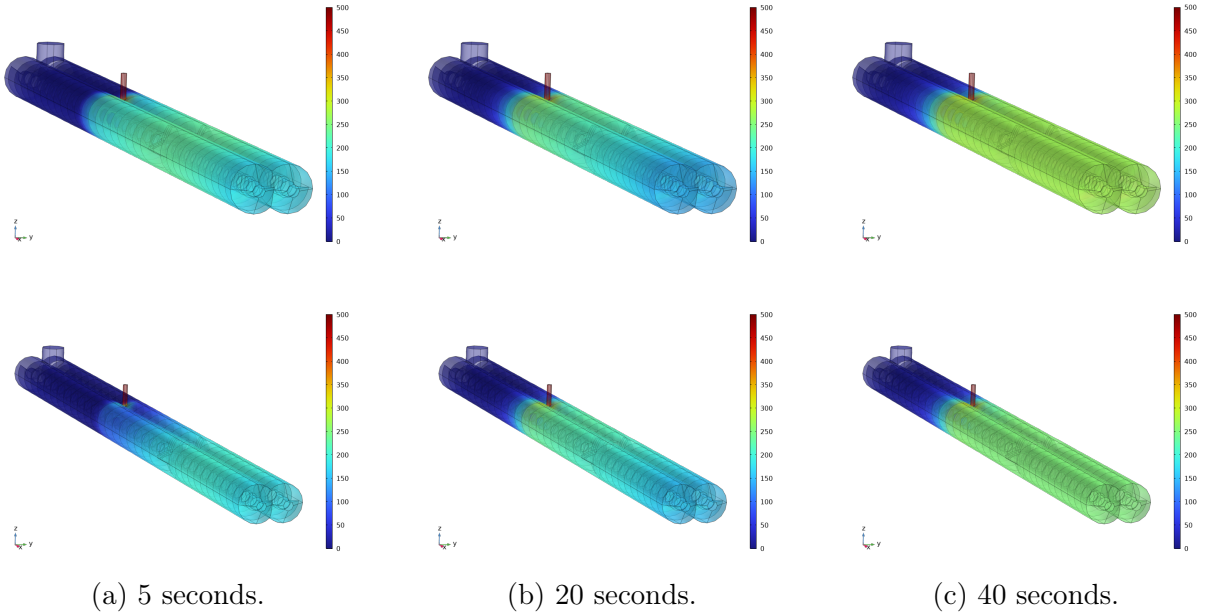


Figure 34: Concentration profile of $cross_{link}$ at 60 RPM (top) and 150 RPM (bottom).

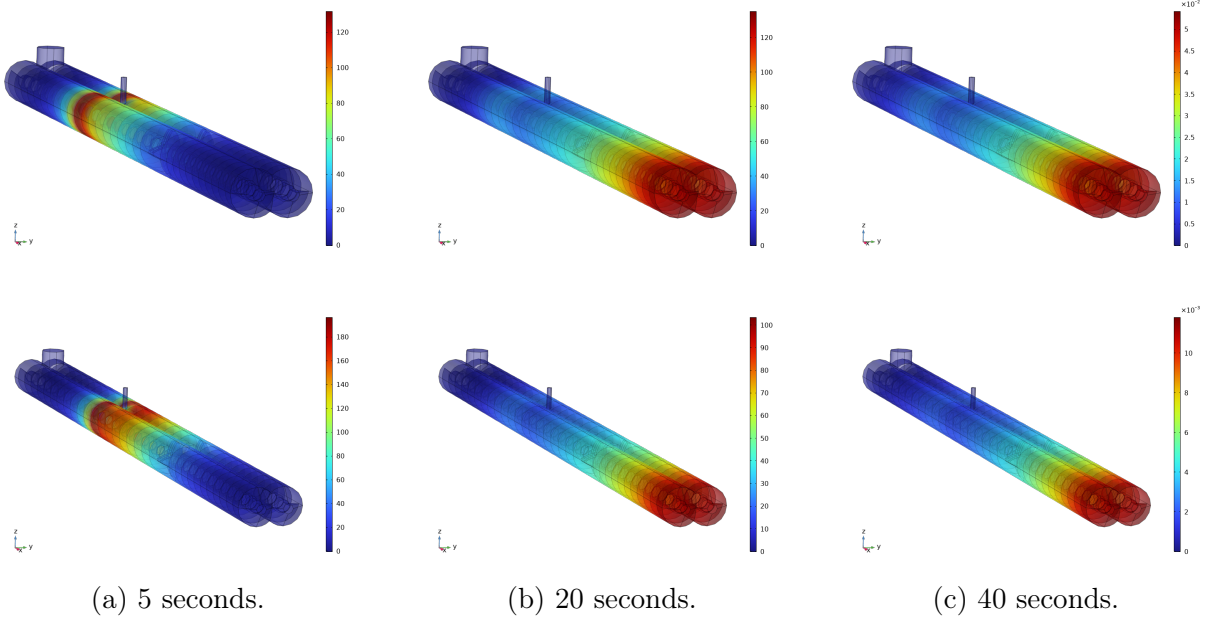


Figure 35: Concentration profile of pol_{cl} at 60 RPM (top) and 150 RPM (bottom).

Varying Heating Configurations

When testing the model against the heating setup, it does not appear any significant difference with the mass transport solutions. From [Figure 36](#) to [Figure 41](#), the graphs do not show neither a qualitative nor a quantitative difference. One of the reasons to be considered is the same observations made in the stationary study, the heating configurations that were modeled do not affect the result in a clear manner. Thus, a proper sensitivity analysis should be included in future research to determine the sensitivity of the model to temperature. Nonetheless, it must be remembered that the simulations of this study use the stationary solutions; hence missing the contribution of the chemistry in the heat module.

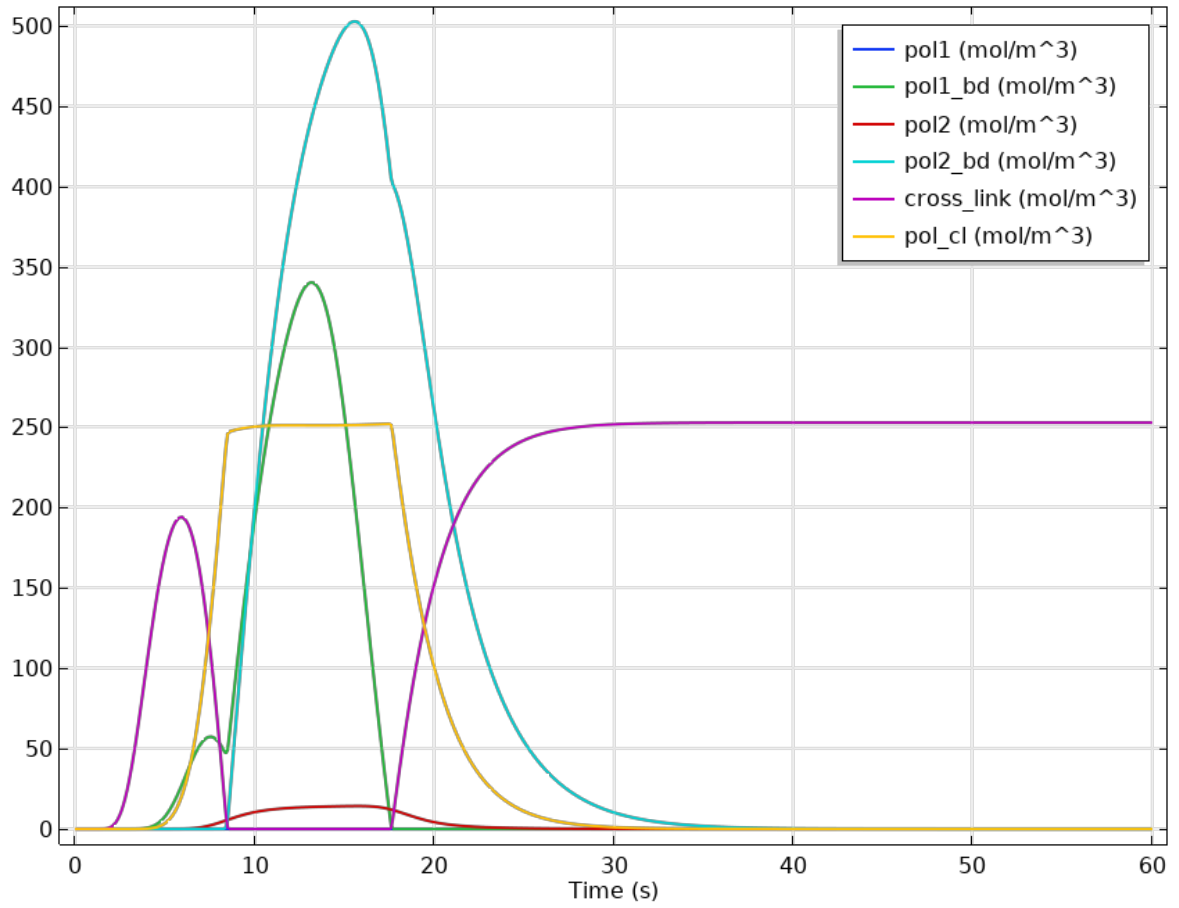
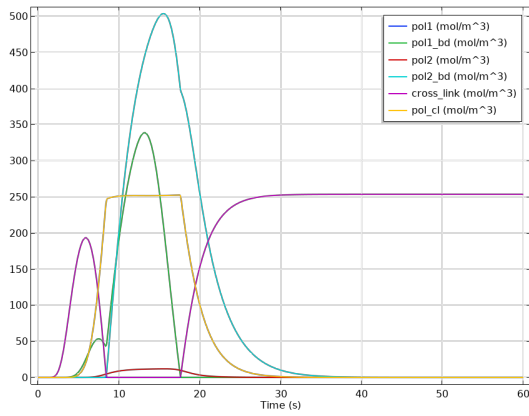
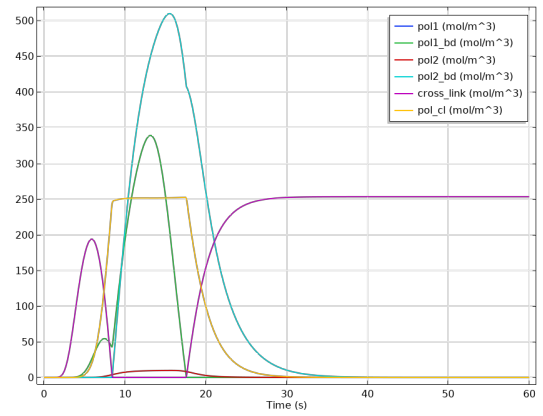


Figure 36: Average concentration at the outlet surfaces over the simulation time with constant heating configuration.



(a) Decreasing trend case.



(b) Increasing trend case.

Figure 37: Comparison of surface average outlet concentrations with a decreasing and increasing heating trend.

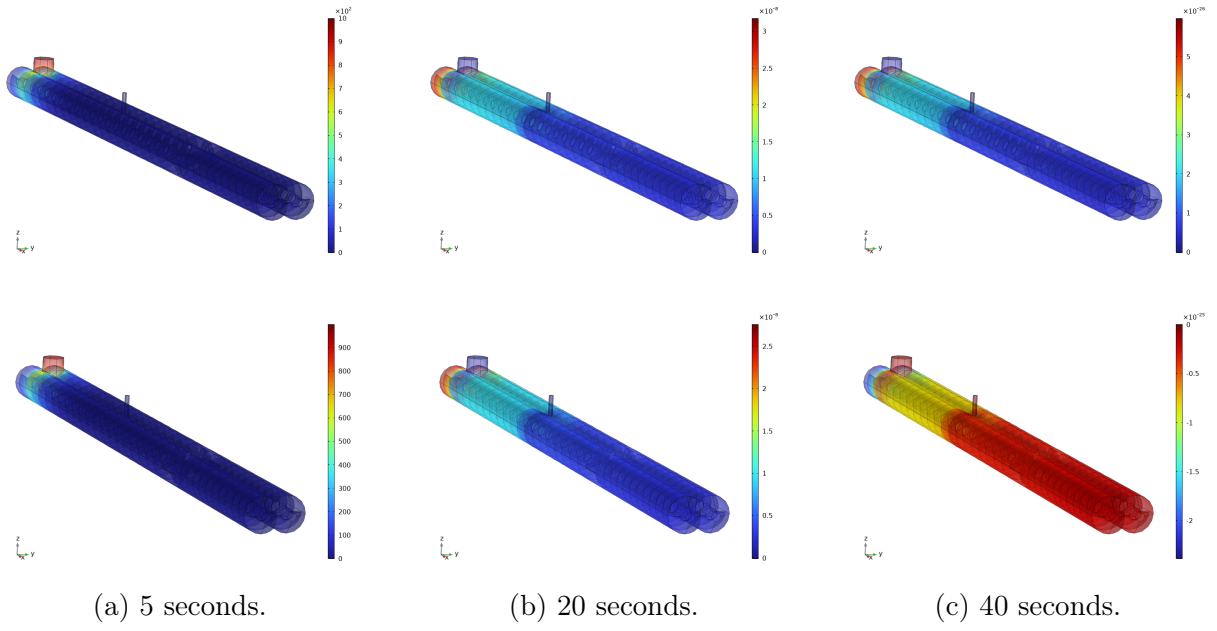


Figure 38: Concentration profile of *pol1* for the decreasing trend (top) and the increasing trend (bottom).

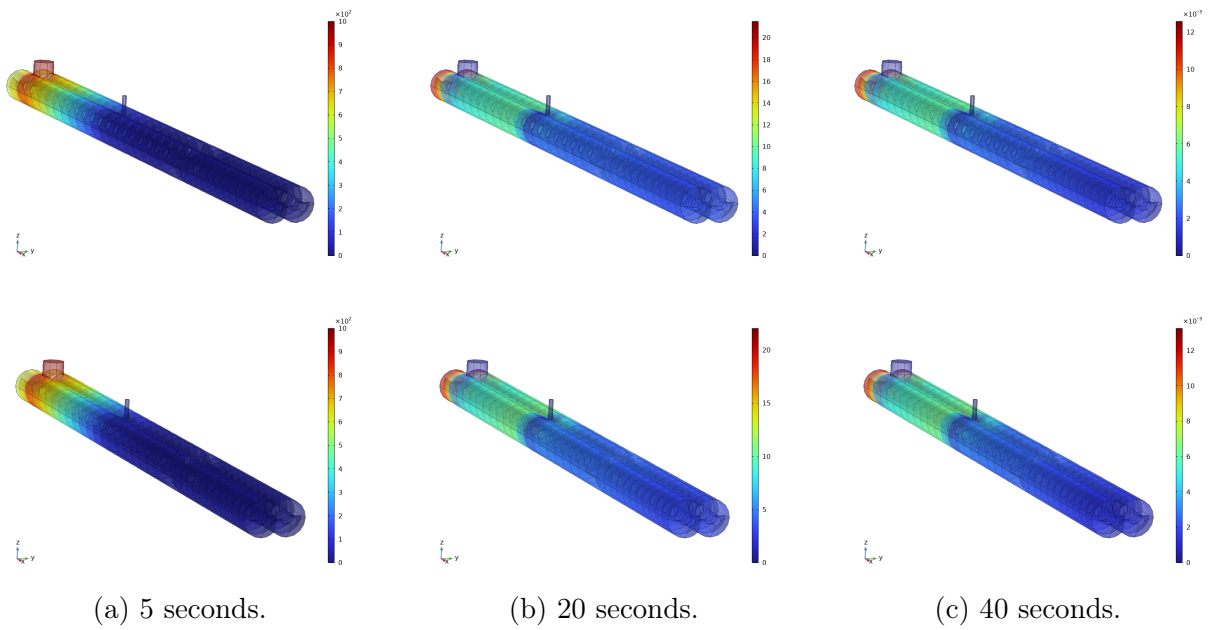


Figure 39: Concentration profile of *pol2* for the decreasing trend (top) and the increasing trend (bottom).

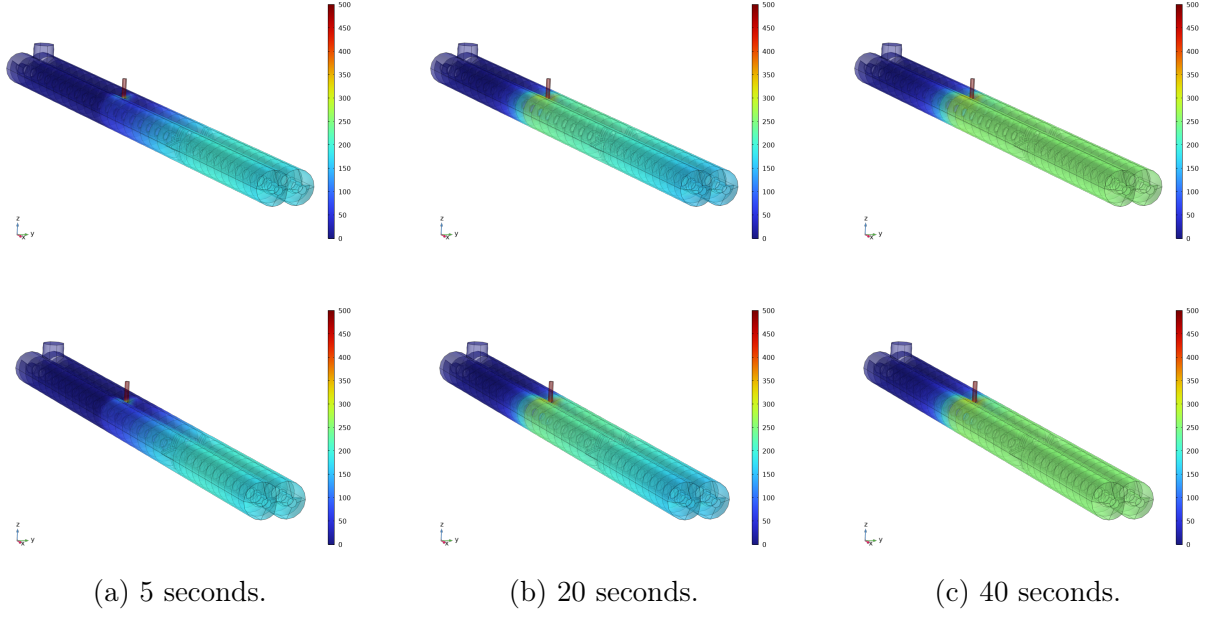


Figure 40: Concentration profile of $crosslink$ for the decreasing trend (top) and the increasing trend (bottom).

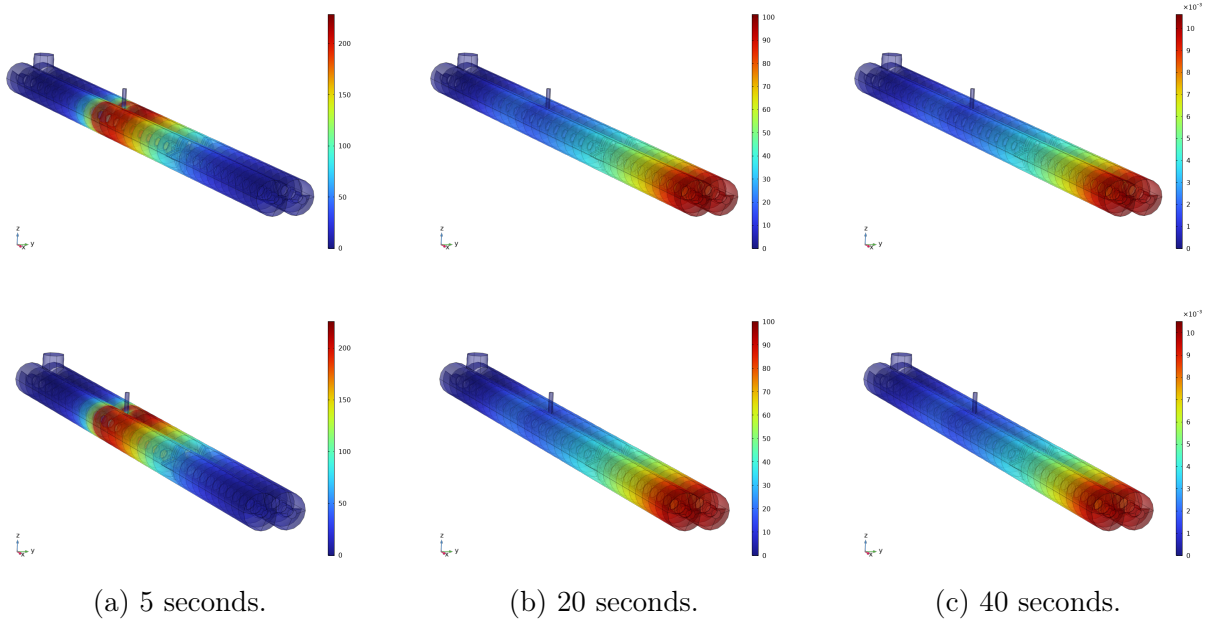


Figure 41: Concentration profile of pol_d for the decreasing trend (top) and the increasing trend (bottom).

Time-dependent, Fully Coupled Flow

As previously anticipated, the final study consists of the transient simulation of all the physics modules. This is the most complete study as all its aspects are coupled. Viscosity varies according to temperature, shear rate, and concentrations. The velocity field varies with temperature and pressure. Finally, the heat transfer includes viscous dissipation as well as the heating elements and the chemical reactions.

Varying RPMs

The evolution in the outlet concentration profile in Figure 42 underlines the importance of the physics coupling. Compared to Figure 30, the reactions occur more abundantly. All concentrations are enhanced, both the reactants and the products, except for $pol1$ which is still consumed instantly. Thus, coupling the physics is a fundamental step that can lead to inaccuracies in the extruder design and optimization, if ignored. Otherwise, Figure 42 confirms that varying the rotation speed is directly correlated to the mechanical degradation of $pol2$. pol_{cl} , as it reacts according to an Arrhenius relation, depends on the RPMs in terms of the velocity field is affected. Higher rotations will transport $pol1_{bd}$ and $pol2_{bd}$ faster but also flush $cross_{link}$, hence creating a situation for which the latter species is the limiting reactant. Figure 43 to Figure 45 complete the analysis of the transport phenomena with the 3D concentration fields of the intermediate and the final products.

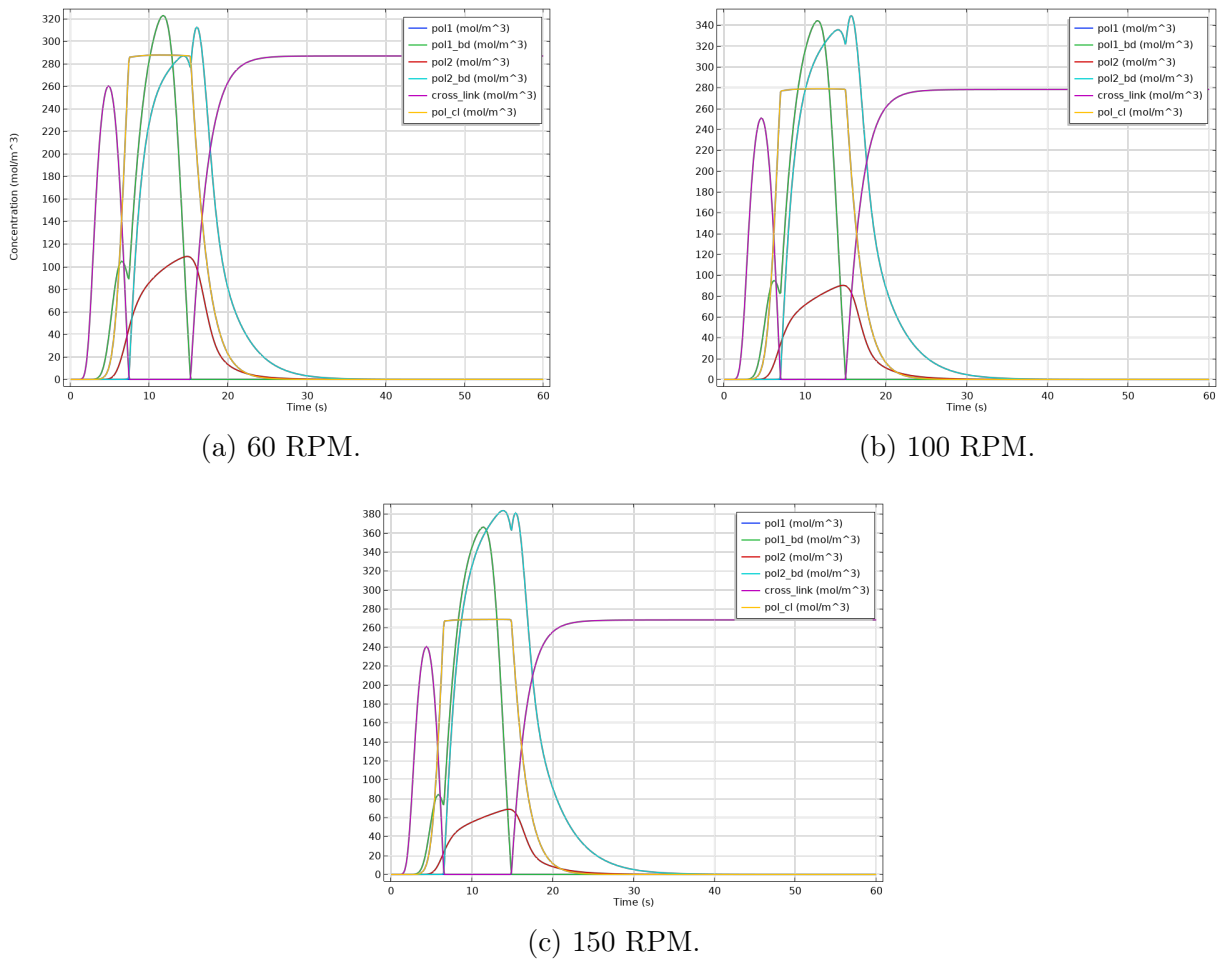


Figure 42: Surface concentration average at the outlet varying rotation speed.

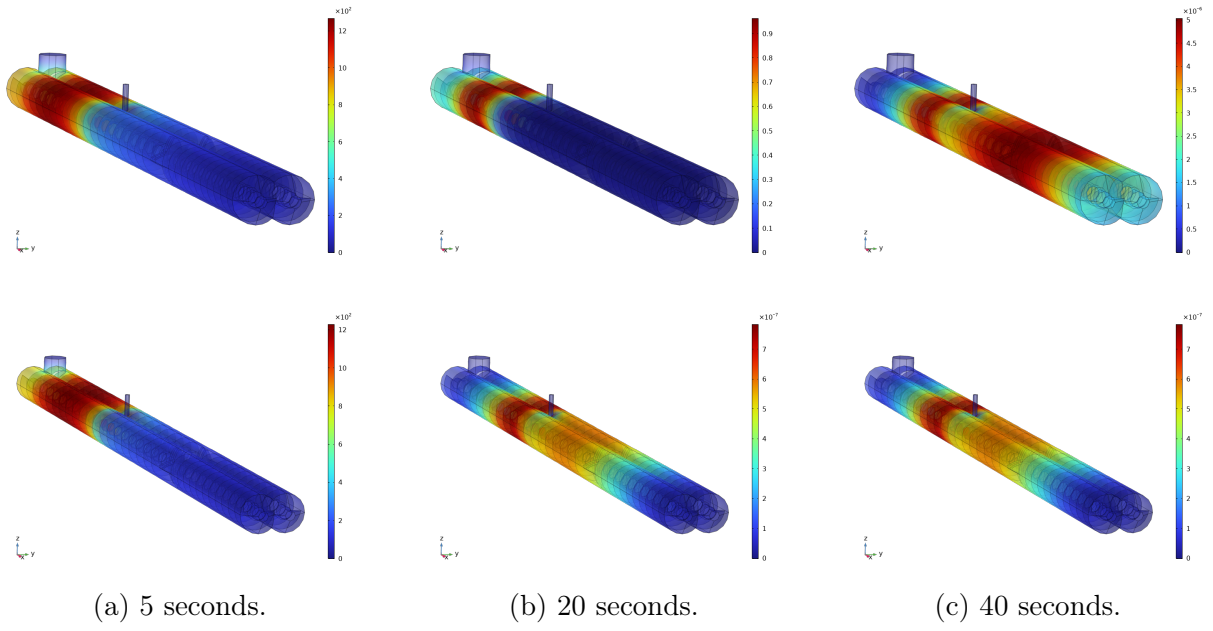


Figure 43: Concentration profile of $pol1_{bd}$ at 60 RPM (top) and 150 RPM (bottom).

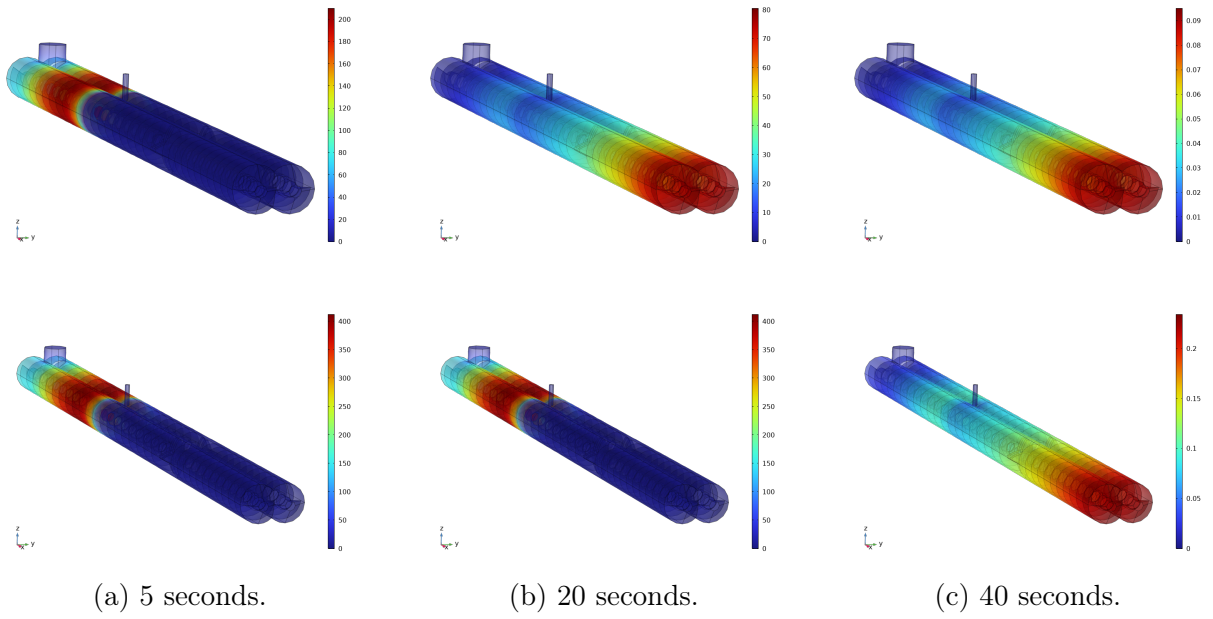


Figure 44: Concentration profile of $pol2_{bd}$ at 60 RPM (top) and 150 RPM (bottom).

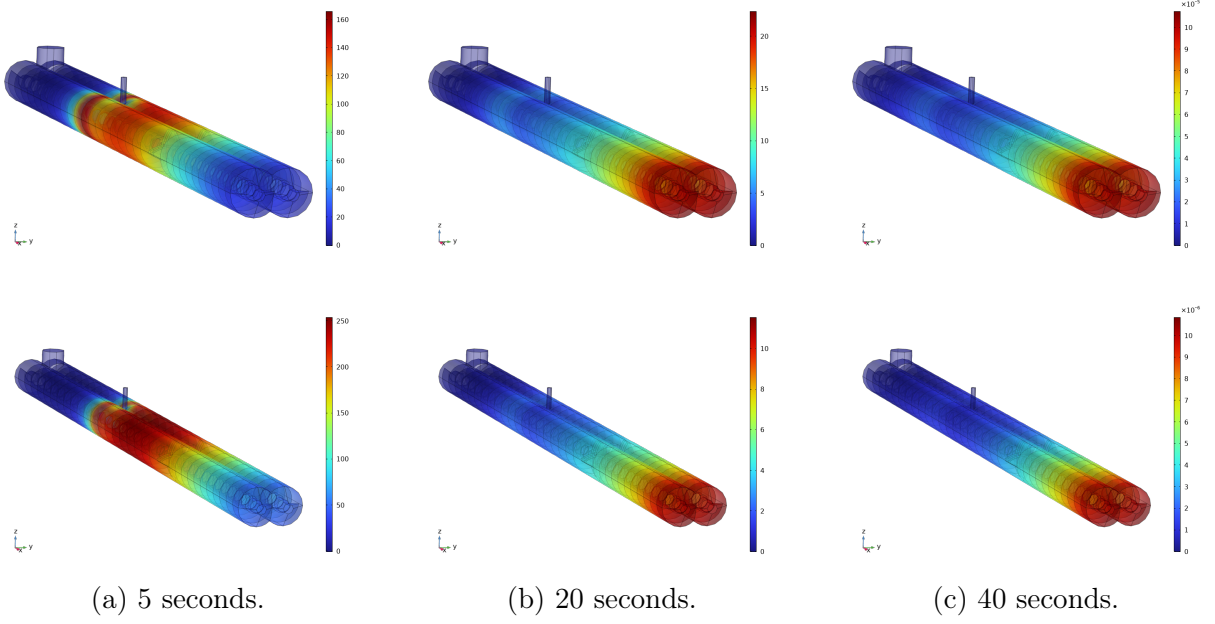


Figure 45: Concentration profile of pol_{cl} at 60 RPM (top) and 150 RPM (bottom).

When fully coupled, the dynamic viscosity profile can be examined with the temperature changes caused by the reactions in Figure 46. As the fluid is shear thickening above a certain threshold, it is expected to observe higher viscosity closer to the screws. Key elements whose role was stressed in previous studies are the metal screws [20]. In the transient fully coupled study, these were found to be decisive in conducting heat back to the fluid and thus becoming implicit heating elements. Their analysis is though assessed in the next section.

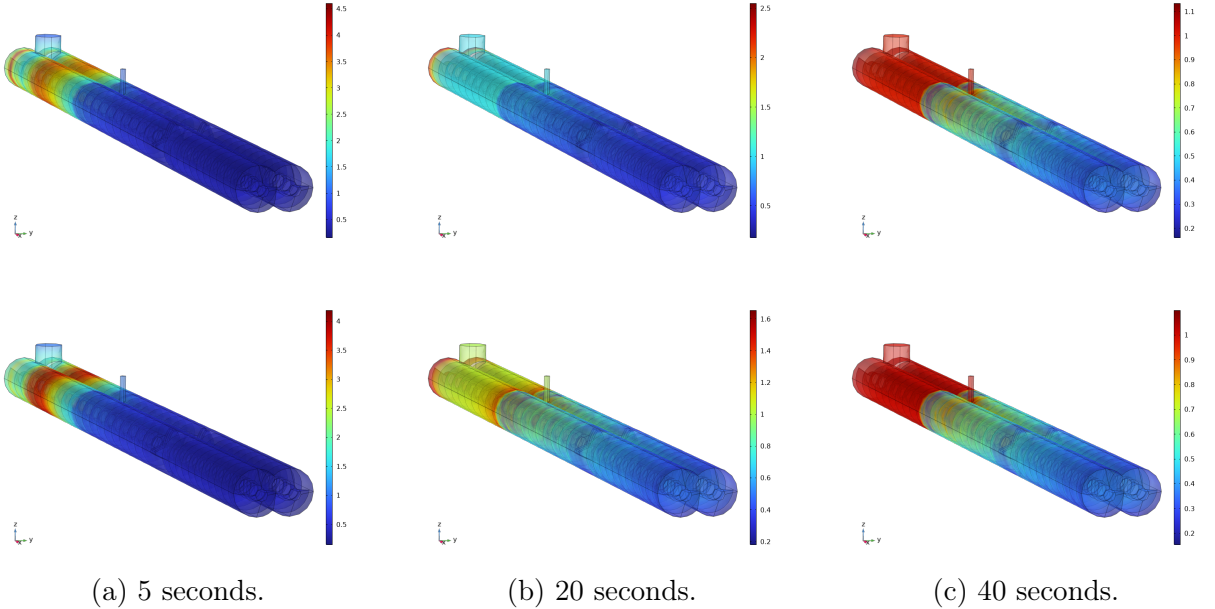
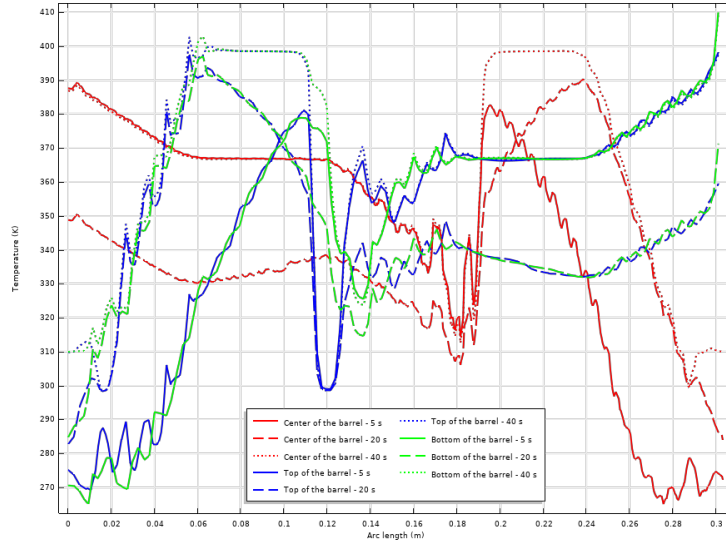


Figure 46: Dynamic viscosity profile for 60 RPM (top row) and 150 RPM (bottom row).

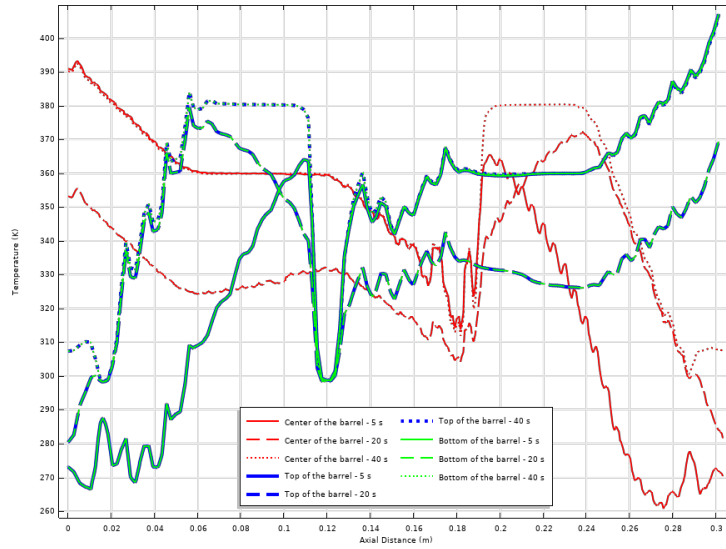
Varying Heating Configurations

When including the heat of reaction in the heat transfer module, the temperature profiles change significantly. Figure 47 displays the temperature as a function of the axial distance again at the top, center, and bottom of the barrel. The measurements at center of the barrel corresponds to the temperatures of the screws. Thus, by plotting at different time steps it can be analyzed the transient evolution of temperature. Given that the heat of reaction and conduction through the screws are now a factor, it is important to contextualize their effect. In particular, the reactions have either a negative contribution to the heat effects, when depolymerization takes place, or positive contribution, when polymerization occurs. In the first part of the extruder the degradation reactions are endothermic, heat is used to break the molecular bonds. In the second part, the formation of pol_{cl} releases energy in the system. This dual effect explains why, in the graph, temperature profiles are lower at $t = 20$ seconds than $t = 0$ seconds before the secondary inlet, which is signaled by the sudden drop in temperature caused by the injection of cold fluid, but higher after it. On top of the difference in the heat of reactions, time plays a fundamental role. As mentioned before, by $t = 40$ seconds the system reaches steady state as the reactions stop. Because of the latter, heat transfer also stops being dominated by the chemistry and the conduction from the screws drives the profile. This can be seen about the location of the primary inlet, where the absence of $pol1$ and $pol2$ translates in the cold fluid being able to heat the same way. Further down the barrel, the screw's role is more relevant as shown in the center of the barrel.

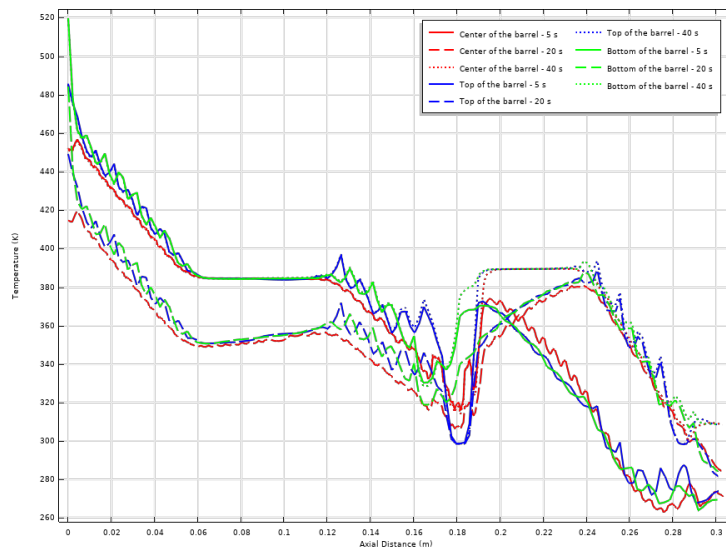
With regard to the polymers' melting conditions, assumed between 393-523 K, it is clear that models of this kind can help ensure proper polymer melt in the context of heat of reaction. If not considered, the first depolymerization reactions could hindered further degradation because of an insufficient activation energy.



(a) Decreasing trend case.



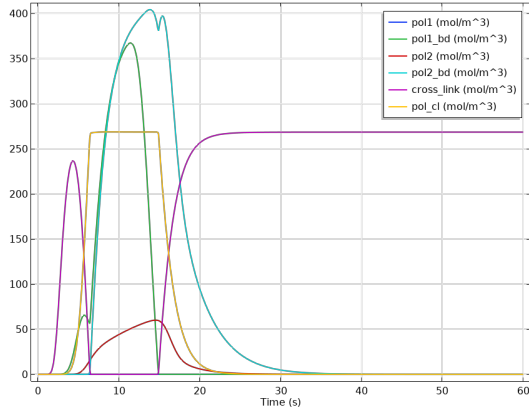
(b) Constant trend case.



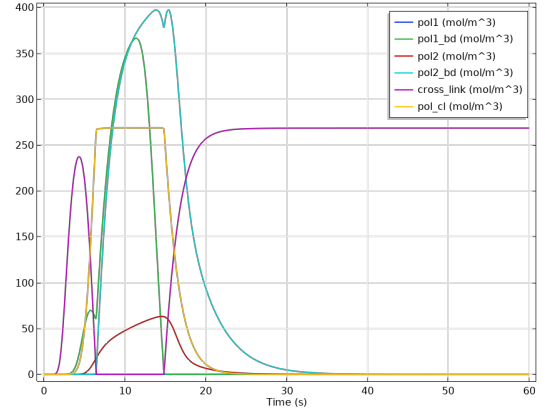
(c) Increasing trend case.

Figure 47: Temperature profile for different heating configurations.

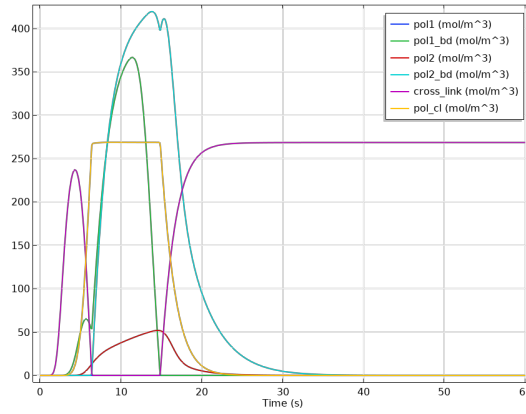
Figure 48 shows how the concentration profile is nearly independent of the temperature changes occurring. Even though it was admitted that the heating configurations tested might not be sufficiently diverse and that they lead to similar thermal behaviors, still the solutions suggest some degree of insensitivity. A discrete difference in the results is that between the polymer concentration profiles for the fully coupled study, Figure 49 to Figure 51, and the transient mass transport study, Figure 38 to Figure 41. This corroborates the well-known idea that solving all interfaces contemporarily achieves the highest degree of accuracy.



(a) Decreasing trend case.



(b) Constant trend case.



(c) Increasing trend case.

Figure 48: Surface concentration average at the outlet varying heating configuration.

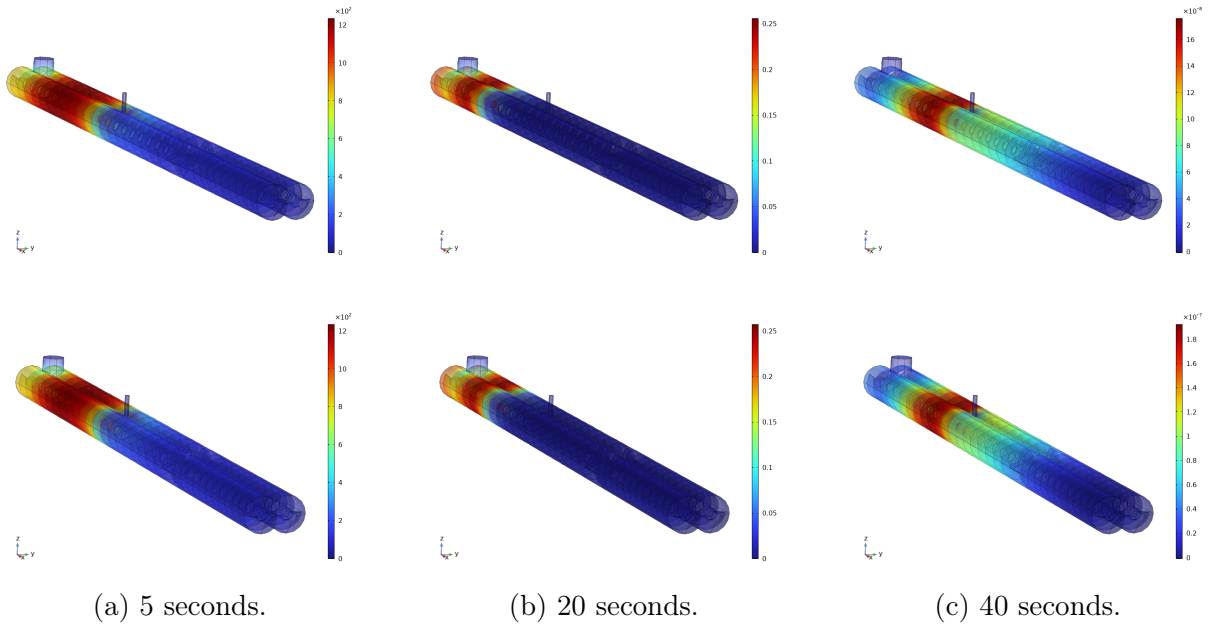


Figure 49: Concentration profile of $pol1_{bd}$ for the decreasing (top) and increasing (bottom) heating configuration.

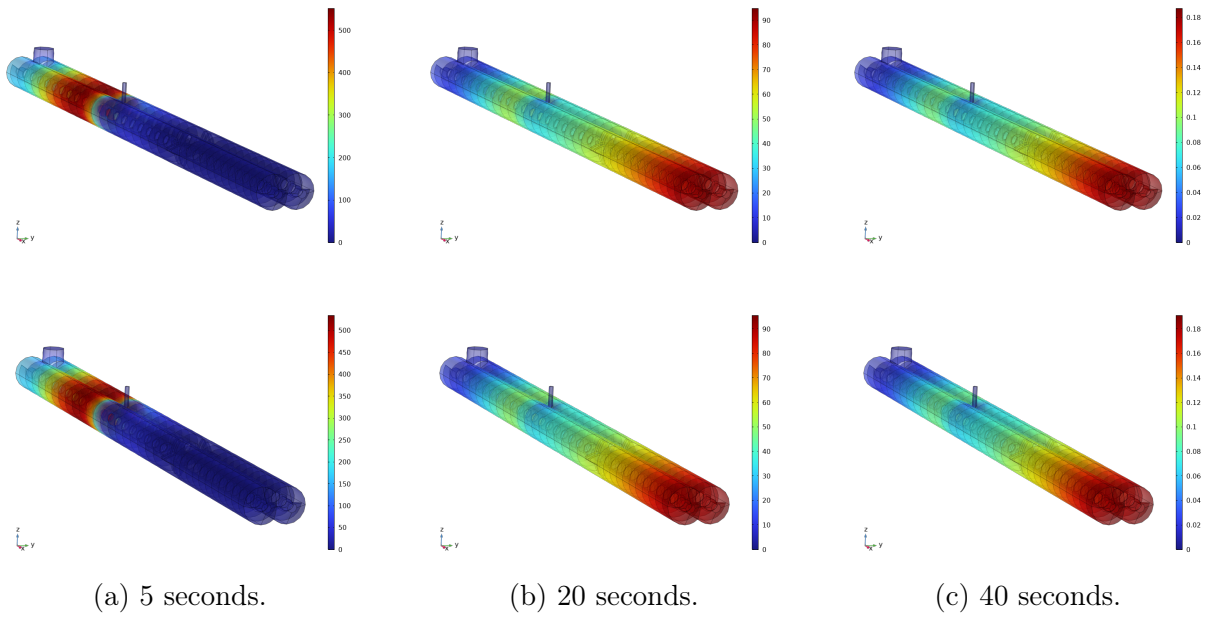


Figure 50: Concentration profile of $pol2_{bd}$ for the decreasing (top) and increasing (bottom) heating configuration.

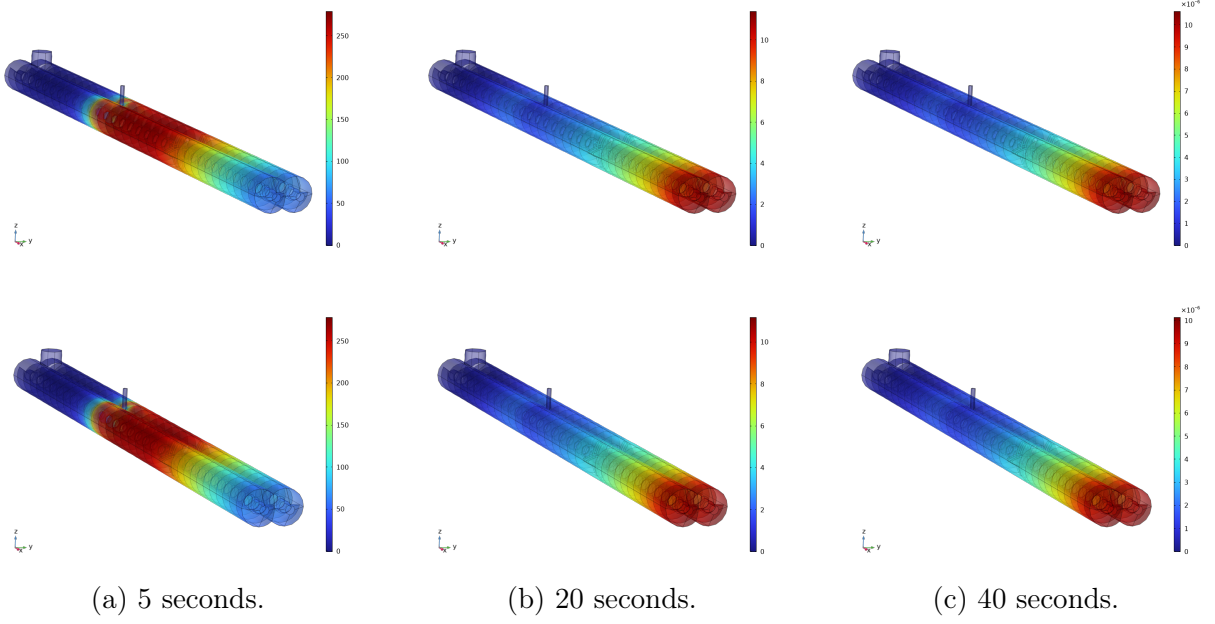


Figure 51: Concentration profile of pol_d for the decreasing (top) and increasing (bottom) heating configuration.

Finally, the clear decrease in the fluid's average viscosity due to the variation in the heating supply is shown in Figure 52. When compared to Figure 46 it can be inferred that the rheological model used is primarily driven by the thermal effects. Thickening behavior close to the screws is still observed in the initial section of the barrel, where temperatures are lower. However, thinning appears visibly more accentuated in the increasing trend case, particularly towards the outlet, due to the higher temperatures. Overall, it is found that the viscosity profiles shown depict well their corresponding heating configuration.

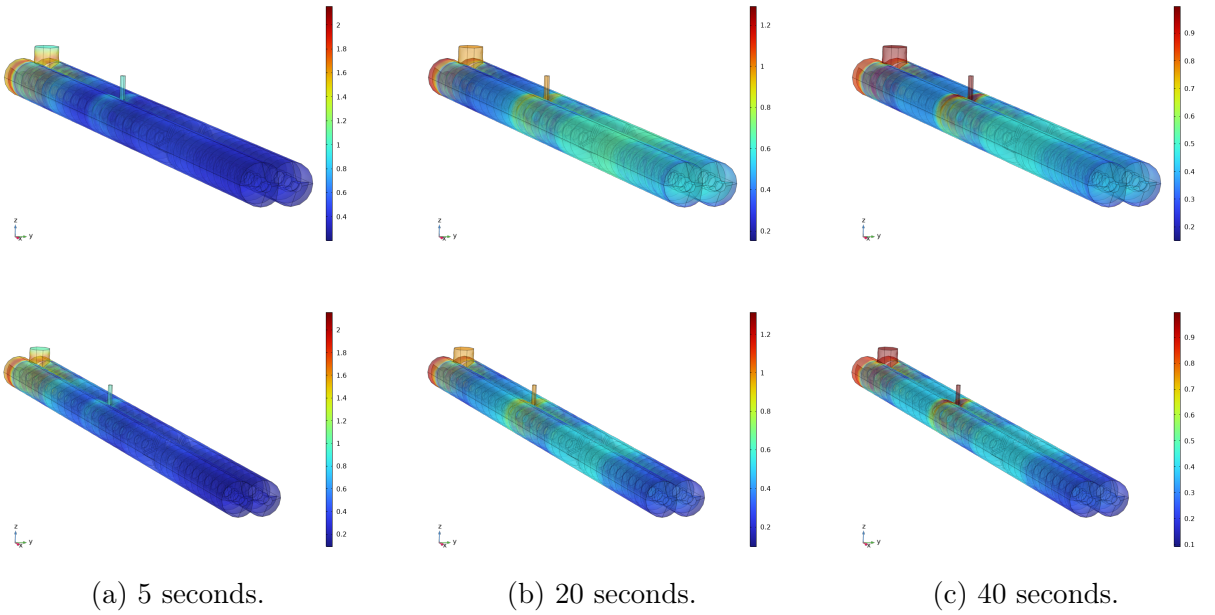


Figure 52: Dynamic viscosity profile for the decreasing trend (top row) and the increasing trend (bottom row).

Conclusion

This thesis represents one of the first attempts at predicting, with CFD, the entirety of a twin-screw extruder geometry. It is definitely the first that does so using complex rheological and kinetic models that link the fluid properties and polymer reaction to the solution composition, temperature, and shear rate. A comprehensive analysis was performed for a fictitious dilute solution containing inelastic non-Newtonian polymers with two depolymerization and one polymerization reactions; the latter occurring between the broken chains and a cross-linking agent. It was found that the position of the inlets along the barrel cannot be neglected and must be tuned in the design phase to avoid flow blockage and subsequent temperature buildup. Moreover, thanks to a thorough analysis of the interdependence of the fluid's properties it was possible to identify the operating range for which the solution's viscosity starts being temperature-driven, as opposed to shear-rate driven. From the transient studies it was estimated the residence time in the extruder, a fundamental operating parameter and one of the main drivers of extrudate quality. Also, by introducing time dependency of the heat effects it was confirmed the fundamental role played by conduction in the metal screws and the one of the heats of reaction. Current results are in line with the theory on CFD and shear-thickening materials. Nonetheless, severe model validation must be done. Future research should focus on calibrating all parameters involved to properly resemble a given solution and the physicochemical properties of its components. This would inevitably require conducting experiments given the complexity and uniqueness of the rheological and kinetic models. Plus, more advanced molecular and reaction dynamics could be considered such as, for instance, molecular entanglement and reaction selectivity. Nonetheless, this work can be seen as a foundation to build upon for engineers and researchers to develop polymer-specific models that can serve the polymer and rubber industry as well as the food industry and the pharmaceutical industry.

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