

Simulation of Hydrolytic Ring Opening Polymerization of Nylon 12 from Laurolactam

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The pandemic caused by COVID-19 resulted in a significant shortage of personal protective equipment (PPE) and additive manufacturing (AM) has been used to produce masks and face shields quickly and with quality. A widely used input is Nylon 12, a polyamide with excellent mechanical properties, low toxicity, better adapting to PPE by AM compared to other polyamides. It is frequently obtained from ring opening polymerization (ROP) route from laurolactam and can be derived from both petroleum and renewable sources. There is a great challenge toward few studies related to the production of Nylon 12 and mainly laurolactam monomer derived from renewable sources. This work aims to simulate the production of Nylon 12 by hydrolytic ROP in the *Aspen Polymer Plus®* simulator. A sensitivity analysis was carried out investigating the variation of the conversion, number average molecular weight, and number average degree polymerization, providing a better understanding of the process. Based on the results, it is concluded that the simulation is viable, since it was observed a formation of a polymer with high conversion and molecular weight according to experimental data.

1. Introduction

The pandemic caused by COVID-19 presents itself as one of the greatest global health challenges of this century. Scientists are studying the characteristics of the virus as speed of spread and the need to mitigate exposure (Advincula et al., 2020). The protection of health professionals is extremely important, requiring the use of personal protective equipment (PPE) such as masks and face shields, however, the global emergency together with an unforeseen situation resulted in the scarcity of these PPE's. Additive manufacturing (AM) emerged as an alternative for the production of PPEs, enabling the production of complex objects with great speed and quality (Amin et al., 2020). The AM process produces 3D objects with different types of materials such as metals, ceramics and plastics. The mechanical properties of objects are heavily affected primarily by the fill design. The greater the fill, the better the object's strength, however, the fill is reduced in less printing time, energy and cost (Patti et al., 2021). According to Mostafa et al. (2018), polyamides are widely used in AM as engineering polymers, in particular Nylon 12, the most used polyamide due to its excellent mechanical properties such as high resistance to solvents and corrosion, great thermal resistance allowing the PPE to be sterilized by autoclave. The crystallinity and melting temperature are lower than other polyamides, requiring less power, therefore energy is spent on the construction of objects. In addition, Nylon 12 has biocompatibility and does not generate toxicity on skin contact (Rahim et al., 2017).

Nylon 12 is a 12 carbon polyamide used as engineering thermoplastic with a wide range of applications, synthesized from ω -aminolauric acid or laurolactam (Griehl and Ruesteivi, 1970). It has excellent mechanical properties, low moisture absorption, durability and good chemical and thermal resistance. It is the most suitable Nylon for use in AM as it exhibits lower crystallinity and melting temperature compared to Nylon 6, which results in the need for less power to melt the material and consequently less energy expenditure to produce three-dimensional objects (Mostafa et al., 2018). Nylon 12 is synthesized from different technological routes, however the most used and industrially efficient is the hydrolytic ring opening polymerization (ROP). This route uses laurolactam monomer, a raw material usually produced from petroleum-derived sources such as butadiene, but there is the possibility of being obtained from renewable sources (Kyulavska et al., 2019). The polymerization is

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divided into three main reactions, first the ring opening reaction (ROR) which consists of the reaction between the cyclic monomer and water which acts as initiator with the ring opening of the monomer forming the amino acid. Then, polycondensation occurs, which consists of the reaction between two or more amino acid molecules, in which the amine functional group reacts with the carboxylic acid functional group, forming a dimer and water. Simultaneously with polycondensation, polyaddition reactions also occur, which are reactions between the amino acid and the lauro lactam monomer that cause the ring opening of the monomer and the addition of this molecule to the structure (Russo and Casazza, 2012).

Thereby, there is a great challenge due to the scarcity of works and articles related to the production of Nylon 12 and especially the lauro lactam monomer derived from renewable sources. Therefore, it is extremely important to study the polymerization process of Nylon 12, with process simulation being a very effective means for analyzing several variables that influence the process. Therefore, this work aims to reproduce the hydrolytic ROP process of Nylon 12, using the *Aspen Polymer Plus*® process simulator, allowing the identification of the relationship between polymer properties and process operating conditions.

2. Methodology

Firstly, the kinetics of the hydrolytic ROP of Nylon 12 is shown, then the operational conditions of the process are described.

2.1 Kinetics

The kinetic mechanism of the polymerization of Nylon 12 proposed for this process is done by the functional groups method and shown in Table 1. The reaction scheme was obtained from the work of Seavey and Liu (2008), who performed the simulation of the hydrolytic ROP of Nylon 6 and adapted for the polymerization of Nylon 12. This can be done because the reactions involving both the polymerization of Nylon 6 and Nylon 12 are similar. Eight reactions are considered in the process, three main ones involving lauro lactama monomer, two cyclic dimer reactions, and three reactions involving acid and amine monofunctional. All reactions take place under uncatalyzed and catalyzed conditions by acid groups, with both being considered in the reaction rate expression.

Table 1: Kinetic mechanism for Nylon 12 hydrolytic ring opening polymerization

Reactions	
1. Ring opening of lauro lactam	$W + LL \xrightleftharpoons[k'_1 = \frac{k_1}{K_1}]{k_1} ADA$
2. Polycondensation	$P_m + P_n \xrightleftharpoons[k'_2 = \frac{k_2}{K_2}]{k_2} P_{m+n} + W$
3. Polyaddition of lauro lactama	$P_n + LL \xrightleftharpoons[k'_3 = \frac{k_3}{K_3}]{k_3} P_{n+1}$
4. Ring opening of cyclic dimer	$W + CD \xrightleftharpoons[k'_4 = \frac{k_4}{K_4}]{k_4} P_2$
5. Polyaddition of cyclic dimer	$CD + P_n \xrightleftharpoons[k'_5 = \frac{k_5}{K_5}]{k_5} P_{n+2}$
6. Acid end-group termination	$HAC + P_n \xrightleftharpoons[k'_2 = \frac{k_2}{K_2}]{k_2} P_{n,x} + W$
7. Amine terminator lauro lactama addition	$CHA + LL \xrightleftharpoons[k'_3 = \frac{k_3}{K_3}]{k_3} P_{n,y}$
8. Amine end-group termination	$CHA + P_n \xrightleftharpoons[k'_2 = \frac{k_2}{K_2}]{k_2} P_{n,y} + W$

W: Water, LL: Lauro lactama, ADA: 12-Aminododecanoic acid, CD: Cyclic dimer, HAC: Acetic acid, CHA: Cyclohexylamine, P_n : Polymer chain with n repeat units, P_m : Polymer chain with m repeat units, $P_{n,x}$: Polymer chain with n repeat units and acetic acid terminated, $P_{n,y}$: Polymer chain with n repeat units and cyclohexylamine terminated.

2.2 Process description

The polymerization process of Nylon 12 in *Aspen Polymer Plus®* was simulated using the experimental plant from the work of Kawakami et al. (1994). It consists of a polymerization column that has three zones (upper, intermediate, lower). Initially, the feed is at 533.15 K and 1 atm, flow rate of 7.35 kg/h and composition of 98.9 % laurolactam, 1.0 % water initiator and 0.1 % monofunctional acid catalyst acetic acid which are fed into the upper zone of the column. In the upper zone most ROR occur which must take place at high temperatures and pressures. The resulting product is transferred to the intermediate zone, which is at lower temperature, where the ROR are completed and the polycondensation and polyaddition reactions in the system start. Finally, in the lower zone at lower temperatures, polycondensation and polyaddition reactions finish.

3. Results and discussion

Figure 1 shows the flowchart of the polymerization process for Nylon 12. The process is fed (FEED) in the simulated upper zone by a continuous stirred tank reactor (CSTR1) which must operate in a vapor-liquid phase, temperature 573.15 K, pressure 5 atm, condensed phase with a volume of 30 m³. The product vapor stream (R1VAP) from the CSTR1 reactor is transferred to a condenser (DISTIL) which recycles the unconverted monomer and water to the feed of the process and discards the excess water (COND) from the process. The product liquid stream (R1OLIGO) is transferred to the intermediate zone that was simulated with another continuous stirred tank reactor (CSTR2) operating in a vapor-liquid phase, temperature 548.15 K, pressure 2 atm, and a condensed phase with a volume of 15 m³. The vapor stream (R2VAP) from the CSTR2 is recycled directly to the FEED. The product liquid stream of the CSTR2 (R2OLIGO) is transferred to the lower zone that was simulated with a plug flow reactor (PFR1) with a thermal fluid of constant temperature of 573.15 K and heat transfer of 0.7 J/s.m².K. The dimensions of the plug flow reactor are 3 meters long and 0.125 meters in diameter. The product stream of the lower zone (POLY1) is the final product that contains the Nylon 12. The conditions of the main streams of the polymerization column are shown in Table 2.

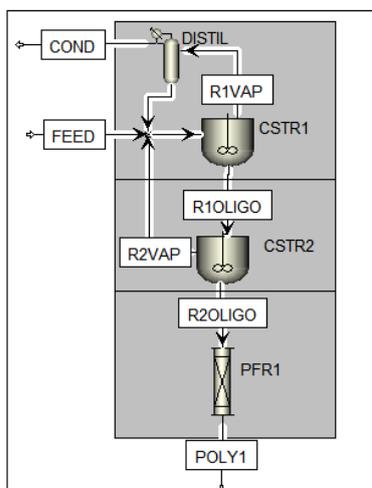


Figure 1: Hydrolytic ROP process flowsheet

Table 2: Main streams of flowsheet

Properties	FEED	R1OLIGO	R1VAP	COND	R2OLIGO	R2VAP	POLY1
Temperature [K]	523.00	573.15	573.15	373.17	548.15	548.15	547.24
Pressure [atm]	1	5	5	1	2	2	2
LL [kg/h]	7.2692	0.851	0.0284	-	0.5652	0.0017	0.4033
W [kg/h]	0.0735	0.0217	0.1934	0.0591	0.0111	0.0126	0.0112
ADA [kg/h]	-	0.0008	-	-	0.0003	-	0.0003
NYLON12 [kg/h]	-	6.3813	-	-	6.6596	-	6.8127
HAC [kg/h]	0.0074	0.0003	0.0011	8.93×10^{-7}	0.0001	-	0.0001
DIMER [kg/h]	-	0.0502	-	-	0.0546	-	0.0634
MWN [g/mol]	-	15,057	-	-	21,880	-	22,866

In the upper section, the conversion of lauro lactam (X_{LL}) to Nylon 12 was 88.23 %. This occurs mainly because this section has, for the most part, hydrolytic ROR and, in parallel, polycondensation and polyaddition reactions. It is observed in Table 2, the R1VAP and R1OLIGO currents are at 573.15 K and 5 atm, indicating that they passed through the CSTR1 reactor at high temperatures and pressures for the hydrolytic ROR to occur. Polycondensation and polyaddition reactions also occur, responsible for the growth of the polymer chain, observed by the high number average molecular weight (\bar{M}_n) of 15.057 g/mol, indicating that there were polycondensation and polyaddition reactions parallel to the hydrolytic ROR in the upper section of the polymerization column. Note that there are two output streams from the CSTR1 reactor, with the R1VAP steam stream having the function of separating water and lauro lactam. This separation of the vapor and liquid streams is very important to be done mainly to separate the process water, to eliminate the excess and to recycle it to the feed stream, as this way the water does not react in the reverse polycondensation reaction that reduces the conversion of Nylon 12 and is reused in feed as an initiator of the hydrolytic ROR.

In the intermediate section, there is an increase in X_{LL} , number average molecular weight (\bar{M}_n) and number-average degree of polymerization (DP_n). This conversion increase to 92.18% indicates that the hydrolytic ROR are finishing and there is a greater occurrence of polycondensation and polyaddition reactions in the process. These reactions, mainly polycondensation, are observed by the large increase in the \bar{M}_n to 21.880 g/mol and the DP_n to 111.11. As in this section mainly polycondensation reactions occur, it is necessary to separate the water to later use it in the process feed. For this reason, the R2VAP steam stream which is composed of water and lauro lactam is recycled to the feed stream.

The lower section had a X_{LL} of 94.41 %. According to the experimental work by Kawakami et al. (1994), at the end of the polymerization column X_{LL} to Nylon 12 is 99.5 %. This discrepancy between conversions is due to factors such as the kinetic parameters used in the simulation. Due to the scarcity of information on Nylon 12 in the literature, such as kinetic parameters, for the simulation the kinetic parameters of the hydrolytic ROP of Nylon 6 from the work of Seavey and Liu (2008) were used. Another factor that may have influenced the result is the limitation of the simulator's operating unit, as the polymerization column was not available in the simulator, it was necessary to perform the simulation using CSTR and PFR reactors to simulate similar column conditions. However, the simulation conversion was satisfactory despite the polymerization column conversion being lower than reported in the literature. The polymer has a low extractable percentage of 6.51%, which represents a low number of unreacted components, and a high \bar{M}_n of 22.866 g/mol, higher than values reported in the literature from 5,000 g/mol to 9,500 g/mol. This high value indicates the formation of a high polymer influencing the qualitative properties of the polymer. The term high polymer refers to the minimum molar mass of a polymer chain that has the physical properties of a polymer, as opposed to a monomer or oligomer.

Using the sensitivity analysis tool, several process variables were analysed, varying the mass flow rate of the feed stream from 0 to 100 kg/h to determine their influence on the process parameters, as shown in Figure 2. Analyses were also carried out in the plug flow reactor to determine the relationship of the variation of the reactor length with the \bar{M}_n and the DP_n . In Figure 2 (A), the effects of the variation in the mass flow rate of the feed stream on the DP_n and on the \bar{M}_n are observed. The R1-MWN and R1-DP curves correspond to the \bar{M}_n and the DP_n of the R1OLIGO stream. Similarly, R2-MWN and R2-DP are from the R2OLIGO stream and R3-MWN and R3-DP are from the POLY1 stream. The profile of the \bar{M}_n and DP_n curves are superimposed due to the \bar{M}_n being dependent on the DP_n , which results in a similar behaviour. It is noted that these properties decrease with the increase of feed mass flow rate, because these are related to the conversion of Nylon 12. As conversion decreases with increasing feed mass flow rate, the \bar{M}_n and DP_n of polymers produced in the reactors also decrease. Figure 2 (B) presents the effects of the variation of the feed mass flow rate on the conversion. The conversion of lauro lactam in all reactors decreases with increasing feed mass flow rate. With more feed mass flow rate, lesser the residence time of the material in the reactors, causing a decrease in the lauro lactam conversion. The effects of the variation of the feed mass flow stream on the extraction value are presented in Figure 2 (C). This polymer property corresponds to the unreacted components of lauro lactam, 12-aminododecanoic acid, dimer and water. There is an increase in the extraction value with feed mass flow rate due to a decrease in conversion with feed mass flow rate.

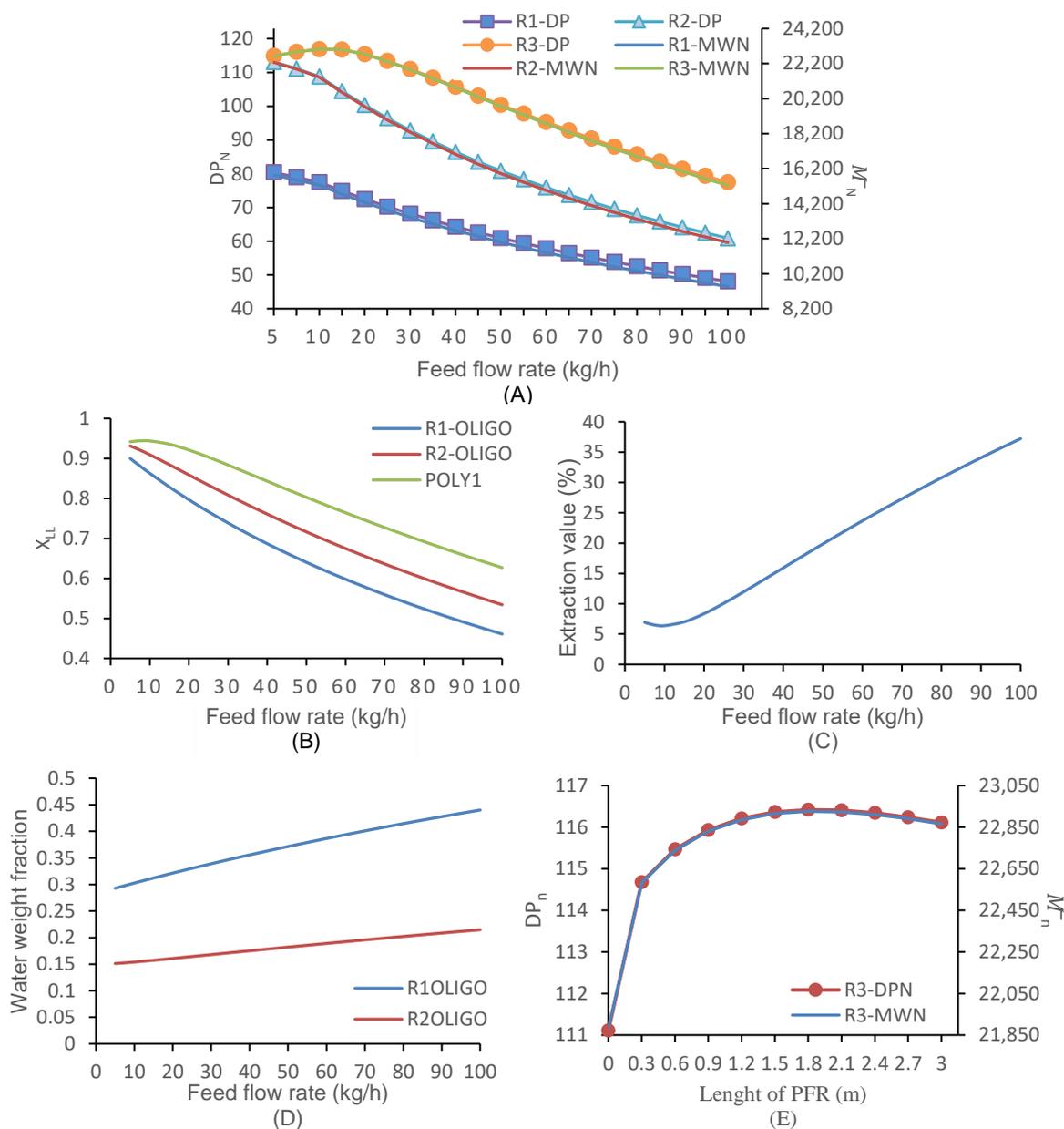


Figure 2: Effect varying the feed mass flow rate in (A) \bar{M}_n and DP_n , (B) X_{LL} , (C) extraction value and (D) water weight fraction and varying the length in (E) \bar{M}_n and DP_n

In Figure 2 (D), the effect of the variation of the feed stream mass flow rate on the water weight fraction in the reactors input streams is shown. With the increase in feed mass flow rate, there is an increase in the water weight fraction in R1OLIGO in the CSTR2 reactor and in R2OLIGO in the PLUG reactor. These increase in the streams R1OLIGO and R2OLIGO occurs because the X_{LL} is decreasing, consequently, more water will be in the process. This occurs because water acts as an initiator for the polymerization of Nylon 12 in hydrolytic ring opening reactions, however, in polycondensation reactions it acts in the reverse direction of the reactions, decreasing the conversion of lauro lactam. The main hydrolytic ring opening reactions take place in the upper section (CSTR1) with the unconverted water being recycled to the feed stream. In the middle and lower section, few hydrolytic ROR occur and polycondensation and polyaddition reactions start, therefore, the presence of water to increase the conversion is undesirable. In the intermediate section, unconverted water is recycled into the FEED, so a greater variation in the R1OLIGO can be seen.

A sensitivity analysis was carried out in the lower section to evaluate the profile of the \bar{M}_n and DP_n as the flow passes through the plug flow reactor, that is, the variation in the length of the reactor as shown in Figure 2 (E). It is observed in the graph that both the R3-DPN and R3-MWN curves overlap, as the \bar{M}_n is dependent on the DP_n and increases as the length of the plug flow reactor increases, reaching an equilibrium value at the end of the reactor. Both curves have an ascending profile in the reactor from 0 to 1.8 meters, indicating that the reactions and conversion to Nylon 12 are taking place. However, it is observed that at the end of the reactor from 1.8 to 3 meters there is a decrease in \bar{M}_n and DP_n , due to the presence of water in the reaction shifting the reaction direction to the reverse direction.

4. Conclusions

The results presented from the simulation of hydrolytic ROP of Nylon 12 performed in the *Aspen Polymer Plus®* simulator demonstrated that the polymerization simulation is viable to be carried out, since it was possible to observe the formation of a polymer with high conversion of 94.41 % and high molar mass of 22.866 g/mol. In the literature, it is reported in the experimental work the formation of Nylon 12 with 99.5 % conversion and molar mass between 5000 g/mol to 9500 g/mol. Evaluating polymer properties such as conversion and molar mass is extremely important, since such properties have a significant impact on the characteristics of the final product and its application. The analysis of the mass flow rate variation profiles with several variables allowed a better understanding of the process. The simulation allowed to identify the relationship between the various polymer variables such as the conversion that decreases with increasing feed mass flow rate, consequently decreasing the \bar{M}_n and DP_n and increasing the extraction value. The simulation proved to be important because it allows to carry out studies related to the hydrolytic ring opening polymerization process of Nylon 12 with greater agility. The results allowed a better understanding of the process and can be applied in the optimization of the experimental plant.

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