Optimization of a Batch Reactor for Biomass-derived Renewable Polyesters

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Abstract - For the first time, we present the process simulation and multiobjective optimization of the batch reactor polyesterification of a library of biomass-derived renewable polyesters: poly(1,3-propylene succinate) (PPS), and poly(1,3-propylene 2,5-furandicarboxylate–co-1,3-propylene succinate) (PPFPS). The simulation environment was implemented in Aspen Plus™ and the ε-constraint method was followed for the multi-optimization problem, considering two objective functions that maximize the number degree of polymerization (DPN) and minimize the heat duty Q of the reactor. The efficient operation points are reported for each case through the construction of Pareto frontiers and the performance of the biobased polyesters was compared to that of petroderived polyethylene teraphthalate (PET) in terms of sustainability indicators and final polymer attributes, such as number molecular weight (M_n), and number degree of polymerization (DPN). The kinetic rate expressions were defined following the functional group approach for step-growth kinetics and the parameters were estimated by fitting a polyesterification model found in the literature to the experimental data. The present work provides comprehensive fundamentals towards a feasible process simulation, process design and scale up of the polyesterification of biomass-derived products.

***Keywords*:** Biomass, polyesters, process simulation, multi-objective optimization, kinetics

1. Introduction

Lately, lignocellulosic biomass sources have become important to lower the dependence of industry on traditional fossil feedstocks. The biorefinery concept arises as a potential and necessary alternative to supply a portfolio of products, including monomers for polymer synthesis. Within polymers, polyesters are an exciting field for the inclusion of bio-building blocks due to their extended applications. We have recently reported the synthesis and kinetic modelling of renewable polyesters based on 2,5-furan dicarboxylic acid (FDCA), succinic acid (SA) and 1,3-propanediol (PDO).[1] As continuous research has been pursued in the synthesis of biomass-derived polyesters, it is imperative to properly scale up the production processes so these are feasible from a sustainable and economical perspective. Therefore, the implementation of a range of process engineering tools, such as modeling, sensitivity analysis, and optimization would allow the determination of the best operation conditions for the production of these polymers, ensuring a proper molecular weight and narrow molecular weight distributions (MWD).[2] Along with the final quality of the synthesised polymers, reduction of production costs needs to be simultaneously considered as well. In this scope, multiobjective optimization (MOO) techniques can be employed when working with simultaneous and opposing performance objectives commonly found in polymerization reactions. This methodology is based upon finding a set of equally good solutions, known as Pareto optimal solutions.[3] In the present work, we report a process engineering study for the batch synthesis of the biomass-derived polyesters poly(1,3-propylene succinate) (PPS) and poly(1,3-propylene 2,5-furandicarboxylate–co-1,3-propylene succinate (PPFPS). Firstly, the reaction modeling covers the estimation of kinetic parameters by fitting a predetermined polyesterification model to the experimental data. Next, the batch process simulation and MOO were performed in Aspen Plus™, concluding with the assessment of sustainability indicators for each case. The analysis for PET

has been included as a comparative petro-derived polyester reference. We focus solely on the chemical synthesis reactor since it is considered the core of any process.

2. Methodology

2.1. Synthesis of Biomass-Derived Polyesters

The polyesters were synthesized from 2,5-furan dicarboxylic acid (FDCA), 1,3-propanediol (PDO) and succinic acid (SA) in a four-neck round bottom flask (250 mL) or a single wall glass reactor (500 mL) by a two-step process comprising polyesterification and azeotropic distillation with xylene. The complete experimental procedure can be found in our previous work.[1] The structures of the biomass-derived polyesters are shown in Figure 1 and the concentrations of the monomers are summarized in Table 1.
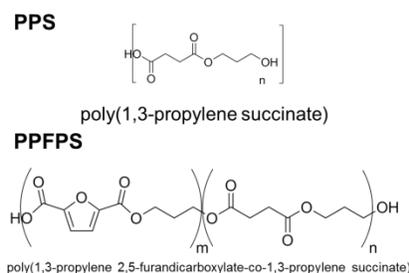

poly(1,3-propylene succinate)

poly(1,3-propylene 2,5-furandicarboxylate-co-1,3-propylene succinate)

Fig. 1: Chemical structures of the biomass derived polyesters.

Table 1: Composition of synthesized polyesters.

Polyester	Molar ratio diol:diacid	FDCA mol%	SA mol%
PPS	1.1	0	100
PPFPS 15/85	1.5	15	85
PPFPS 70/30	1.5	70	30
PPFPS 85/15	1.5	85	15

2.2. Development of Kinetic Model

For the simulation in Aspen Plus™, we considered the functional group approach and followed the procedure used by Seavey et al.[4] for PET. Firstly, the main species and segments are defined. The conventional species considered are water, PDO, SA, and FDCA. The diol and diacids polymerize to form the corresponding polyesters, which are composed of terminal (T-) and bound (B-) segments for both the diacids and the diols, as shown in Figure 2. As in the case of PET, two main reactions are considered: esterification or water formation and transesterification. The assumptions considered were equal reactivity hypothesis;[5] the rate coefficients k_i of the species are equal to those of the segments; and reversible reactions are disregarded. With the assumptions and species defined, Aspen Plus™ automatically generates a set of 12 reactions for homopolyesters and 24 for the PPPFS copolyesters. In order to estimate the reaction coefficients k_i, a polyesterification model from the literature was fitted to the experimental carboxylic acid data, which is calculated from the experimental acid value.[1] This model was proposed by Lehtonen,[6] and was considered because the kinetic parameters included in the ordinary differential equation were the ones required by Aspen Plus™ for the step-growth polymerization. The rate equation is then defined as Eq. (1):

$$r = k_o e^{\frac{-E_a}{RT}} \left(C_{COOH} C_{OH} - \frac{C_{COOR} \cdot C_{H_2O}}{K} \right) \tag{1}$$

Where k_o is the pre-exponential factor in kg·mol^{-1}min^{-1}; E_a is the activation energy in J·mol^{-1}; R is the universal gas constant in J·mol^{-1}K^{-1}; K is the equilibrium constant; C_{COOH}, C_{OH}, C_{H2O} and C_{COOR} are the concentrations of

carboxylic acid, hydroxyl, water and ester, respectively, in mol·kg^{-1}. Figure 3 shows that the experimental conversion is satisfactorily fitted to the esterification model throughout the entire reaction time
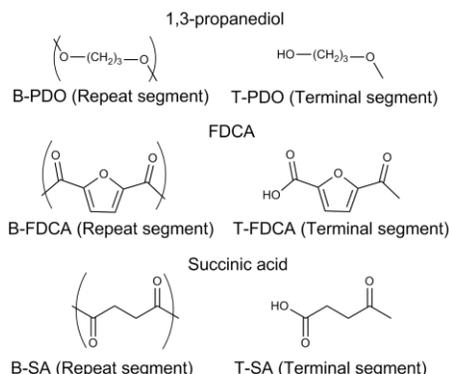

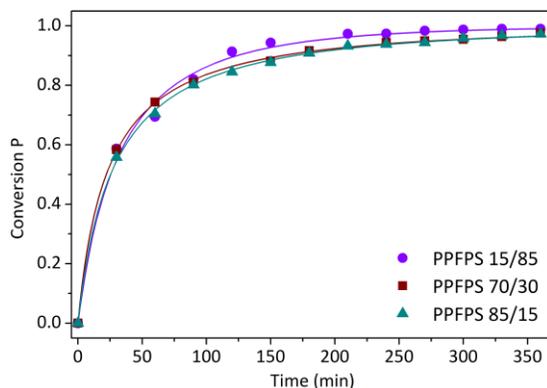Fig. 2: Chemical structures of the repeat and terminal segments.

.   Fig. 3: Conversion of COOH groups, fitted to the model.

2.3. Simulation and Multiobjective-Optimization

The two objective functions ψ_1 and ψ_2 considered for the batch biomass-derived polyesterification refer to both the polymer quality and the costs of production derived from energy usage as defined by equations 2 and 3 below:

$$\psi_1 = \max(DPN) \tag{2}$$

$$\psi_2 = \min(Q) \tag{3}$$

Where DPN is the number degree of polymerization and Q is the heat duty in kBTU·h^{-1}.

2.4. Sustainability Indicators

The simulations were assessed thus according to environmental, energy and economic bases in terms of common sustainability indicators for chemical processes.[7] We considered two indicators: Specific energy intensity (R_{SEI}) and global warming potential (GWP), which refer to the net energy used as primary fuel and total mass of CO_2 equivalents per mass of final polyester, respectively. The worst case scenarios for the indicators refer to R_{SEI} of 1.95×10^3 MJ·kg^{-1} and all GWP released. The estimation of the sustainability indicators after the optimization was done considering natural gas as base fuel under the Environmental Protection Agency (EPA) rule E9-5711, included in the Aspen Plus™ interface.

3. Results and Discussion

3.1. Simulation and Multiobjective Optimization (MOO)

The batch simulation and ϵ-constraint optimization performed in Aspen Plus™ for the different polyesters provided the optimum operation conditions and the results of the mass balances for each of the monomers, segments concentration profiles, energy balances, and polymer attributes such as number molecular weight M_n and DPN. We considered a production of 40 t·d^{-1} as the base case. The Polymer Non-Random Two Liquid (PolyNRTL) activity coefficient method was used for the thermodynamic properties coupled with the Van Kravelen group contribution method.[8] The molecular weight of most polyesters used in coatings range between 2 and 6 kDa.[9] Table 2 summarizes the efficient or compromise solutions obtained from the MOO as well as the sustainability indicators considered. The GWP results are normalized from 0 to 100% sustainability. The Pareto frontier for PPS is depicted in Figure 4a, whereas the M_n/DPN and segment concentration profiles are shown for PPFPS 70/30 (Figure 4b) and PPFPS 15/85 (Figure 4c), respectively. All the optimum process temperatures of our polyesters were in the range of 191-220 °C, while PET is processed well above that range, at 269 °C, which falls within the operating conditions found in the literature.[4] The simulated final M_n and DPN were around 4.2 kDa and 40, respectively, suitable for coil coatings. The polymeric attributes for PET were lower, with a final M_n of 3.6 kDa and degree of polymerization of 38. In terms of heat duty, although the energy consumption is similar between PET and our polyesters, the main advantage relies in terms of the sustainability indicators. They suggested that the production of PPFPS 70/30 releases less CO_2 among all polyesters, as its normalized GWP is 91% of sustainability, although PPFPS 15/85 is the most energy-efficient process, as the specific energy intensity is 1.60 MJ·kg^{-1}. The production of PET presented the highest energy consumption and CO_2 release among all the polymers studied (1.90 MJ·kg^{-1} and 88%, respectively) suggesting that our polyesters would be a sustainable and efficient alternative to conventional PET for the intended application.

Table 2: Composition of synthesized polyesters.

Polyester	Temperature, °C	M_n, kDa	DPN	Polymer, kg·hr^{-1}	Heat Duty, MJ·hr^{-1}	GWP, Normalized	R_{SEI} MJ·kg^{-1} polymer	R_{SEI} Normalized
PPS	191	4.2	43	1360	2200	0.89	1.80	0.092
PPFPS 15/85	212	4.2	43	1400	2200	0.90	1.60	0.082
PPFPS 70/30	220	4.0	43	1400	2200	0.91	1.70	0.087
PPFPS 85/15	215	4.0	42	1400	2300	0.90	1.70	0.087
PET	269	3.6	38	1280	2400	0.88	1.90	0.097

4. Conclusions

The process simulation and optimization were successfully implemented in Aspen Plus™ for the polyesterification of biomass-derived monomers FDCA, succinic acid and 1,3-propanediol. The kinetic parameters E_a, k_o, and K were estimated in Matlab™ for each polyester system by fitting the experimental batch data to a polyesterification model proposed in the literature and regressing the data using the weighting sum squares method. The *a* posteriori optimization ϵ-constraint method was followed to determine the utopia points and compromise solutions.

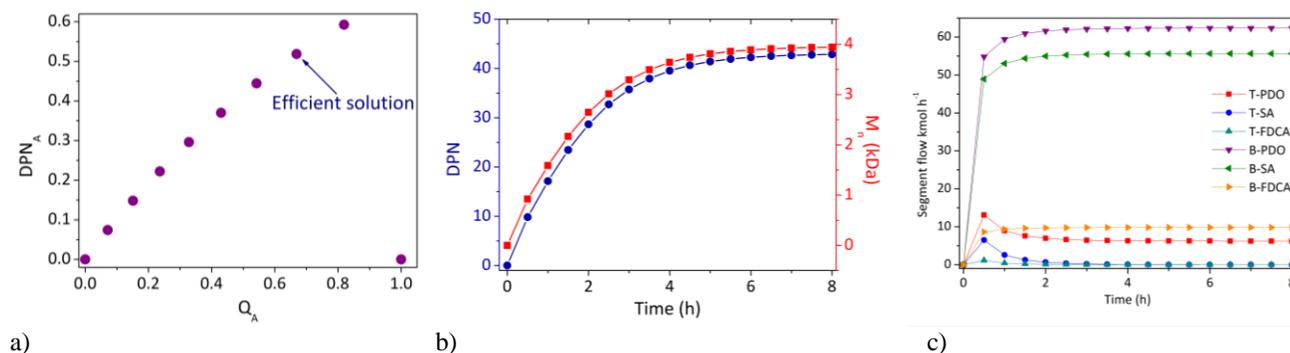a)   b)   c)

Fig. 4: a) Pareto frontier for PPS. b) DPN and Mn profiles for PPFPS 70/30. c) Segment flow profiles for PPFPS 15/85.

The optimum process temperatures were in the range of 191 °C to 215 °C whereas the processing temperature for PET was 269 °C. The number molecular weight M_n and degree of polymerization DPN of the polyesters were in the range of 4.0 and 4.2 kDa and 42-43, respectively, suitable for coating resins. The final production of about 1400 $kg_{polymer} \cdot h^{-1}$. PET targeted lower polymer quality, with M_n of 3.6 kDa and DPN of 38. The environmental impact of the processes was addressed by the principles of sustainability performance indicators, which showed that PET production releases more CO_2 and is the least energy efficient of the production processes. The present process engineering study for this biomass-derived family of polyesters provides and insightful and useful source for further polymerization process design and implementation stages. Different reactor configurations and biomass-derived polyesterification systems will be evaluated in the future.

Acknowledgements

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