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Simulation-based Analysis of Propylene Glycol Production from Lactic Acid

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Propylene glycol is an intermediate molecule with wide applications in the chemical industry. Its most successful renewable production technology is based on hydrogenolysis of glycerol, subproduct of the biodiesel industry, which has been commercially produced since the early 2010s. The biodiesel market, however, is highly dependent on government incentives and raises the fuel versus food debate. Other renewable raw materials that can be obtained from lignocellulosic sources, such as cellulose and lactic acid, have been studied for propylene glycol production through similar technology but focusing on catalyst development. In that regard, this work developed a conceptual design and simulation using Aspen Plus® for propylene glycol production from lactic acid. To assess its potential as feedstock, mass and energy balances were compared with those reported in the literature for glycerol-based propylene glycol. The results demonstrate that there is room for improvement towards a competitive lactic-acid based biorefinery, especially in terms of energy consumption.

1. Introduction

The growing interest in the replacement of petrochemicals and fuels with renewable equivalents has fostered research on new routes to enable this transition, especially those based on biochemical conversion. However, despite promising theoretical yields (Straathof, 2017), depending on the targeted product, current microorganisms have much lower performance than required to enable their commercial application. This is the case for glycols such as propylene glycol (1,2-propanediol, 1,2-PDO). So far, the highest reported yield is 0.48 g/g at very low productivity of 0.043 g/L/h (Jain, 2015).

Chemical catalysis has been an important player in renewables production. Bio-propylene glycol is commercially produced from biodiesel-derived glycerol since the beginning of the decade through hydrogenolysis reactions over metal catalysts (Cu, Ni, Ru). Nonetheless, the biodiesel market is highly dependent on government policies and subsidies and current hydrogenolysis catalysts require high-purity glycerol (Kong 2016).

Other feedstocks have been explored to produce 1,2-PDO through similar reactions, such as lignocellulosic biomass and glucose, but they still suffer from catalyst stability and low selectivity (Zheng *et al.*, 2017). Another promising intermediate for 1,2-PDO production is lactic acid (LA), because of its high theoretical yield from lignocellulosic sugars and its high reactivity to a variety of products (Dusselier *et al.*, 2013). However, research has been dedicated mostly to lab-scale studies and catalyst development.

In this context, this work aims to develop a preliminary conceptual design to assess the potential of lactic acid transformation to 1,2-PDO through process simulation, in order to obtain the main process parameters (material and energy balances) and identify process bottlenecks when compared to glycerol as a feedstock, which is an established process. The development of conceptual designs will allow a more thorough economic and environmental feasibility analysis of such processes.

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2. Methods

2.1 Process Description

Scenario LA-1

Lactic acid (88 wt%) is heated to 50 ºC and mixed with a recycle stream composed of water and unreacted LA, resulting in a feed stream of 38 wt% LA. H_2 enters the reactor (R) at 200 ºC and a molar ratio H_2/LA of **2.5**, resulting in a temperature profile of 112-161 ºC to avoid the undesired overhydrogenolysis of 1,2-PDO to propanols and propionic acid above 180 ºC (Cortright *et al.*, 2002). The resulting mixture (PROD) is separated in a flash drum (F1), after which the unreacted H_2 is compressed and heated to the required reactor inlet conditions. Given the high boiling point and the thermal sensitivity of LA (Komesu *et al.*, 2018) and the intermediate 1,2-PDO boiling point (188 ºC), in order to separate the 1,2-PDO product and unreacted LA, these are sent to a reactive distillation column (ACET). In the reactive distillation, 1,2-PDO reversibly reacts with excess acetaldehyde (AC/PDO = **8**) to produce 2,4-dimethyl-1,3-dioxolane (DMD), an acetal with a lower boiling point (92 ºC) (Dhale *et al.* 2004). Part of the bottom stream is recycled to the reactor to maintain the temperature profile and increase overall yield, and the distillate is separated in a distillation column (AC-REC) to recover the excess acetaldehyde.
The obtained DMD reacts with excess water (H_2O/DMD = **3**) in a reactive distillation column (HYDR), producing 1,2-PDO and acetaldehyde. Unreacted DMD and acetaldehyde are recovered through distillation (AC-DMD-R), while high-purity 1,2-PDO (99.5 mol%) is obtained in a final distillation (PDO-REC). The process flowsheet is represented in Figure 1.

Scenario LA-2

Lactic acid (88 wt%) at 25 ºC is mixed with H_2, which enters the reactor (R) at 200 ºC and a molar ratio H_2/LA of **10**, resulting in a reactor temperature profile of 97-180ºC. The resulting mixture (PROD) is separated in a flash drum (F1), after which the unreacted H_2 is compressed and heated to the required reactor inlet conditions. The liquid products are sent to a reactive distillation column (ACET). In the reactive distillation, 1,2-PDO reversibly reacts with excess acetaldehyde (AC/PDO = **7**) to produce 2,4-dimethyl-1,3-dioxolane (DMD). The obtained DMD reacts with excess water (H_2O/DMD = **3**) in a reactive distillation column (HYDR), producing 1,2-PDO and acetaldehyde. Acetaldehyde are recovered through distillation (AC-REC), while high-purity 1,2-PDO (99.5 mol%) is obtained in a final distillation (PDO-REC).

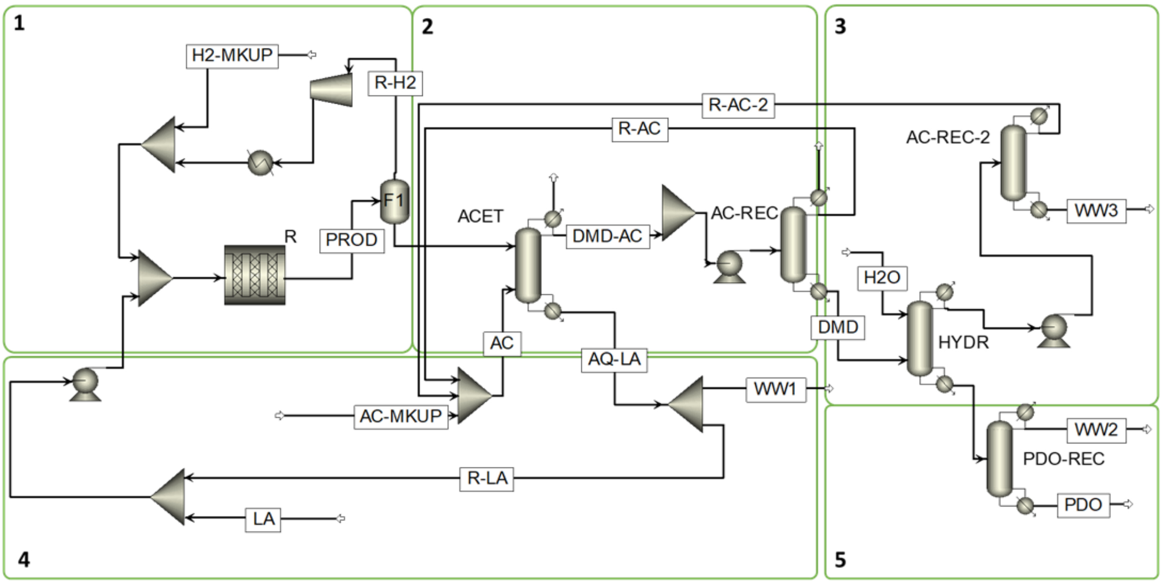

Figure 1: Process flowsheet for lactic acid hydrogenation simulation (Scenario LA-1): 1) Hydrogenation and H_2 recycle; 2) Acetalization and acetaldehyde recovery and recycle; 3) Acetal hydrolysis and acetaldehyde recycle; 4) Lactic acid recycle; 5) PDO purification.

2.2 Process Simulation

Simulations were performed using software Aspen Plus® v8.6, with UNIQUAC for liquid-phase activity and Redlich-Kwong Equation of State for vapor phase (UNIQ-RK) calculations. The pure component and binary interaction parameters employed were those available on the software database and those reported by Chopade *et al.* (2003) for DMD and water. When binary parameters were not available, they were estimated using UNIFAC group contribution method.
LA hydrogenolysis simulation was based on the kinetic model reported by Xi *et al.* (2011) for reaction over Ru/AC catalyst in trickle-bed reactors at 83 bar and do not consider the formation of other byproducts. The kinetic parameters are presented in Table 1 and the main simulation parameters employed are listed in Table 2. Flash temperature for H_2 recovery was determined in order to obtain a 99 mol % H_2 stream.

Table 1: Kinetic model for lactic acid hydrogenolysis over Ru (Xi et al. 2011)

Reaction			Rate Equation		
$LA + 2H_2 \overset{r_1}{\rightarrow} PDO + H_2O$			$r_1 = \frac{k(C_{LA})_L(C_{H_2})_L}{\left(1 + K_{H_2}(C_{H_2})_L + K_{LA}(C_{LA})_L\right)^2}$		
Rate Parameters					
$k = k_0 \exp\left(-\frac{E_A}{RT}\right)$		$K_{H_2} = K_0 \exp\left(-\frac{\Delta H}{RT}\right)$		$K_{LA} = K_0 \exp\left(-\frac{\Delta H}{RT}\right)$	
k_0 ($(m^3)^2$/kmol/h)	E_A (kJ/mol)	K_0 (m^3/kmol)	ΔH (kJ/mol)	K_0 (m^3/kmol)	ΔH (kJ/mol)
0.007	12.4	1.92×10^{-11}	-79.8	8×10^{-8}	-47.8

Table 2: Main equipment and simulation conditions

Equipment (Block)	Parameters	
	LA-1	LA-2
R (RPlug)	Adiabatic:; D = 1.1 m; L = 4.4 m; Catalyst mass = 1700 kg; Pressure Drop – Ergun equation; Dp = 1.368 mm; ρp = 800 kg/m^3; P0 = 83 bar (Xi *et al.* 2011)	
	T = 112 – 161°C	T = 97 – 180 °C
F1 (Flash2)	P = 82.8 bar; T = 60 °C	P = 83 bar, T = 60 °C
ACET (RadFrac)	10 stages (3-9 reactive); RR = 0.52; D/F = 0.52; Liquid holdup = 1350 L; D = 1.7 m; P = 2.5 – 2.54 bar	12 stages (3-11 reactive) RR = 0.6; D/F = 0.77; Liquid holdup = 1200 L; D = 1.62 m; P = 1.2 – 1.27 bar
AC-REC (RadFrac)	20 stages; RR = 0.42; D/F = 0.66; P = 3 – 3.13 bar; D = 1.09 m	20 stages; RR = 0.407; D/F = 0.754; P = 3 – 3.13 bar; D = 1.11 m
HYDR (RadFrac)	20 stages (2-15 reactive); RR = 4; D/F = 0.496; Liquid holdup = 600 L; P = 1 – 1.06 bar; D = 1.11 m	20 stages (2-15 reactive); RR = 4; D/F = 0.5; Liquid holdup = 600 L; P = 1 – 1.06 bar; D = 1.12 m
AC-REC-2 (RadFrac)	14 stages; RR = 1; D/F = 0.51; P = 3 – 3.09 bar; D = 0.58 m	14 stages; RR = 1.13; D/F = 0.5; P = 3 – 3.09 bar; D = 0.59 m
PDO-REC (RadFrac)	8 stages; RR = 0.572; D/F = 0.714; P = 1 – 1.05 bar; D = 0.59 m	8 stages; RR = 0.255; D/F = 0.545; P = 1 – 1.05 bar; D = 0.577 m

Propylene glycol reversible acetalization occurs with excess aldehyde, according to Eq (1). Both acetalization and hydrogenolysis reactive distillation simulations were performed based on the kinetics reported by Dhale *et al.* (2004), according to Eqs (2) and (3), obtained using structured packing Katapack®-S filled with cationic exchange resin Amberlyst 15. For liquid holdup, packing sizing and pressure drop calculations in the simulator, an HETP of 1 m, surface area of 125 m^2/m^3 (Coker, 2010) and void fraction of 0.622 (Kolodziej *et al.*, 2002) were assumed. For acetaldehyde recovery distillations, both columns were designed (number of stages, reflux ratio and feed stage) using Winn Underwood Gilliland shortcut design calculation (DSTWU block) to obtain a 99 mol % acetaldehyde distillate stream with 98% recovery, whose results were used to perform more rigorous simulation to achieve both specifications (RADFRAC block). In the final PDO purification distillation (PDO-REC), shortcut design was also used to recover 99.95% of the feed PDO with 99.5 mol % purity and also used in rigorous simulation to achieve the required specifications.

$$PDO + AC \underset{Hydro}{\overset{Acet}{\rightleftarrows}} DMD + H_2O \tag{1}$$

$$r_{Acet}\left(\frac{kmol}{m^3\ s}\right) = 0.3\exp\left(-\frac{1515}{T}\right)(C_{PDO})_L(C_{AC})_L \tag{2}$$

$$r_{Hydro}\left(\frac{kmol}{m^3\ s}\right) = 1.8\exp\left(-\frac{2942}{T}\right)(C_{DMD})_L(C_{H_2O})_L \tag{3}$$

3. Results and Discussion

Table 3 presents the main results for the proposed processes, assuming an annual capacity of 20,000 ton/y of 1,2-PDO (2478 kg/h). Due to lactic acid polymerization undesired reactions and catalyst deactivation at high temperatures, two approaches can be used in order to dilute the feedstock and reduce the temperature increase due to the heat of reaction. The first (LA-1) consists on using very dilute LA aqueous solutions (typical conditions in the literature are usually 1 M solutions (ca. 10 wt %) (Xi *et al.*, 2011). However, large excess water leads to high energy consumption and low DMD yield in the reactive distillation step because it shifts the reaction equilibrium (Eq. (1)) towards 1,2-PDO. Therefore, more concentrated feedstock solutions can improve the reactive distillation efficiency. However, more detailed experimental studies and kinetic models are necessary to establish the maximum LA concentration allowed for hydrogenation.

The second approach (LA-2) uses high hydrogen to lactic acid molar ratios, acting as water does in the previous case. In scenario LA-2, the H_2/LA ratio was determined based on the temperature profile along the reactor for scenario LA-1. Using excess hydrogen enabled a lower excess of acetaldehyde in the following acetalization step (ACET), which in turn resulted in a reduction of 15 % in heating demand in this step. Given that water and acetaldehyde are only partially miscible (Dhale *et al.,* 2004), the use of more concentrated LA solutions might be challenging for reactive distillation, because lower water and higher acetal concentrations along the column incurs in the formation of two liquid phases. In order to prevent the formation of these two-phases, lower operating pressure is required in the ACET reactive column, leading to lower condenser temperatures (30 ºC at 1.2 bar, versus 50 ºC at 2.5 bar). Therefore, the use of reactive distillation for 1,2-PDO purification requires more thorough studies in order to assess its feasibility in large-scale processes.

Table 3: Main equipment energy requirement for 1,2-PDO production from LA

Equipment (Block)	Conversion (mol %)		Energy Requirement (Heating – H, Cooling – C)			
	LA-1	LA-2	LA-1		LA-2	
			H (MW)	C(MW)	H (MW)	C(MW)
R (RPlug)	98.24	99.7	-	-	-	-
F1 (Flash2)	-	-	-	1.50	-	1.16
ACET (RadFrac)	99.7	98.6	8.74	4.18	7.53	4.12
AC-REC (RadFrac)	-	-	2.49	2.31	2.64	2.13
HYDR (RadFrac)	91.73	92.57	0.58	4.16	0.66	4.19
AC-REC-2 (RadFrac)	-	-	0.69	0.49	0.72	0.52
PDO-REC (RadFrac)	-	-	0.75	0.61	0.71	0.57

Table 4 presents a comparison of the mass and energy balances reported in the literature by Gonzalez-Garay *et al.* (2017) and those obtained in this work. From the results, there is a clear indication of the large impact feedstock concentration has on the results. While scenario GLY-1 uses a 75 wt% glycerol solution, scenario GLY-2 considers a high purity glycerol feed, both with an assumed H_2/GLY molar ratio of 5, which is much lower than the one experimentally reported by Akiyiama *et al.* (2009), of 141 for scenario GLY-2.

The results also demonstrate that the reactive distillation steps have a large energy consumption (>18 MJ/kg), driven by the high excess of acetaldehyde and water required. These steps are necessary in order to separate the 1,2-PDO product from the unreacted lactic acid by converting it into a product more volatile than water, which results in a bottom stream of dilute lactic acid in water and a top product of excess acetaldehyde and DMD. However, the results here presented were not optimized or heat-integrated, as in the case of Gonzalez-Garay *et al.* (2017) results (>4 MJ/kg). Nonetheless, the need for complex separation steps makes the lactic acid-based biorefinery very challenging, both in terms of lactic acid production and its transformation to other materials (Dusselier *et al.*, 2013).

The production of high-purity lactic acid also requires reactive distillation and removal of large amounts of water, with an estimated heating demand of 16.54 MJ/kg (Su *et al.*, 2013). Therefore, if 1,2-PDO were produced directly from dilute, lower purity lactic acid, as proposed by Binczarski *et al.* (2016), who treated lactate from sugar beet pulp fermentation broth through adsorption on activated carbon to be converted into 1,2-PDO over Ru catalyst, achieving high yield (87.7 mol %). This could represent a large reduction in the feedstock cost.

Table 4: Comparison of material and energy balances required to produce 1 kg of 1,2-PDO

	GLY-1 (Gonzalez-Garay *et al.*, 2017)	GLY-2 (Gonzalez-Garay *et al.*, 2017)	LA-1 (this work)	LA-2 (this work)
Raw materials				
Glycerol sol. 90 wt%	1.4238	1.3707	-	-
Lactic acid 88 wt%	-	-	1.691	1.696
Molar yield (%)	94.6	98.09	0.912	0.910
H_2	0.0297	0.0321	0.058	0.058
Water	0.0093	-	0.371	0.480
Acetaldehyde	-	-	0.097	0.061
Wastewater	0.4305	0.3798	1.218	0.648
Heating demand (MJ)	4.635	4.819	18.831	17.965
Cooling demand (MJ)	5.970	6.157	18.833	18.085
Electricity (kW)	0.0578	0.0582	0.020	0.012

4. Conclusions

In this work, a conceptual design for the production of 1,2-propanediol from lactic acid and its simulation were developed in order to provide a preliminary assessment of its feasibility in terms of commercial application. Both experimental results published in the literature and the simulation indicate that 1,2-propanediol can be obtained from this feedstock with high overall yield (>91 mol%). However, its high energy requirement (18 MJ/kg of heating demand versus 4.6 MJ/kg from glycerol) indicate that more thorough studies are necessary in order to obtain more competitive process configurations and determine optimal reaction conditions. Process optimization and heat-integration studies in addition to economic analyses can indicate promising pathways for this application.

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