**Process designs for converting biobased propylene glycol to acrylic acid via lactic acid and allyl alcohol**

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**Highlights**

* Techno-economical evaluation per route shows that reaction section is critical part
* Comparison between two processes to conclude which is inherently favored
* Separation section is remarkably similar for both processes
* Economic evaluation shows need for 50% drop in PG price for an economically viable process

**1. Introduction**

The price of Propylene Glycol (PG) is expected to drop dramatically with the increasing use of biomass as feedstock, since it is a byproduct of sugar hydrogenolysis [1, 2]. This could make PG a promising raw material to be upgraded to Acrylic Acid (AcrA). Two process designs for the conversion of PG to AcrA are proposed, either by oxidation of PG to lactic acid (LA) and dehydration to AcrA or by dehydration of PG to allyl alcohol (AA) and oxidation to AcrA [3] . A conceptual design for both routes was proposed, followed by a techno-economical evaluation on a basic engineering level. Both processes were evaluated individually on heat integration, sustainability, CAPEX and OPEX. The minimum PG price to reach economic break-even for the two routes was compared for a capacity of 150 kta for glacial acrylic acid (>99.5 % purity) from a 50/50 mol% water/PG feed.

**2. Methods**

Douglas methodology is followed - with different levels of detail, based on hierarchy of decision. During the process, several options are evaluated and the best alternative is chosen based on theoretical analysis and simulated results[4]. Consequently, a Process Flow Diagram is developed and evaluated using Aspen Plus V10 software. An improved heat integration system is suggested for both processes using pinch analysis. Finally, an economic analysis is performed to calculate the CAPEX and OPEX related to the process.

**3. Results and discussion**

Both flowsheet designs start with two reactors without a separation and recycle in between. Due to limited information of all the reactions, the same overall reaction yield for both processes is assumed in the paper. Despite the various by-products, the separation section for both processes is remarkably similar. Water removal is the key function of the first separation unit which in both processes is a liquid-liquid extractor. For the LA route, DIPE was found to be the most optimal solvent, whereas for the AA route octanol was found to be the most suitable, based on energy consumption and solvent recovery. Further purification is performed by (vacuum) distillation. AcrA recovery for the LA route and AA route are 99.7% and 99.1%, respectively, showing only minor differences in the separation.

Significant differences can be found in the heat integration. A high-temperature oxidation reaction (325 °C) in AA route provides valuable energy and covers almost all the hot utilities needed. The liquid phase oxidation in the LA route results in availability of energy at 80 °C, which is too low for steam generation and needs cooling by an external utility. Evaporation of the product stream in the LA route is expected to give polymerization issues. A novel spray evaporator unit was proposed to solve this problem by inducing instantaneous evaporation of both LA and water. This is however an expensive and high energy consuming unit.

Both processes will profit tremendously by reducing the required amount of water dilution. Table 1 shows the water usage per ton product for both routes. Less water present in the system reduces the volume of operation units, lowering the CAPEX and OPEX significantly. The difference in solvent loss (Table 1) between the two routes is mainly the result of a difference in the thermodynamic modelling of the extraction.

For both routes, the reactor section is a major cost contributor accounting roughly 50% of the investment. However, since the reactor design suffers from a lack of information, this cost factor is highly uncertain. Advances in the reaction section, such as higher catalytic performance, might lead to a significant reduction of the total investment. The largest difference between the routes is in the use of an air separation unit for the LA route, whereas the AA route uses air. This leads to a preliminary estimate of the total investment of 203 M$ for the LA route and 170 M$ for the AA route. Raw materials are by far the largest costs for operation in both routes. The AA route benefits from lower costs for utilities, since heat can be integrated better and the LA route uses a spray evaporator, which is a large energy consumer. In the end the necessary break-even price of PG on a preliminary basis for the LA and AA route is 940 $/ton PG and 1070 $/ton PG, respectively. With the current uncertainty margins of ± 30% in all economic calculations, a conclusion concerning a more attractive process would be premature.

**Table 1.** Important comparison parameters for both designs.

|  |  |  |
| --- | --- | --- |
| Description | LA route | AA route |
| Acrylic Acid recovery (%) | 99.7 | 99.1 |
| Heat integrated (MW) | 55 | 89 |
| Hot Utility (MW) | 4 | 13 |
| Cold Utility (MW) | 141 | 52 |
| Water usage (ton water/ton product) | 5.1 | 3.9 |
| E-factor (kg waste/kg product) | 1.1 | 1.0 |
| Solvent losses (kg/ton product) | 139 | 23 |

**4. Conclusions**

The constructed processes show similarities regarding the flowsheet, proposed unit operations, CAPEX and sustainability. Liquid-Liquid extraction is used in both processes as the main separation unit due to the presence of large amounts of water. The reaction section design suffers from a lack of information but forms a critical difference between the two routes. The break-even feedstock price of PG is quite similar for both routes at this point. Further investigations should show which process is more feasible. Producing AcrA via high temperature dehydration and subsequent high temperature oxidation is shown to be inherently favoured, due to the opportunity to integrate the reaction heat available at high temperature. To conclude, the price of PG has to drop dramatically to replace the conventional production of acrylic acid with one of the routes proposed here.

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**References**

1. Ruppert, A.M., K. Weinberg, and R. Palkovits, *Hydrogenolysis Goes Bio: From Carbohydrates and Sugar Alcohols to Platform Chemicals.* Angewandte Chemie International Edition, 2012. **51**(11): p. 2564-2601.

2. Lahr, D.G. and B.H. Shanks, *Effect of sulfur and temperature on ruthenium-catalyzed glycerol hydrogenolysis to glycols.* Journal of Catalysis, 2005. **232**(2): p. 386-394.

3. Pramod, C.V., et al., *Bio-based acrylic acid from sugar via propylene glycol and allyl alcohol.* Catalysis Science & Technology, 2018. **8**(1): p. 289-296.

4. Perkins, J.D., *Conceptual design of chemical processes J. M. Douglas, McGraw-Hill, New York, 1988. pp. xviii + 601, . ISBN 0-07-017762-7.* Journal of Chemical Technology & Biotechnology, 1989. **46**(3): p. 249-249.