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Reactive Extraction for Downstream Separation of 1,3-Propanediol

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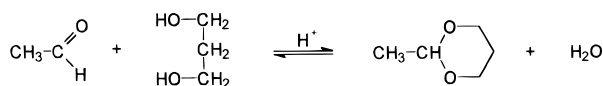
The downstream separation of 1,3-propanediol from dilute aqueous solution was studied. A process combining reversible reaction of 1,3-propanediol with acetaldehyde to 2-methyl-1,3-dioxane and a simultaneous extraction of the product by organic solvent appears to be technically feasible and attractive. The dioxane yield was 91–92%, the overall conversion of 1,3-propanediol was ca. 98%, and recovery of dioxane into the organic extractant was 75%.

Introduction

1,3-Propanediol (1,3-PD) is a chemical intermediate used in organic synthesis and as a monomer for the production of biodegradable polymers (1). Currently its relatively small-scale production is based on acrolein or ethylene oxide, petroleum derivatives. Recent industrial efforts to commercialize a poly(propylene terephthalate), 1,3-PD-based polyester (2, 3) are expected to boost a demand for this chemical.

The production of 1,3-PD by a biological route is potentially an attractive process. The microbial conversions of glycerol to 1,3-PD by bacteria from several genera including *Citrobacter*, *Clostridia*, *Enterobacter*, and *Klebsiella* have already been intensively studied (4–7). This bioconversion is of increasing interest as a result of the growing volume of glycerol generated by the oleochemical industry.

The final concentration of 1,3-PD in the fermentation broth is kinetically constrained to about 65–70 g/L (5, 8, 9). Most recently, Cameron et al. (9) reported on the metabolic engineering approach, which allowed a final 1,3-PD titer of about 100 g/L. Bearing in mind the low volatility and hydrophilic properties of 1,3-PD, the recovery of this diol from the complex and dilute fermentation broths is critical for the development of a commercially viable process. The replacement of conventional distillation techniques by the energy efficient solvent extraction may significantly reduce the cost of the product separation. However, the distribution of 1,3-PD into extraction solvents appears to not be good enough (10) to make this approach efficient. Another way to tackle this problem is to convert 1,3-PD into a substance without hydroxyl groups and then to recover it by means of liquid extraction. A suitable reaction is presented below. It involves acid-catalyzed, reversible reaction of 1,3-PD with acetaldehyde, leading to 2-methyl-1,3-dioxane (2MD). A similar processing strategy has already



been successfully applied for the recovery of 1,2-propanediol from dilute streams (11).

The preliminary results of investigations of extractive reaction approach for the separation of 1,3-PD from a dilute, aqueous solution are presented in this research note.

Materials and Methods

Materials. Acetaldehyde (99%), 1,3-propanediol (98%), ethylbenzene (99%), *o*-xylene (97%), toluene (99.5%+), and Dowex 50-WX4-200 ion-exchange resin were provided by Aldrich. Amberlite IR-120 (H⁺), a strongly acidic cation-exchange resin, and a 4 Å molecular sieve were obtained from Fluka. The resins were used as obtained. Other chemicals used were purchased from commercial suppliers at the highest available purity.

Preparation of 2-Methyl-1,3-dioxane. The reaction was carried out in a 250-mL round-bottom flask, equipped with a reflux condenser, a dropping funnel, and a thermometer. A mixture of 100 g (1.32 mol) of 1,3-PD, 12.5 g of Dowex ion-exchange resin, and 6.25 g of potassium bromide was stirred in the reaction vessel immersed in an ice bath. A 75-mL (1.34 mol) volume of acetaldehyde was slowly added to the mixture, to avoid boiling as the exothermic reaction proceeded. The stirring was continued for 20 min in the ice bath and then for 1 h at room temperature. The ion-exchange resin and potassium bromide were separated from the reaction mixture by filtration. The permeate was allowed to separate into two layers: a top organic contained mainly 2MD, and the bottom consisted of unreacted substrates. The two liquid phases were separated using the separatory funnel. Then the organic phase was dried over a 4 Å molecular sieve for about 17 h. The dried organic phase was shaken with Na₂CO₃ to remove acid residues. Following the filtration, the liquid phase was distilled on the Vigreux column at atmospheric pressure. The distillation produced 32.88 g of 2MD (0.32 mol) with the boiling point in the range of 111–112 °C. The purity of the dioxane was 99% (GC).

Extractant Selection. Potential extractants for 2MD were screened by means of the ESP program (12), which uses the UNIFAC group contribution method (13) to calculate multicomponent liquid–liquid equilibria. This program has already been found to be very effective in the selection of suitable solvents in related situations, e.g., extractive biocatalysis and extractive fermentation (14–16). The ranking focused on the mass distribution

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Table 1. Extraction Characteristics of Selected Solvents with Calculated Mass Distribution Ratios for 2-Methyl-1,3-dioxane (D_{2MD}), 1,3-Propanediol ($D_{1,3-PD}$), and Acetaldehyde (D_{MeCHO})

| extractant | D_{2MD} | $D_{1,3-PD}$ | D_{MeCHO} | bp (°C) | water solubility (wt %) | density (kg/m ³) |
|------------------|-----------|--------------|-------------|---------|-------------------------|------------------------------|
| <i>o</i> -xylene | 47.17 | 0.001 | 0.29 | 144.4 | 0.01 | 880 |
| toluene | 60.74 | 0.003 | 0.49 | 110.6 | 0.05 | 866 |
| ethylbenzene | 19.49 | 0.003 | 0.88 | 136.2 | 0.01 | 866 |

coefficient D , which is crucial for determining the viability of the liquid extraction process.

Reactive Extraction Experiments. Equal volumes (50 mL) of an appropriate organic solvent and an aqueous solution containing 39.95 or 59.60 g of 1,3-PD/L and 235 or 352 g of acetaldehyde/L were stirred vigorously in the equipment described in the previous section. The temperature was maintained at 31.5 or 40 °C. The reaction was catalyzed by a Dowex or Amberlite ion-exchange resin. Samples of the two-phase mixture were taken regularly for GC analysis. 2MD was analyzed in both phases, and 1,3-PD was determined in the aqueous phase only. The analysis was performed on a HP5890 series II gas chromatograph equipped with a thermal conductivity detector and a 30-m HP-1 column (0.53 mm diam, 0.88 μ m film thickness). The injector and detector were set at 250 and 300 °C, respectively. The oven temperature was programmed from 70 to 200 °C. Helium was used as a carrier gas. Data acquisition and processing were carried out using a Millennium 2010 chromatography manager (Waters, Milford, MA).

Results and Discussion

Extractant Selection. The largest distribution ratios for 2MD, D_{2MD} , have been obtained for several chlorinated compounds. However, they were excluded because of the relatively high cost. A closer inspection of the ESP ranking revealed that aromatic hydrocarbons might also be applied in the proposed reactive extraction process,

similarly as they were in the separation of 1,2-propanediol from a dilute aqueous solution (11). These compounds exhibit fairly large values of D_{2MD} , low affinity for acetaldehyde and 1,3-PD, and low water solubility. The first property allows reduction of the extractant flow rate, and the second allows as much acetaldehyde as possible in the aqueous reaction phase. The calculated distribution ratios between the organic and aqueous phases for the compounds of interest are given in Table 1.

Extractive Reaction Experiments. The initial experiment was carried out without extractant to examine the kinetics of the 2-methyl-1,3-dioxane formation. The reaction was catalyzed by a Dowex resin, added in an amount of 1, 2.5, or 5 g, i.e., 20, 50, or 100 g of resin per L of the aqueous solution, and the initial concentration of 1,3-PD in the reaction system was 59.6 g/L. In all cases conversion was in the range of 91–94%. The time plot of the dioxane and 1,3-PD concentrations during the run with 1 g of catalyst is shown in Figure 1. As can be seen the reaction attains a near-equilibrium state in ca. 20 min. A similar behavior was also observed in the experiments performed at higher catalyst concentrations and at lower temperatures. In the latter cases conversions were a bit larger, up to 96%, and this behavior is typical for exothermic reactions. As the mechanism of reaction is not clear, one cannot rule out the formation of byproducts. The chromatographic analysis performed during the course of reaction revealed that this indeed occurs. However, attempts to identify the compound proved unsuccessful.

Preliminary extractive reaction experiments have been performed using the selected aromatic hydrocarbons, i.e., ethylbenzene, toluene, and *o*-xylene. As can be seen from Figure 1 the conversion achieved in the process with *o*-xylene was 98%, and the yield was ca. 92%. As could be expected, the extraction shifted the equilibrium position, and this resulted in the larger conversion. The extraction equilibrium was attained in ca. 10–15 min. The recovery of dioxane into *o*-xylene was 70–75%. The rate of reaction, catalyzed by a Dowex resin, appeared

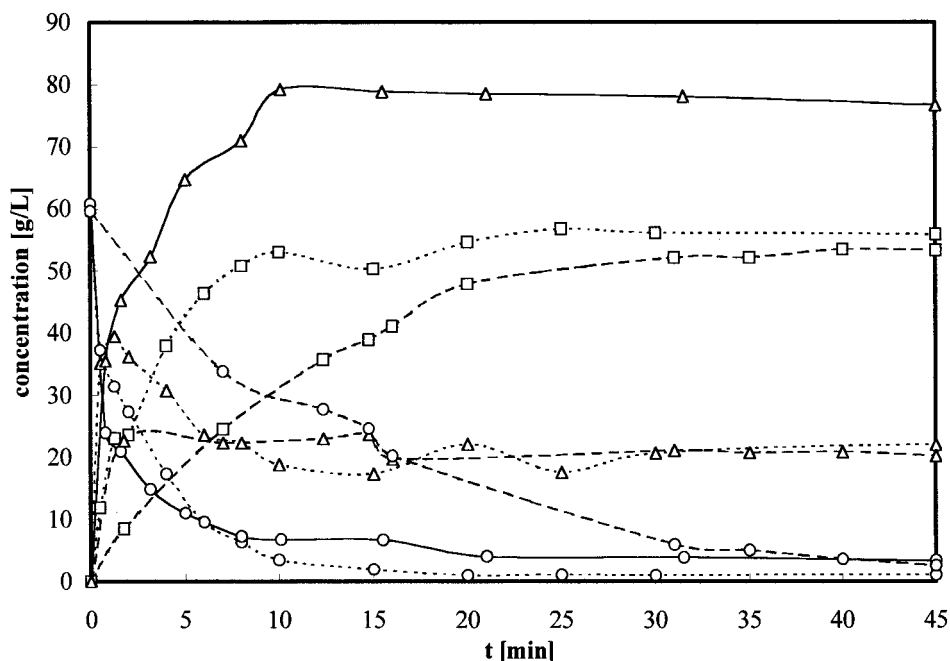


Figure 1. Time courses of the reaction of 1,3-PD with acetaldehyde (solid lines) and of the reactive extraction catalyzed by Dowex (---) or Amberlite (- - -) resin using *o*-xylene as an extractant at 40 °C. Symbols: Δ , aqueous phase 2MD concentration; \square , organic phase 2MD concentration; \circ , aqueous phase 1,3-PD concentration.

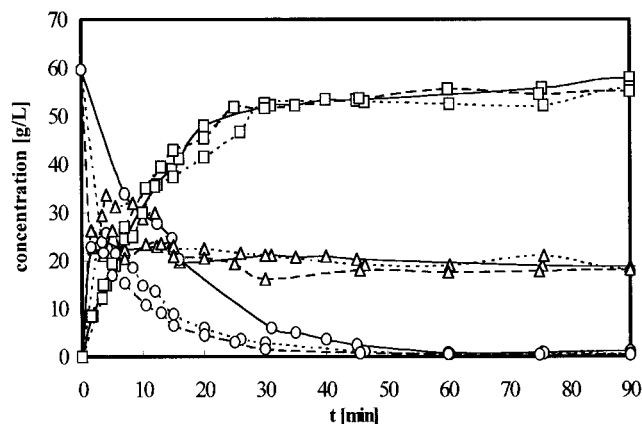


Figure 2. Time plots of dioxane and 1,3-PD concentrations during the reactive extraction process with different extractants (— *o*-xylene, ---- ethylbenzene, - - - toluene) at 40 °C. Initial concentration of 1,3-PD: 59.6 g/L. Symbols as in Figure 1.

to be higher than that of the one catalyzed by Amberlite. Despite notable differences in the reaction kinetics, the overall conversions and the obtained extraction efficiencies (the ratio of the mass of dioxane in the organic phase to the total mass of dioxane produced) were almost the same. However, owing to the higher cost of a Dowex resin, the Amberlite catalyst was used in the subsequent experiments. As the higher concentration of the catalyst appeared to have little bearing on the kinetics of the extractive reaction process, the experiments were carried out using 1 g of catalyst.

Figure 2 presents the time plot of the extractive reaction process at 40 °C using three different organic solvents. As can be seen, the final concentrations of dioxane in the aqueous and organic phases are almost the same, regardless of the extractant applied. The extraction efficiency into *o*-xylene, ethylbenzene, and toluene was 75%, 72%, and 76%, respectively. The conversion was 98–99%, and the yield was 91–92%. The extraction equilibrium was attained in ca. 10–20 min. The similar values of conversions and extraction efficiencies were obtained from the experiments carried out at 31.5 °C. Thus, the choice of the latter temperature may be recommended.

A series of experiments has been also performed for 1,3-PD concentration representing a typical composition of the fermentation broth from the bioconversion of glycerol, i.e., 39.95 g/L, which would correspond to 57.2 g of 1,3-PD per L of aqueous solution (5). The results are given in Figure 3. The overall conversions were ca. 98%, and the recovery of dioxane into the organic phase was 69%, 71%, and 74% for *o*-xylene, ethylbenzene, and toluene, respectively.

The results obtained clearly demonstrate that the selected solvents show similar extraction potentials for the separation of 2-methyl-1,3-dioxane. However, the use of a higher-boiling solvent such as *o*-xylene or ethylbenzene should facilitate the easier, downstream separation of dioxane from the organic phase.

In conclusion, the experiments performed have shown that the conversion of 1,3-propanediol to 2-methyl-1,3-dioxane combined with the simultaneous separation of the product from the reaction mixture by liquid extraction is technically feasible. The aromatic hydrocarbons function well as extractants. The dioxane separated from the organic solvents could be hydrolyzed to 1,3-propanediol. The reactive extraction approach can be incorporated into the overall downstream separation scheme for the recovery of 1,3-propanediol from the dilute aqueous streams

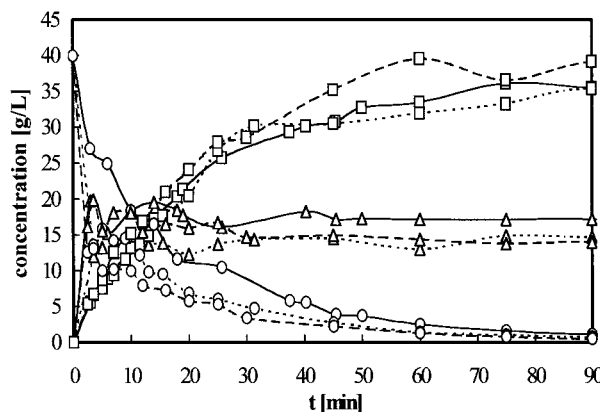


Figure 3. Time plots of dioxane and 1,3-PD concentrations during the reactive extraction process with different extractants (— *o*-xylene, ---- ethylbenzene, - - - toluene) at 31.5 °C. Initial concentration of 1,3-PD: 39.95 g/L. Symbols as in Figure 1.

generated by the fermentation processes. The research on the complete evaluation of the downstream separation of 1,3-propanediol from the fermentation broths is under way in our laboratory.

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References and Notes

- (1) Witt, U.; Müller, R.-J.; Augusta, J.; Widdecke, H.; Deckwer, W.-D. Synthesis, Properties and Biodegradability of Polyesters Based on 1,3-Propanediol. *Macromol. Chem. Phys.* **1994**, *195*, 793–802.
- (2) Potera, C. Genencor & DuPont Create "Green" Polyester. *Genet. Eng. News* **1997**, *17* (June 1), 17.
- (3) McCoy, M. Chemical Makers Try Biotech Paths. *Chem. Eng. News* **1994**, *22*, (June 2), 13–19.
- (4) Forsberg, W. C. Production of 1,3-Propanediol from Glycerol by *Clostridium acetobutylicum* and other *Clostridium* species. *Appl. Environ. Microbiol.* **1987**, *53*, 639–643.
- (5) Saint-Amans, S.; Perlot, P.; Goma, G.; Soucaille, P. High Production of 1,3-Propanediol from Glycerol by *Clostridium butyricum* VPI 3266 in a Simple Controlled Fed-Batch System. *Biotechnol. Lett.* **1994**, *16*, 831–836.
- (6) Barbirato, F.; Bories, A.; Camarasa-Claret, C.; Grivet, J. P. Glycerol Fermentation by a New 1,3-Propanediol Producing Microorganism: *Enterobacter agglomerans*. *Appl. Microbiol. Biotechnol.* **1995**, *43*, 786–793.
- (7) Biebl, H.; Zeng, A.-P.; Menzel, K.; Deckwer, W.-D. Fermentation of Glycerol to 1,3-Propanediol and 2,3-Butanediol by *Klebsiella pneumoniae*. *Appl. Microbiol. Biotechnol.* **1998**, *50*, 24–29.
- (8) Zeng, A.-P.; Biebl, H.; Deckwer, W.-D. Microbial Conversion of Glycerol to 1,3-Propanediol: Recent Progress. In *Fuels and Chemicals from Biomass*; Saha, B. C., Woodward, J., Eds; ACS Symposium Series; American Chemical Society: Washington, DC, 1997; Vol. 666, pp 264–279.
- (9) Cameron, D. C.; Altaras, N. E.; Hoffman, M. L.; Shaw, A. J. Metabolic Engineering of Propanediol Pathways. *Biotechnol. Prog.* **1998**, *14*, 116–125.
- (10) Malinowski, J. J. Evaluation of Liquid Extraction Potentials for Downstream Separation of 1,3-Propanediol. *Biotechnol. Tech.* **1999**, *13*, 127–130.

- (11) Broekhuis, R. R.; Lynn, S.; King, C. J. Recovery of Propylene Glycol from the Dilute Aqueous Solutions via Reversible Reaction with Aldehydes. *Ind. Eng. Chem. Res.* **1994**, *33*, 3230–3237.
- (12) Kollerup, F.; Daugulis, A. J. Ethanol Production by Extractive Fermentation—Solvent Identification and Prototype Development. *Can. J. Chem. Eng.* **1986**, *64*, 598–600.
- (13) Magnussen, T.; Rasmussen, P.; Fredenslund, A. UNIFAC Parameter Table for Prediction of Liquid–Liquid Equilibria. *Ind. Eng. Chem. Process Des. Dev.* **1981**, *20*, 331–339.
- (14) Bruce, L. J.; Daugulis, A. J. Solvent Selection Strategy for Extractive Biocatalysis. *Bioetchnol. Prog.* **1991**, *7*, 116–124.
- (15) Daugulis, A. J.; Axford, D.; Ciszek, B.; Malinowski, J. J. Continuous Fermentation of High-Strength Glucose Feeds to Ethanol. *Biotechnol. Lett.* **1994**, *16*, 637–642.
- (16) Malinowski, J. J.; Daugulis, A. J. Liquid–Liquid and Vapour–Liquid Behaviour of Oleyl Alcohol Applied to Extractive Fermentation Processing. *Can. J. Chem. Eng.* **1994**, *71*, 431–436.

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