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Article

Reactive Extraction Process for Separating 2,3-Butanediol from Fermentation Broth

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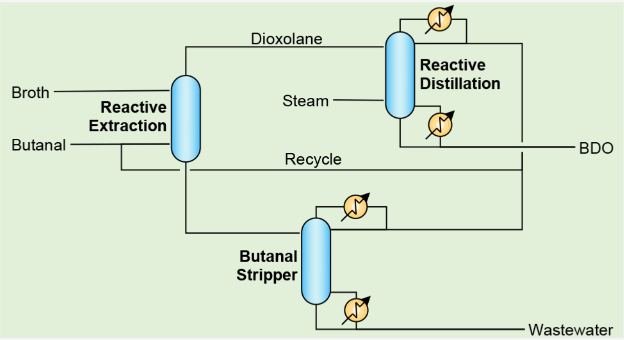
ABSTRACT: Separating 2,3-butanediol (BDO) from fermentation broth is challenging. Water is more volatile than BDO, so energy consumption for distillation is high. One alternative is a reactive extraction process. BDO in the broth reacts with an aldehyde or ketone to form an insoluble dioxolane, which can be decanted from the broth. The dioxolane is subsequently heated with water or steam, resulting in decomposition of the dioxolane into BDO and the aldehyde or ketone, which are separated to recover BDO and the aldehyde or ketone for recycling. Although variations of this process have been demonstrated, no information on efficiency, cost, or sustainability has been reported. Energy efficiency, cost, and sustainability of a reactive extraction process were evaluated. The total energy consumed by the reactive extraction process is about 17% of the net heating value of BDO, and the separation cost is $0.22/kg BDO.



1. INTRODUCTION

Biobased 2,3-butanediol (BDO) is a potential intermediate in the production of carbon-neutral fuels and chemicals. However, separating BDO from fermentation broth is challenging. Current fermentation technology can produce a broth containing approximately 10 wt % BDO. Because water is more volatile than BDO, which has a normal boiling point of 177 °C, energy consumption for ordinary distillation is prohibitively high. Additionally, the high distillation temperatures (130−165 °C) can produce oligomers that require subsequent hydrogenation. Alternatives for BDO recovery are an active area of research. Shao and Kumar[1] evaluated the energy efficiency of pervaporation and vacuum membrane distillation for the separation of BDO from a fermentation broth. Hong et al.[2] analyzed the energy efficiency and economics of a multieffect evaporator followed by distillation. Harvianto et al.[3] published a techno-economic analysis of distillation and solvent extraction with oleyl alcohol. Lee et al.[4] studied solvent extraction with 2-heptanol. Church et al.[5] reported estimates of energy consumption for two-stage vacuum distillation and vacuum distillation plus pervaporation.

Reactive extraction is an older process that has not received as much attention as a means of recovering BDO. In this process, BDO reacts with an aldehyde or ketone to form an insoluble dioxolane that can be decanted from the broth. The dioxolane is then heated with water to reverse the reaction, allowing for the high-purity BDO recovery and recycling of the aldehyde or ketone. In 1946, Senkus[6] published laboratory and pilot plant results for a reactive extraction process for separating BDO from a fermentation broth using formaldehyde as the reactant. This process used sulfuric acid to catalyze dioxolane formation and hydrochloric acid to catalyze the reverse reaction. A few years later, Tink[7,8] developed a similar process using n-butanal as the solvent and a mineral acid as the catalyst. Use of mineral acids made these processes economically unattractive.

More recently, Li et al.[9] studied the reactive extraction of BDO using n-butanal as the reactant and extractant. They reported a 95% conversion of BDO to dioxolane using the ion-exchange resin HZ-732 as the catalyst and a 99% recovery of BDO from the dioxolane in a reactive distillation. Staple et al.[10] used Amberlyst 15 resin to produce dioxolanes from BDO and various aldehydes. They reported a conversion of BDO to dioxolane of 93% to 97% depending on the aldehyde. The focus of Staple et al.[10] was production of dioxolanes as potential fuels, so they did not consider BDO recovery via reactive distillation.

The use of acid-based ion-exchange resins as the catalysts could make the chemistry of reactive extraction both energy efficient and economical. However, only Li et al.[9] have published a study of the use of resin-catalyzed dioxolane chemistry as a method of BDO recovery, and their study does

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not address energy efficiency or cost. This study was undertaken to determine the process sustainability of a reactive extraction process for separating BDO from a fermentation broth regarding the potential energy efficiency and cost to determine whether additional consideration of this process is warranted.

2. ANALYSIS SCOPE AND BASIS

The fermentation broth is a complex mixture that contains water, fermentation products, insoluble solids, unconverted sugars, dissolved electrolytes, and soluble biomass components.[11] BDO is the primary fermentation product. The broth can also contain formic acid, acetic acid, lactic acid, succinic acid, ethanol, and acetoin.[3] Moreover, based on an analysis of the mineral content of corn stover, the broth may also contain calcium, potassium, magnesium, and sodium.[12]

Solids and dissolved minerals are a problem for reactive extraction. Solids would likely plug the catalytic beds, and dissolved minerals will deactivate the acid resin catalyst. Therefore, it was assumed that fermentation broth is filtered and deionized before it is fed to the reactive extraction process. The filtration and deionization processes are not included in the scope of this analysis, which is consistent with other published studies.[1−4] Based on the biorefinery analysis,[11] the flow rate of filtered, deionized broth is 193,111 kg/h. The broth is assumed to contain 10 wt % BDO plus organic impurities. Table 1 shows the detailed composition of the fermentation broth used in this analysis. The temperature and pressure of the broth are 33 °C and 4.05 bar. The target BDO recovery for the reactive extraction process is 95%. The products of the separation process are 99 wt % BDO and wastewater. The specified flow rate, BDO concentration, and target recovery correspond to a BDO production rate of 440 tonne/day.

Table 1. Assumed Feed Composition Based on Refs 3 and 11

component	concentration (wt %)
water	85.75
BDO	10.00
formic acid	0.027
acetic acid	0.89
lactic acid	0.071
succinic acid	0.20
ethanol	1.05
acetoin	0.93
arabinose	0.27
xylose	0.26
glucose	0.55

3. THE REACTIVE EXTRACTION PROCESS

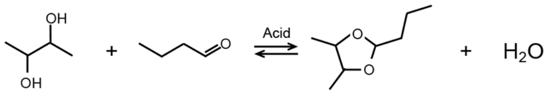
3.1. Choice of Solvent. The choice of the aldehyde or ketone for the solvent is important to the success of the reactive extraction process. The available data[6,10] indicate that dioxolanes form more readily with higher molecular weight aldehydes and ketones, but the reverse reaction is more favorable for low molecular weight aldehydes and ketones. The solubility of the aldehyde or ketone in water and its boiling point are also important considerations. The more soluble the aldehyde or ketone is in water, the greater the losses to the aqueous fermentation broth. For energy efficient stripping of the aldehyde or ketone from the spent fermentation broth, its boiling point should be less than that of water. The optimum choice of solvent involves trade-offs involving chemical equilibrium, solubility, and boiling point.

Table 2 gives the solubility and boiling point of various aldehydes and ketones. Based on the available information, n-butanal is the best choice of solvent. Both Staples et al.[10] and Li et al.[9] achieved high yields of dioxolane using n-butanal. Li et al.[9] also achieved high recovery of BDO in a reactive distillation. Solubility and boiling point also favor n-butanal. It has the lowest solubility of aldehydes and ketones with boiling points less than water, which should minimize the energy consumption and cost of stripping the aldehyde or ketone from the spent fermentation broth and recycling it.

Table 2. Solubility and Boiling Points of Aldehydes and Ketones

aldehyde or ketone	solubility in water at 25 °C (g/L)	boiling point (°C)
acetaldehyde	miscible	21
propanal	306	39
acetone	miscible	56
2-butanone	223	80
n-butanal	71	75
isobutanal	145	63
2-pentanone	43	102
3-pentanone	46	102
n-pentanal	12	103

3.2. Process Description. Figure 1 is a process flow diagram (PFD) of the reactive extraction process. For simplicity, this diagram does not show all heat exchangers or pumps. The broth is mixed with the reactive n-butanal solvent and fed to a multistage reactive extraction unit consisting of a series of reactors, which convert the BDO and solvent into a dioxolane, 2-propyl-4,5-dimethyl-1,3-dioxolane, and water.



(1)

Decanters separate the dioxolane-rich organic phase from the aqueous phase. The organic phase and steam are fed to a reactive distillation where the reverse reaction occurs and the BDO and n-butanal are separated. The n-butanal is recycled to the reactive extraction. The spent fermentation broth contains 82% of the unreacted n-butanal, which is recovered in the Butanal Stripper and recycled.

3.2.1. Reactive Extraction. In the reactive extraction, the n-butanal acts as both a reactant and an extractant. The butanal reacts with the BDO in the fermentation broth. As an organic liquid that is relatively insoluble in water, it aids in the separation of the dioxolane from the aqueous phase.

Both counter-current and crossflow configurations were considered for the reactive extraction. The optimum was found to be a three-stage crossflow configuration (Dioxolane Reactors 1−3 in Figure 1) with an equal n-butanal flow to each stage. This conclusion is consistent with the analysis of Li et al.[9] The dioxolane forming reaction is exothermic, so active cooling is needed to obtain favorable equilibrium conversion. The optimum temperature was determined to be 35 °C, the lowest practical temperature that can be maintained without a

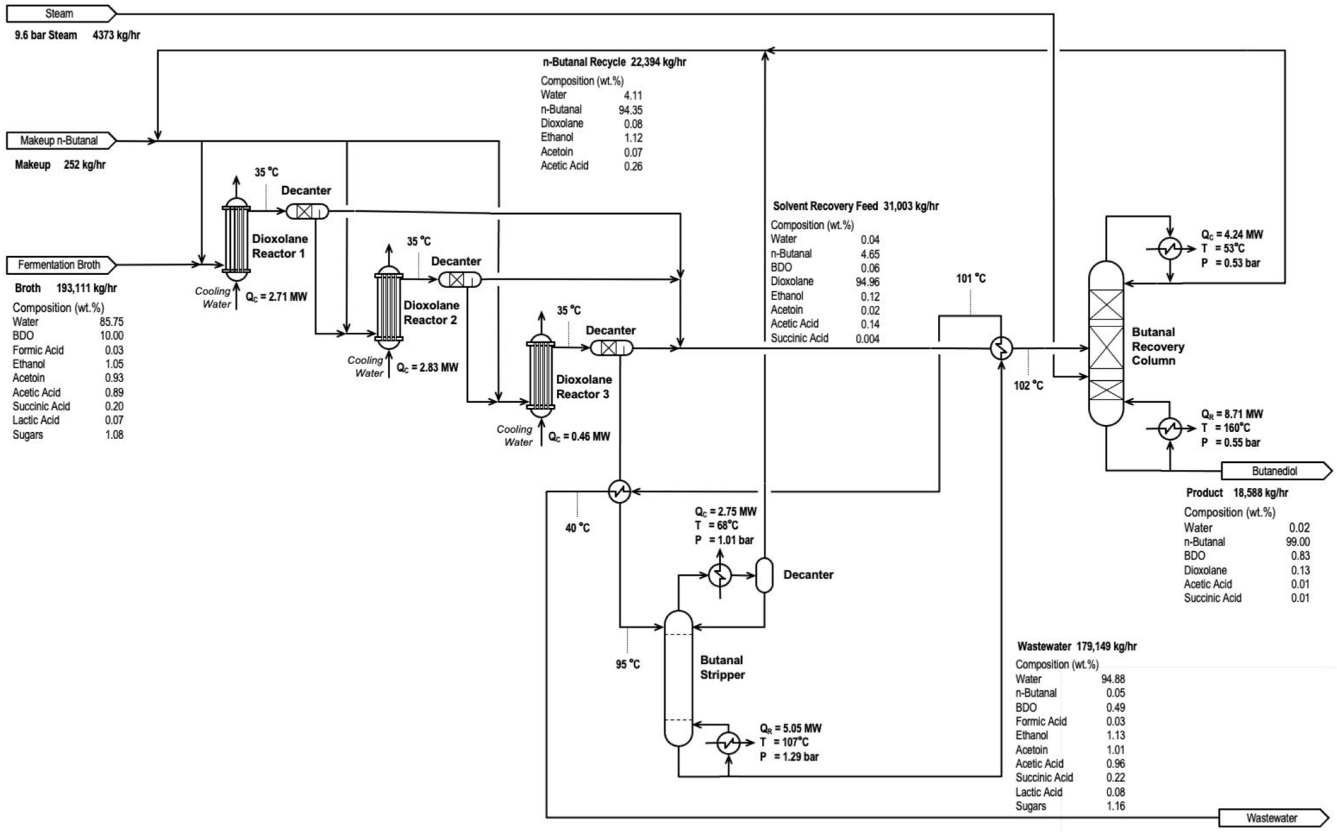


Figure 1. A simplified process flow diagram for the reactive extraction process.

chilled water system. The optimum n-butanal feed to the process was determined to be 140% of the stoichiometric amount with equal flow to each stage of the reactive extraction. Reasonable residence times can be achieved using Amberlyst 14 as the catalyst.

Each stage of the process consists of a static mixer, a fixed bed reactor with internal cooling tubes, and a decanter. The broth and n-butanal for each stage are fed to the static mixer to ensure that the organic phase is dispersed in the aqueous phase before they are fed to the Dioxolane Reactor. The spent broth contains 98% of the unreacted BDO, unreacted butanal, and trace amounts of dioxolane. The organic product is 95 wt % dioxolane with the balance being butanal plus small quanitites of BDO, and other organic impurities. The unconverted sugars and most of the other organic impurities in the broth are expected to remain in the aqueous phase.

3.2.2. Butanal Recovery. Like dioxolane production, the decomposition of dioxolane into BDO and n-butanal is equilibrium limited. This thermodynamic limitation can be overcome by continually removing the n-butanal product in a reactive distillation which drives the reaction to completion. Li et al.[9] reported 99% BDO recovery in a reactive distillation. The reactive distillation column consists of three sections−the upper rectifying section that separates n-butanal and water from BDO and the unreacted dioxolane, the middle reaction section where the dioxolane reacts with water to form BDO and n-butanal, and the lower stripping section that removes water and n-butanal from the BDO product. The dioxolane is fed to the column near the middle of the reacting section. The column temperature profile in Figure 2 illustrates these three sections. The dioxolane feed is heated to 102 °C and fed to the column near the middle of the reacting section. Water needed for the dioxolane decomposition reaction is fed to the column as saturated steam at 9.6 bar at the bottom of the reacting section, and the feed rate is 119% of the stoichiometric amount.

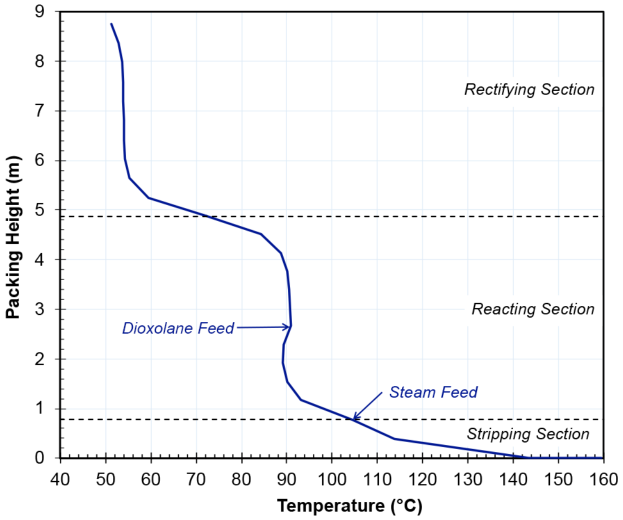


Figure 2. Predicted temperature profile for the Butanal Recovery Column.

Senkus[6] and Li et al.[13] used mineral acid catalysts to recover BDO and n-butanal from the dioxolane, so the reaction will likely require an acid catalyst. In this study, the acid form of a weak cation exchange resin is proposed as the catalyst. Structured packing is used to minimize the pressure drop in the column. Sulzer Katapak-SP or a similar product could hold the resin catalyst in the reacting section of the column.

It has been reported that BDO can oligomerize if heated, but the mechanism for oligomerization is not clear. BDO is thought to form oligomers with sugars, but sugars are expected to remain in the aqueous phase. An oligomerization mechanism of concern for the reactive distillation is the acid-catalyzed dehydration of BDO to 2-butanone and its reaction with BDO to form a dioxolane.[14] This reaction is expected to be minimal because the dioxolane from the reactive extraction contains only a small portion of the organic acids in the fermentation broth. Also, keeping the reaction zone cool by operating the column under vacuum will help minimize the possibility of oligomerization.

The column is designed to achieve a BDO purity of 99 wt %. The primary impurity is n-butanal. The BDO product also contains small amounts of organic contaminants and trace amounts of water. The simulation predicts an overall dioxolane conversion of greater than 99.9% in the reactive distillation.

3.2.3. Butanal Stripping. The spent fermentation broth exiting the third stage Dioxolane Reactor contains 3.4 wt % n-butanal, which is nearly 80% of the excess dioxolane. To prevent excessive losses of n-butanal and excessive organic loading of the wastewater treatment plant, the n-butanal is stripped from the spent broth. The spent broth is heated to 95 °C and fed to the top stage of a 17-stage distillation column. The condensate forms two liquid phases—an organic phase containing 95 wt % n-butanal and an aqueous phase containing 11 wt % n-butanal. The organic condensate is decanted from the aqueous condensate and recycled to the Dioxolane Reactors. The aqueous phase is the reflux to the Butanal Stripper. The Butanal Stripper is designed to reduce the n-butanal content of the wastewater to less than 0.05 wt %.

3.2.4. Heat Integration. Hot wastewater from the bottom of the Butanal Stripper can be recovered to reduce overall energy consumption by preheating the feeds to the Butanal Recovery Column and Butanal Stripper. This simple waste-heat recovery scheme is illustrated in Figure 1. First, the hot wastewater at 107 °C is used to preheat the dioxolane from 35 to 102 °C. This energy exchange only reduces the wastewater temperature to 101 °C, so it can be used to preheat the spent fermentation broth from 35 to 95 °C while cooling the wastewater to 40 °C. Preheating the feeds reduces energy consumption in both distillation columns.

3.3. Utilities. The primary focus of this study is on utilities that significantly impact energy consumption, which are steam, electricity, and cooling water. Cooling water is an important consideration because cooling water systems are significant consumers of electricity. This study does not consider plant utilities such as instrument air and wastewater treatment.

3.3.1. Steam. Steam provides process heat to the distillation column reboilers in the process. It is also the source of water for the reactive distillation used to recover BDO and butanal from the dioxolane. Saturated steam is provided to the reboilers and the process at 9.63 bar. Producing 9.63 bar saturated steam for process heat requires 2020 kJ/kg of steam, and producing 9.63 bar saturated steam as a process feed requires 2671 kJ/kg of steam. The difference in energy requirements is the result of process differences. Steam fed to the reboiler condenses in the reboiler at 178 °C, and it is recycled to the boiler at that temperature. The steam that is fed to the reactive distillation is consumed by the process. Makeup water to generate steam for the reactive distillation is fed to the boiler at approximately ambient temperature. Because of the lower boiler feed temperature, more energy is needed to produce saturated steam at 9.63. bar. To estimate the equivalent fuel value of the steam, the boiler is assumed to be 80% efficient.

3.3.2. Electricity. The primary consumers of electricity are pumps and cooling towers. Pump powers are estimated based on typical pressure drops through process equipment and piping. Pumps are assumed to have a hydraulic efficiency of 55%, and motors are assumed to have an efficiency of 95%. The fuel equivalent of electrical power is based on US power consumption and generation from 2017 through 2019. [The years 2020 and 2021 were not included in the determination of average fuel consumption for electrical power generation. Because of the impact of Covid-19 restrictions on energy consumption, these years may not represent typical US power consumption.] The fuel equivalent for electricity is the total electrical power consumption per unit of fuel consumed for thermal power generation, including nuclear power. This ratio was determined to be 1.85 kW_{fuel}/kW_e based on data from the US Energy Information Agency (EIA).

3.3.3. Cooling Water. A forced-draft cooling tower provides cooling water to the process at 25 °C. The design temperature rise is 5.5 °C. The primary consumers of electricity in the cooling water system are the cooling tower fans and the cooling water pumps. Energy consumption by the cooling tower fans is approximated as 0.0115 kW_e/kW_{th}. The cooling water pumps are assumed to consume 0.133 kW_e/m^3 of cooling water.

4. PROCESS MODEL

4.1. Physical Properties. This analysis is based on chemical and phase equilibria calculations. Therefore, thermodynamic properties are essential to the analysis. Reliance on thermodynamic properties is problematic because key physical properties of dioxolane are not available. To simplify the analysis, arabinose, xylose, and glucose were lumped together as a single component, which was modeled as glucose.

4.1.1. Pure Component Properties. A broad range of pure component properties is required to model the reactive extraction process. The key properties are the liquid phase thermodynamic properties and vapor pressure. Basic data exists for all compounds except the dioxolane. The enthalpy of formation for the dioxolane in the liquid phase was determined from the measured enthalpy of combustion.[10] Critical temperature, critical pressure, and normal boiling point were estimated using the group contribution method of Marrero and Gani.[15] Vapor pressure as a function of temperature was estimated from the normal boiling point and the critical point. The density of liquid dioxolane was obtained from ref 10. Liquid heat capacity for the dioxolane was estimated from data for similar compounds using group contribution principals.[16]

4.1.2. Fluid-Phase Equilibria. Fluid-phase equilibrium was modeled using the Redlich−Kwong equation of state[17] for the vapor phase and the UNIQUAC equation[18] for the liquid phases. UNIQUAC was chosen for the liquid phase because the combinatorial term better models the size difference between the dioxolane and the other major components in the mixtures. Parameters for the combinatorial contribution to the UNIQUAC activity coefficient model were determined using the UNIFAC group contribution method.[19] Data exists for only 8 of the 55 binary pairs in the mixture. Of the four major components, data are available for only two of the six possible binary pairs—liquid—liquid equilibrium data for the n-butanal/water system[20] and vapor—liquid equilibrium data for the BDO/water system.[21,22] The UNIQUAC parameters for the missing binary pairs were derived from UNIFAC parameters for liquid—liquid equilibria.[23] Liquid—liquid equilibrium parameters were used for the model because the liquid—liquid phase separation is more important to the reactive extraction process than vapor—liquid equilibrium. Mixing UNIQUAC and UNIFAC maximizes the use of the available data while using UNIFAC for the missing binary pairs.

4.1.3. Chemical Equilibria. Because Gibbs free energy of formation data is not available for BDO and the dioxolane, the equilibrium constant was estimated from the limited reaction data available. The only data available for the reaction of BDO with n-butanal are found in refs 9 and 10. The data, however, are inconsistent. Equilibrium coefficients, as determined from data in ref 10, are orders of magnitude larger than equilibrium coefficients based on data from ref 9. Also, the data given in ref 9 are not consistent. Two possible reasons exist for the inconsistencies. First, the published data may not represent chemical equilibrium. Second, activity coefficients are needed to estimate the equilibrium constant from the available data, and the UNIQUAC model and parameters are inaccurate.

To obtain a model that is consistent with the expected process performance, the equilibrium constant at 25 °C was estimated from the cross-flow reactive extraction data of Li et al.[9] The enthalpy of reaction as a function of temperature was determined from the enthalpies of formation and the liquid heat capacity. The equilibrium constant as a function of temperature was determined using the standard thermodynamic relationship between the equilibrium constant and enthalpy of the reaction

$$\frac{\mathrm{d}}{\mathrm{d}t}\ln(K_a) = \frac{\Delta H_{rx}}{R \cdot T^2} \tag{2}$$

where K_a is the equilibrium constant, T is the temperature in K, ΔH_{rx} is the enthalpy of reaction in kJ/kmol, and R is the gas constant in kJ/kmol K. The results of integrating eq 2 for the reaction between BDO and n-butanal are well represented by the following approximate equation.

$$\ln(K_a) = -39.354 + 14692/T \tag{3}$$

The equilibrium constant estimate depends on the values of the activity coefficients. To obtain results consistent with the published data, eq 3 must be used with the activity coefficient model and the model parameters used in its derivation.

4.2. Material and Energy Balance Calculations.

Material and energy balances for the reactive extraction process were performed using ChemCAD 7.1.5. The calculations were performed using only standard unit operation models in ChemCAD.

The standard distillation module with equilibrium reactions was used for the Butanal Recovery Column (see Figure 1). The model contained 23 equilibrium stages with a total condenser and a kettle reboiler. The top nine stages and the bottom three stages were standard distillation stages with no chemical reaction. The 11 stages in the middle were reactive stages with chemical equilibrium for the dioxolane in the liquid phase. The dioxolane was fed to the column on stage 16, and steam was fed above stage 21. Estimates of the height equivalent of a theoretical stage were obtained from the Sulzer literature[24] for Mellapak for the nonreacting sections and Katapak SP for the reacting sections.

Two liquid phases form in the Butanal Stripper condenser. Therefore, the column model included liquid—liquid phase equilibrium in the condenser. The organic phase is the distillate, which is recycled to the Dioxolane Reactors, and the aqueous phase is the reflux. The modified O'Connell correlation was used to estimate the actual number of stages in the column.[25]

The model includes estimates of pressure drops through heat exchanges, packed bed reactors, and distillation columns. The estimates are not rigorous but values typical of specified equipment type,[24,26] and they are used only to obtain an order-of-magnitude estimate of process pump power consumption.

4.3. Summary of Results.

Figure 1 contains a summary of the material balances for the reactive extraction process. The process is estimated to obtain an overall BDO recovery of 95.3%. Over 98% of loss is unreacted BDO in the wastewater. The remainder of the loss is unreacted dioxolane in the product.

Table 3 is a summary of process energy. Fuel to produce steam accounts for about 97% of total energy consumption.

Table 3. Energy Balance Summary

	quantity	value
heating	solvent recovery reboiler (kW)	8,701
	butanal stripper reboiler (kW)	5,044
	total (kW)	**13,745**
cooling	dioxolane reactors (kW)	6,013
	solvent recovery condenser (kW)	4,234
	butanal stripper condenser (kW)	2,752
	other (kW)	3,133
	total (kW)	**15,929**
steam	process heating (kg/h)	24,496
	process feed (kg/h)	4,373
cooling water	flow (m^3/h)	2,540
electricity	process pumps (kW_e)	110
	cooling water (kW_e)	189
	total (kW_e)	**295**
fuel/thermal energy	steam (kW_{fuel})	21,237
	electricity (kW_{fuel})	547
	total (kW_{fuel})	**21,784**
	total (kJ/kg BDO)	**4,262**

Electricity to run the pumps and cooling water system is only a minor contributor to overall energy consumption. With heat, total equivalent fuel consumption for the thermally integrated process is 4,260 kJ/kg BDO in the product stream, which is 17% of the lower heating value (LHV) of the recovered BDO. Figure 3 shows the breakdown of fuel consumption by process area. Heat integration of the process is essential to the process. If heat integration is eliminated, fuel consumption increases by 90% to 7,880 kJ/kg BDO or 32% of the LHV of the recovered BDO.

5. ECONOMIC ANALYSIS

The objective of the economic analysis was to estimate the incremental cost of separating the BDO from the fermentation broth. The analysis is an assessment of the initial viability of the process, and the results are one metric for comparison with other BDO separation processes. The reactive extraction process is in the early stages of development with a low degree

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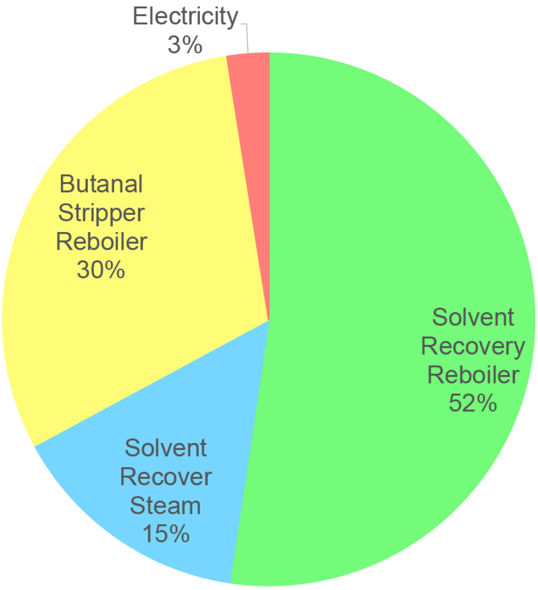

Figure 3. Breakdown fuel consumption by process areas.

of process definition typical of an AACE International Class 4 or 5 estimate.[27] A reasonable process flow diagram was developed from the available data, and an equipment-factored method was used to estimate costs. This method of analysis is typical of a Class 4 estimate. However, significant uncertainty exists. Therefore, the accuracy of estimate is between that of a Class 4 and Class 5 estimate or approximately −40% and +60%.

In this study, the reactive extraction process is assumed to be a stand-alone process. Separation cost is defined as the cost of producing the purified BDO product for a specified internal rate of return and excludes the cost associated with the producing fermentation broth, removing solids and cations from the broth, and upgrading of the BDO into other products. This definition includes variable and fixed operating costs as well as capital investment and financing costs. Although analyzed as a stand-alone process, the reactive extraction process is part of a larger biorefinery that produces steam and electricity from process waste.[11] A techno-economic analysis of an integrated biorefinery with the reactive extraction process will be included in the paper that is currently being prepared for publication.

5.1. Capital Investment. Purchased and installed equipment costs inside battery limits (ISBL) were estimated using Woods' method.[28] Cost estimates for structured packing were based on data reported by Dejanovic et al.[29] Estimates were based on a March 2022 *Chemical Engineering* Plant Cost Index, which is 784.5. Table S4 in the Supporting Information is a list of installed costs for ISBL equipment.

ISBL installed equipment cost is not the total capital cost associated with the BDO separation process. The separation process places demand on space and process utilities. These capital costs are related to utilities and other outside battery limits (OSBL) facilities and account for increased service capacity or lost opportunity costs. An example of a direct cost would be additional cooling water system capacity. An example of lost opportunity would be steam consumed as process heat instead of being used for the cogeneration of electricity. Another example of lost opportunity would be land occupied by the separation process that could be used for future expansion. A factor method was used to estimate OSBL costs as well as other expenses not included in the ISBL cost. OSBL cost factors are based on the tabulation in Peters et al.[30] OSBL cost factors used in this analysis are based on the utility requirements of the BDO separation process and the expected demands for the utilities. For example, the lower value of the range of value given in Peters et al. is used if the demand for a particular utility is expected to be small. Factors for home office expenses, contractor fees, and so forth are based on Woods' recommendations.[28] Other contributions to fixed capital investment (FCI) include home office expenses, contractor fees, and contingencies. Total capital investment (TCI) is the additional costs of legal fees, spare parts, working capital, and startup expenses. Table S5 in the Supporting Information is a summary of costs contributing to FCI and TCI and their bases.

5.2. Operating Costs. *5.2.1. Variable Operating Costs.* Variable operating costs include n-butanal makeup, utilities, and replacement of the ion exchange resins used as catalysts. Wastewater treatment is not included in variable costs because it depends on fermentation broth volume and BDO recovery rather than the specific process. Therefore, it is not an incremental cost associated with the BDO separation process. Variable operating costs estimates are based on March 2022 prices and a process availability of 90% and are summarized in Table S6 in the Supporting Information.

The prices for 1-butanal and ion exchange resins are averages based on a survey of industrial suppliers. The price of steam is based on the cost of natural gas needed to generate 1 tonne of steam with a boiler efficiency of 80%. The natural gas price is the average industrial natural gas price for the Midwest region of the United States (US) in March 2022 or \$7.06/MJ. The price data was obtained from the US Energy Information Agency (EIA). The price of boiler chemicals was determined to be insignificant based on data given by Davis et al.[11] The biorefinery is assumed to be a net electrical power generator.[11] Therefore, the cost of electricity is based on the lost revenue from electrical power sales, which was assumed to be the wholesale price of electricity. The price of electricity used in this study is the average wholesale price for the US Midwest during the first quarter of 2022. Cooling water costs include the power for the cooling tower fans and cooling water pumps, makeup cooling water assuming 4.5 cycles of concentration, and cooling water chemicals. The price of makeup water was assumed to be \$0.88/m^3 based on 2022 Des Moines, Iowa water rates, and cooling water chemical costs were estimated for data given by Davis et al.[11]

5.2.2. Fixed Operating Costs. Fixed costs include labor, supervision, maintenance, and fixed charges. Royalties and general expenses are not included in fixed operating costs because they are only applicable at the biorefinery level. Three operators are required per shift to operate the reactive extraction process based on the type and number of units in the process.[31] The total number of operators was based on five complete crews, which is the number needed for continuous operations without requiring operators to work overtime. The hourly rate for the operator is the average for a chemical operator in the US Midwest for 2021, as reported by the US Bureau of Labor Statistics. Other fixed charges were determined using a factor method. Fixed operating costs and their basis are summarized in Table S7 in the Supporting Information.

5.3. Separation Cost Estimate. The separation cost, as defined in the introduction to this section, is equal to the minimum BDO selling price as determined from a discount cash flow analysis. Capital investment, operating costs, and financial parameters in the cash flow analysis are summarized in Table 4.

Table 4. Parameters for the Discount Cash Flow Analysis

parameter	value
capital costs	
FCI (million \$)	\$53.86
TCI (million \$)	\$67.68
operating costs	
variable costs (million \$/yr)	\$9.41
fixed cost (million \$/yr)	\$6.54
financial parameters	
construction time (months)	30
start-up time (months)	3
first year's capacity	80%
equity financing	60%
interest rate on loans	5.5%
term of loan (yrs)	7
process depreciation time (yr)	7
tax rate	25.8%
plant life (yrs)	30
internal rate of return	10%

Depreciation is calculated using the Modified Accelerated Recovery System, as dictated by the US Internal Revenue Service. Depreciation is only used in this analysis to calculate corporate taxes. The tax rate is assumed to be 25.8%, which is the maximum federal corporate tax of 21% plus the state corporate tax rate of 4.8%. The average state tax rate is used because the location of the biorefinery has not been specified. The estimated separation cost is \$0.22/kg of BDO. Figure 4 shows the cost breakdown. Capital costs are the largest single contributor to separation costs. Other cost factors are functions of FCI—maintenance, operating supplies, insurance, taxes, and interest in loans. Capital costs and capital related costs comprise about 63% of the separation costs. Efforts to reduce separation costs must focus on reducing capital costs. The dioxolane reactors account for about 42% of the installed equipment costs. Therefore, efforts to reduce cost should focus on optimizing reactor design.

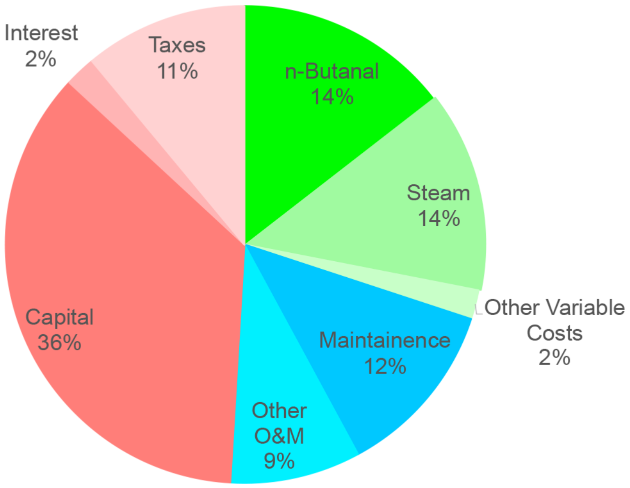

Figure 4. Separation cost breakdown.

5.4. Sustainability. Sustainability in process design is core to the mission of developing renewable fuels and chemicals and should be considered best practice in the early stage of a process design.[32,33] One outcome of the sustainability evaluation is to allow researchers to identify challenges and opportunities for achieving the best possible sustainability targets and exert any design changes in process areas in need of sustainability improvement. This study presents key sustainability metrics for the reactive extraction process for BDO separation and recovery from a fermentation broth. The conceptual process sustainability was evaluated using the foreground process data derived from the process model (Tables 3 and 5). Embodied emissions and resource consumption from the reactive extraction process system related to material and energy inputs were also included. The boundary for all metrics is the BDO separation and recovery, which was the focus of this research. Upstream processes (i.e., fermentation broth production and transportation) and downstream processes (i.e., BDO product distribution and transportation) were not considered in this study. For environmental impact metrics——global warming potential (GWP) and cumulative fossil energy (CFE) demand, we used the GREET emission factors[34] with Ecoinvent[35] processes used to fill the data gap. The functional unit is 1 kg of BDO produced. Table 5 summarizes the key sustainability metrics for the process.

Table 5. Summary of Sustainability Metric per kg of BDO for the Reactive Extraction Process

sustainability metric	value
BDO separation cost	\$0.22/kg
global warming potential	0.31 kg CO_{2e}/kg
cumulative fossil energy	5.1 MJ/kg
total thermal energy	4.3 MJ/kg
percent of BDO LHV	17.2%
consumptive water use	0.14 m^3/kg
wastewater	9.7 L/kg

The life cycle GWP was determined to be 0.31 kg CO_{2e}/kg, where CO_{2e} is CO_2 equivalent. Similarly, the life cycle CFE demand was estimated to be 5.1 MJ/kg. Both GWP and CFE include the emissions associated with the production of material and energy inputs to the reactive extraction process (e.g., the production of n-butanal and ion-exchange resin). Steam production is the predominant contribution to GWP and CFE being 92% and 90% of these metrics, respectively. As fossil energy is a nonrenewable resource, it is prudent to decrease its demand to improve the energy sustainability aspect of the separation process. This can be accomplished by switching to a renewable energy source such as biogas or reducing the total direct thermal energy usage, currently at 4.3 MJ/kg and corresponding to 17.2% of the LHV of BDO.

The consumptive water use for the current BDO separation process was determined to be 0.14 m^3/kg and is equal to the makeup water to the cooling tower due to the evaporative loss. The U.S. Geological Survey defined consumptive water use as "water that is evaporated, transpired, incorporated into products or crops, consumed by humans or livestock, or otherwise removed from an immediate water environment".[36] The BDO separation process also generates wastewater, with

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Table 6. Comparison of the Reactive Extraction Process to the Baseline Distillation Process

process	BDO capacity (tonne/day)	BDO recovery (%)	BDO purity (%)	fuel consumption (kJ/kg BDO)	reported cost estimate ($/kg BDO)	harmonized cost estimate ($/kg BDO)
reactive extraction	440	95.3	99.0	4,262	$0.22	$0.22
distillation[2]	41	90	99.0	32,200	$0.66	$0.47
two-stage vacuum distillation[5]	>420	>90	50	29,300	N/A	N/A
membrane distillation[1]	0.32	75	99.5	148,000	N/A	N/A
mulitstage evaporation + distillation[2]	40.6	90	99.0	50	$0.44	N/A
vacuum distillation + pervaporation[5]	>420	>90	50	25,600	N/A	N/A
pervaporation[1]	0.32	75	99.5	38,000	N/A	N/A
solvent extraction with oleyl alcohol[2]	41	90	99.0	14,200	$0.39	$0.46
solvent extraction with 2-heptanol[3]	21.5	93.3	99.1	15,300	$1.30	$0.46

an intensity of 9.7 L/kg. Both consumptive water usage and wastewater generation are critical to process sustainability. The former relates to water removal from the available supplies without returning to a water resource system by mechanisms such as evaporation and cooling tower drift. The latter's environmental footprint could include acidification and eutrophication that disrupt the natural balance of aquatic life.[37] Furthermore, sustainability metrics are not limited to environmental impacts. The economic aspect of the sustainability is also important and can be represented by the BDO product separation cost, which is $0.22/kg BDO product.

6. DISCUSSION

The key metrics for evaluating processes for separating BDO from fermentation broths are recovery, energy consumption, and separation cost. Energy consumption is a good surrogate for the sustainability metrics. Steam production accounts for more than 90% of total energy consumption, and steam production accounts for 90% or more of the GWP and CFE. Therefore, a BDO separation process with low energy consumption will also have a low GWP and CFE. Consumptive water use is dominated by cooling tower losses, and cooling requirements correlate with heating requirements; hence, a BDO separation process with low energy consumption will also have low consumptive water use.

Comparisons of recovery and energy consumption are straightforward because they are independent of scale and easily verified by independent analysis. Separation costs are more difficult to compare because estimates depend on the date, location, scale of the process, and methodological assumptions. Table 6 compares the analysis results for the reactive extraction process with published results for seven other processes for recovering BDO from fermentation broth—ordinary distillation,[3] two-stage vacuum distillation,[5] multistage evaporation followed by distillation,[2] vacuum distillation plus pervaporation,[5] membrane distillation,[1] pervaporation,[1] and solvent extraction with oleyl alcohol,[3] and solvent extraction with 2-heptanol.[4]

Reactive extraction exhibits the lowest energy consumption of the eight processes summarized in Table 6. Energy consumption for reactive extraction is a factor of about 3.5 less than solvent extraction plus distillation, the next lowest alternative. While this conclusion must be tempered by the fact that the analyses summarized in this paper are based on different BDO recoveries and purities and increasing recovery and purity will the increase energy consumption, none of the analyses summarized in Table 6 achieved a BDO recovery greater than 95%. Consequently, differences in recovery will not readily change the qualitative conclusion. Of the analyses summarized in Table 6, only the analyses of pervaporation and membrane distillation were based on a BDO purity greater than 99 wt %. Sensitivity studies have shown that increasing the BDO purity to 99.5% for the reactive extraction process increases energy consumption by less than 1%. Therefore, differences in purity do not affect the conclusions.

Because energy consumption is a surrogate for GWP, GFE, and consumptive water use, the low energy consumption for reactive extraction is a strong indicator that its sustainability measures are much lower than the other processes listed in Table 6. Because energy consumption for reactive extraction is much lower than the other process, the error introduced by using energy consumption as a surrogate for sustainability is unlikely to impact the overall conclusion.

Of the alternatives to reactive extraction recovery, costs are only available for distillation, multistage evaporation followed by distillation, and solvent extraction plus distillation. However, the cost estimates of Hong et al.,[2] Harvianto et al.,[3] and Lee et al.[4] differ from those of this analysis. The differences include the date of the study, utility costs, inclusion of fixed costs, and financial assumptions. To make valid cost comparisons, distillation and solvent extraction costs were computed using the process data and capital costs estimates of Harvianto et al.[3] and Lee et al.[4] with the financial and cost assumption of this study. Table 6 contains the results of this harmonization of cost estimates. Utility costs in this study were evaluated for a US-based biorefinery that generates steam and electricity from waste. Steam costs in this study are lower than the values assumed by Harvianto et al.[3] and Lee et al.,[4] and electricity costs are greater. The harmonized separation costs are lower for distillation and solvent extraction with 2-heptanol because costs are dominated by steam consumption. Harvianto et al.[3] used vacuum distillation to recover the solvent in their extraction process. Considerable electrical power is needed to operate the vacuum system, so the higher electrical power cost used in the reanalysis results in an increase in separation costs. The paper of Hong et al.[2] did not include sufficient cost data to harmonize their results with this study.

The separation costs for reactive extraction are lower than both distillation and solvent. However, the analysis for reactive extraction is based on a process with a BDO capacity of more than an order of magnitude larger than the other process. Variable operating costs account for 85% and 67% of the separation costs of distillation and solvent extraction with oleyl alcohol, respectively, so separation costs should be relatively insensitive to capacity. Separation costs for solvent extraction with 2-heptanol and reactive extraction are dominated by capital related costs (i.e., capital, taxes, interest, and maintenance), so separation costs are expected to be sensitive to capacity. Figure 5 shows the separation cost as a function of capacity for the four processes. At low BDO production capacities, solvent extraction with 2-heptanol has a clear cost advantage. As capacity increases, the separation costs for reactive extraction decrease sharply because of the increased economy of scale. Above a BDO production capacity of 200 tonne/day, separation costs for reactive extraction and solvent extraction with 2-heptanol are within the −40%/+60% error of the cost estimation method.

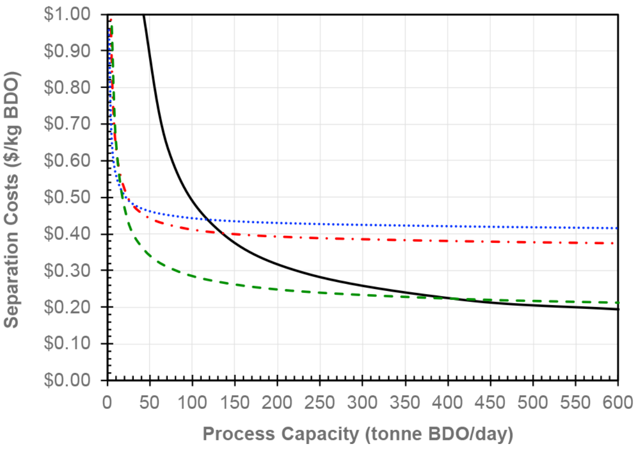

Figure 5. BDO separation costs in 2022 US dollars as a function of process capacity for reactive extraction (—), distillation (···, blue), solvent extraction with oleyl alcohol (-·-·-, red), and solvent extraction with 2-heptanol (---, green).

7. CONCLUSIONS

The techno-economic and sustainability analyses of the reactive extraction process show that the reactive extraction is a promising process for recovering BDO from a fermentation broth. The analysis shows that 95% BDO recovery at 99 wt % purity is possible while consuming significantly less energy than other published processes. Sustainability metrics are also favorable for the reactive extraction process. Because energy is a reasonable surrogate for the sustainability, low energy consumption also indicates that reactive extraction has more favorable sustainability metrics than the other reported process. At low production capacities, the other processes are more economical than reactive extraction. For large-scale BDO production, the separation cost for reactive extraction is lower than distillation and solvent extraction with oleyl alcohol, at it is comparable to solvent extraction with 2-heptanol for large-scale BDO production.

The primary source of uncertainty in this analysis of the reactive extraction process for BDO recovery is the lack of thermodynamic data for the dioxolane intermediate. Although experimental data indicates that the process should work, the lack of reaction equilibrium data for the dioxolane forming reaction and the lack of phase equilibrium data for a mixture containing the dioxolane make estimating energy consumption and costs challenging. The limited kinetic data available makes equipment sizing uncertain and, therefore, capital cost estimates uncertain. Two process related uncertainties could affect the practicality of the reactive extraction processes—catalyst life and the impact of minor components and impurities in the fermentation on the process. Although significant uncertainty exists, the lack of reliable quantitative data is not unique to the reactive extraction process. The current sustainability metrics results can serve as the baseline for future comparison (e.g., tracking development and improvement) and as a basis for comparing with other BDO separation approaches.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.2c04307.

> Thermodynamic model parameters, process flow diagrams with material and energy balances, and purchased and installed equipment cost estimates, details of the FCI and TCI estimates, variable operating cost estimates, and fixed operating cost estimates (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

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■ ABBREVIATIONS

AACE = Association for the Advancement of Cost Engineering
BDO = 2,3-butanediol
EIA = Energy Information Agency
CFE = cumulative fossil energy
FCI = fixed capital investment
GREET = Greenhouse Gases, Regulated Emissions, and Energy Use in Technologies
GWP = global warming potential
ISBL = inside battery limits
LHV = lower heating value
OSBL = outside battery limits
PFD = process flow diagram
TCI = total capital investment
UNIQUAC = universal quasi-chemical
UNIFAC = UNIQUAC functional group activity coefficient
US = United States

■ REFERENCES

(1) Shao, P.; Kumar, A. Process Energy Efficiency in Pervaporative and Vacuum Membrane Distillation Separation of 2,3-Butanediol. *Can. J. Chem. Eng.* **2011**, *89*, 1255−1265.

(2) Hong, J.; Long, N. V. D.; Harvianto, G. R.; Haider, J. Design and Optimization of Multi-Effect-Evaporation-Assisted Distillation Configuration for Recovery of 2,3-Butanediol from Fermentation Broth. *Chemical Engineering & Processing: Process Intensification.* **2019**, *136*, 107−115.

(3) Harvianto, G. R.; Haider, J.; Hing, J.; Long, N. V. D.; Shim, J.-J.; Cho, M. H.; Kim, W. K.; Lee, M. Purification of 2,3-Butanediol from Fermentation Broth: Process Development and Techno-Economic Analysis. *Biotechnology for Biofuels.* **2018**, *11*, 18.

(4) Lee, S. C.; Woo, H. C.; Kim, Y. H. Energy-Efficient Process of 2,3-Butanediol Using 2-Heptanol Extraction. *Chemical Engineering & Processing: Process Intensification.* **2021**, *160*, 108286.

(5) Church, A.; Sun, N.; Yan, J.; Karp, E.; Tan, E.; McNamara, I.; Freeman, C.; Liu, J.; Glezakou, V.; Zhang, D.; Dunn, J.; Valentino, L. 2−3-Butanediol (BDO) Separations. March 11, 2021. Separations Consortium, Technology Area Session: Performance-Advantaged Bioproducts, Bioprocessing, Separations, and Plastics. https://www.energy.gov/sites/default/files/2021-04/beto-18-peer-review-2021-bioproduct-church.pdf (accessed 2021-12-30).

(6) Senkus, M. Recovery of 2,3-Butanediol Produced by Fermentation. *Ind. Eng. Chem.* **1946**, *38*, 913−916.

(7) Tink, R. *Extraction of Polyhydroxy Compounds from Dilute Aqueous Solutions by Acetal Formation.* M.S. Thesis, University of Saskatchewan, Saskatoon, Saskatchewan, 1950.

(8) Ledingham, G.; Neish, A. Fermentative Production of 2,3-Butanediol. In *Industrial Fermentations*; Chemical Publishing Company: 1954; Vol. *2*, pp 27−94.

(9) Li, Y.; Zhu, J.; Wu, Y.; Liu, J. Reactive Extraction of 2,3-Butanediol from Fermentation Broth. *Korean Journal of Chemical Engineering.* **2013**, *30*, 154−159.

(10) Staples, O.; Moore, C.; Leal, J.; Semelsberger, T.; McEnally, C.; Pfefferie, L.; Sutton, A. A Simple, Solvent Free Method for Transforming Bioderived Aldehydes into Cyclic Acetals for Renewable Siesel Fuel. *Sustainable Energy & Fuels.* **2018**, *2*, 2742−2746.

(11) Davis, R.; Grundl, N.; Tao, L.; Biddy, M.; Tan, E.; Beckham, G.; Humbird, D.; Thompson, D.; Roni, M. *Process Design and Economics for the Conversion of Lignocellulosic Biomass to Hydrocarbon Fuels and Coproducts: 2018 Biochemical Design Case Update*; NREL/TP5100-71949; National Renewable Energy Laboratory: Golden, CO, 2018; DOI: 10.2172/1483234.

(12) Sawyer, J. Nutrient Removal When Harvesting Corn Stover, *Integrated Crop Management.* 2007, IC-298(22), 251, August 6, 2007. https://crops.extension.iastate.edu/encyclopedia/nutrient-removal-when-harvesting-corn-stover (accessed 2022-11-8).

(13) Li, Y.; Wu, Y.; Zhu, J.; Liu, J.; Shen, Y. Separating 2,3-Butanediol from Fermentation Broth Using n-Butyraldehyde. *Journal of Saudi Chemical Society.* **2016**, *20*, S495−S502.

(14) Harvey, B.; Merriman, W.; Quintana, R. Renewable Gasoline, Solvents, and Fuel Additives from 2,3-Butanediol. *ChemSusChem.* **2016**, *9*, 1814−1819.

(15) Marrero, J.; Gani, R. Group-Contribution Based Estimation of Pure Component Properties. *Fluid Phase Equilib.* **2001**, *183*−*184*, 183−208.

(16) Kolska, Z.; Kukal, J.; Zabrabsky, M.; Ruzicka, V. Estimation of the Heat Capacity of Organic Liquids as a Function of Temperatue by a Three-Level Group Contribution Method. *Ind. Eng. Chem. Res.* **2008**, *47*, 2075−2085.

(17) Redlich, O.; Kwong, J. On the Thermodynamics of Solutions V; An Equation of State; Fugacities of Gaseous Solutions. *Chem. Rev.* **1949**, *44*, 233−244.

(18) Abrams, D.; Prausnitz, J. Statitsitical Thermodynamics of Liquid Mixtures: A New Expression for the Excess Gibbs Energy of Partly or Completely Miscible Systems. *AIChE J.* **1975**, *21*, 116−128.

(19) Reid, R.; Prausnitz, J.; Poling, B. *The Properties of Gases & Liquids*, 4th ed.; McGraw-Hill Book Company: New York, 1987; pp 314−332.

(20) Yu, C.; Wu, S.; Zhao, Y.; Zeng, Z.; Xue, W. Liquid-Liquid Equilibrium Data of the Water + Butyric Acid + {Butanal or n-Butanol} Ternary Systems at 293.15, 308.15, and 323.15 K. *Journal of Chemical & Engineering Data.* **2017**, *62*, 2244−2252.

(21) Blom, R.; Mastaka, G.; Efron, A.; Reed, D. Liquid-Vapor Equilibrium in Mixtures of 2,3-Butylene Glycol and Water. *Ind. Eng. Chem. Res.* **1945**, *37*, 870−872.

(22) Othmer, D.; Schlechter, N.; Koszalka, W. Composition of Vapors from Boiling Binary Solutions. *Industrial and Engineering Chemistry Research. W.* **1945**, *37*, 895−900.

(23) Magnussen, T.; Rasmussen, P.; Fredenslund, A. UNIFAC Parameter Table for Prediction of Liquid-Liquid Equilibria. *Industrial and Engineering Chemistry Process Design and Development.* **1981**, *20*, 331−339.

(24) *Structured Packings-Energy-Efficient, Innovative & Profitable*; E10686; Sulzer Ltd.: Winterhur, Switzerland, 2020.

(25) Duss, M.; Taylor, R. Predict Distillation Tray Efficiency. *Chemical Engineering Progress.* **2018**, *112* (6), 24−30.

(26) Woods, D. *Rules of Thumb in Engineering Practice*; Wiley-CVH Verlag GmbH & Co: Weinheim, Germany, 2007; pp 45−54, DOI: 10.1002/9783527611119.ch2.

(27) *Cost Estimation Classification System-As Applied in Engineering. Procurement, and Construction for the Process Industries*; Recommended Practice No. 18R-98; AACE International: Fairmont, WV, USA, 2005.

(28) Woods, D. *Rules of Thumb in Engineering Practice*; Wiley-CVH Verlag GmbH & Co: Weinheim, Germany, 2007; pp 376−436, DOI: 10.1002/9783527611119.app4.

(29) Dejanovic, I.; Matisjseciv, L.; Jansen, H.; Olujic, Z. Designing a Packed Dividing Wall Column for an Aromatics Processing Plant. *Ind. Eng. Chem. Res.* **2011**, *50*, 5680−5692.

(30) Peters, M.; Timmerhaus, K.; West, R. *Plant Design and Economics for Chemical Engineers*, 5th ed.; McGraw-Hill: Boston, 2002; pp 239−349.

(31) Brown, T. Estimating Product Cost. *Chemical Engineering.* **2000**, *107* (8), 86−89.

(32) Tan, E. An Integrated Sustainability Evaluation of High-Octane Gasoline Production from Lignocellulosic Biomass. *Biofuels, Bioproducts, and Biorefining.* **2019**, *13*, 1439−1453.

(33) Smith, R.; Tan, E.; Ruiz-Mercado, G. Applying Environmental Release Inventories and Indicators to the Evaluation of Chemical Processes in Early Stage Development,. *ACS Sustainable Chemical Engineering.* **2019**, *7*, 10937−10950.

(34) *Greenhouse gases, Regulated Emissions and Energy use in Transportation (GREET) model.* https://greet.es.anl.gov/ (accessed 2022-10-27).

(35) Wernet, G.; Bauer, C.; Steubing, B.; Reinhard, J.; Moreno-Ruiz, E.; Weidmema, V. The Ecoinvent Database Version 3 (Part 1): Overview and Methodology. *Internation Journal of Life Cycle Assessment* **2016**, *21*, 1218−1230.

(36) Shaffer, K. *Consumptive Water Use in the Great Lakes Basin*; Fact Sheet 2000−3032; US Geological Survey: Washington, DC, 2008. http://pubs.usgs.gov/fs/2008/3032/pdf/fs2008-3032.pdf (accessed 2022-11-9).

(37) Li, S.; Tan, E.; Dutta, A.; Snowden-Swan, L.; Thorson, M.; Ramasamy, K.; Bartling, A.; Brasington, R.; Kass, M.; Zaimes, G.; Hawkins, T. Techno-Economic Analysis of Sustainable Biofuels for Marine Transportation. *Environmental Science & Technology*. **2022**, *56*, 17206.

https://doi.org/10.1021/acs.iecr.2c04307
Ind. Eng. Chem. Res. 2023, 62, 5241−5251