Simulation with Computational Fluid Dynamics of Succinic Acid and Co-Product Biorefinery Process

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Abstract
Succinic acid is a di-carboxylic acid with tremendous future market potential, and there is increasing interest to produce it from microorganisms using cheap renewable resources like biomass. However, commercialization of bio-succinic acid is currently challenged by limited profitability of processes devoted solely to succinic acid, high downstream process costs, and minimal available industrial-scale simulation. To address these limitations, a novel industrial-scale biorefinery process to convert corn-stover into succinic acid and co-products was simulated using an integrated mathematical model developed from reported laboratory-scale experimental data. The upstream section of the biorefinery featured handling, pre-treatment, conversion, and separation of corn stover feedstock into a liquid fraction for ethanol processing and a solids fraction containing mainly cellulose that was further hydrolyzed into glucose for succinic acid processing. Subsequent units of operation were then simulated for a baseline process: Microfiltration was used to remove residual insoluble lignin, and glucose was then continuously fermented by the strain *M. Succiniciproducens MBEL55E* to produce succinate and by-products acetate, lactate, and formate. Additional steps to recover and purify succinic acid included cell microfiltration for cell removal, moving-bed adsorption for sugar removal and decolorization, nanofiltration for separation of succinate primarily from other salts, ion exchange for acidification and purification, and finally crystallization. The finite volume method of Computational Fluid Dynamics (CFD) was coupled with kinetic, stoichiometric, mass, and energy balance equations to simulate the effects of inlet temperature impeller speed, diameter, and spacing, as well as inlet temperature and fermentor volume, on fermentor cooling jacket heat transfer area. Predicted dissolved CO$_2$ concentrations in the fermentor were in agreement with those in literature. The effects of microfiltration recirculation rate, microfiltration stage numbers, and adsorber sorbent particle diameter on dimensional requirements and power consumption were additionally evaluated. Yields and estimated volume and area requirements for units of operation were obtained for the baseline process and for those involving the simulated variable changes. This work represents the first reported industrial-scale bio-succinic acid process model.

Key words: Succinic acid; Biorefinery; Manheima succiniciproducens; Process simulation

Introduction
Succinic acid is a di-carboxylic acid which can be used as a C4 chemical building-block for manufacturing industrially valuable chemicals like adipic acid, N-methyl pyrrolidinone, 2-pyrrolidinone, succinate salts, 1,4-butanediol, maleic anhydride, tetrahydrofuran and gamma-butyrolactone, as well as ion-chelators, surfactants, detergents, synthetic resins, biodegradable polymers, pharmaceuticals, antimicrobials, food acidulants, flavor-enhancers, and green solvents [1-3]. Current succinic acid production ranges from 25,000–36,000 t/year, and market price ranges from $5.90–9.00(U.S.)/kg depending on purity [3, 4]. Succinic acid market and price were predicted to range from 180,000–27,000,000 t/year [1, 5], and from $0.50–1.50(U.S.)/kg, respectively [2, 5].

Conventional production of succinic acid involves chemically processing fossil-based resources like petroleum through oxidation of n-butane or benzene via maleic anhydride, followed by hydrolysis and dehydrogenation [2, 6]. However, there is increased commercial and scientific interest to instead produce succinic acid from microorganisms using cheaper renewable resources like biomass. In 2004, the U.S. Department of Energy designated succinic acid as one of the top value-added chemicals from biomass [7]. Prospects of global bio-based succinic acid markets motivated companies BioAmber, DSM and Roquette, BASF and CSM, and Myriant to announce construction of new plants since 2010 [8-10]. We previously demonstrated a process involving pre-treatment and hydrolysis of inexpensive and renewable ligno-cellulosic waste and residue like corncob from agricultural and food industries to yield substrates for microbial fermentative production of succinic acid and co-products [11].

Commercialization of bio-succinic acid is nonetheless currently challenged by limited profitability when a plant is devoted solely to succinic acid [5]. Succinic acid production should therefore occur in an integrated biorefinery, where co-production of ethanol, other carboxylic acids, and on-site steam and electricity via processing of recovered lignin residues enhance profitability. Commercialization is also challenged by high downstream costs associated with isolation, purification, and sterilization of end-products accounting for up to 80% of total production cost [12]. For example, succinic acid precipitation by Ca$^{2+}$-containing species results in excessive sludge waste and also adversely affects the fermented cellular metabolism and cell membrane fluidity and permeability [12-14]. Reactive extraction with tri-n-octalamine (TOA) [15] can remove glucose but suffers from organic solvent toxicity and waste. A promising batch laboratory-scale process involving four-acid products *Actinobacillus succinogenes* fermentation and downstream centrifugation, filtration, activated carbon adsorption, cation-exchange chromatography, vacuum distillation, crystallization, filtrat-

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Received November 01, 2011; Accepted December 08, 2011; Published December 10, 2011

Citation: Wensel P, Yu L, Chen S (2011) Simulation with Computational Fluid Dynamics of Succinic Acid and Co-Product Biorefinery Process. J Bioprocess Biotechniq S2:002 doi:10.4172/2155-9821.S2-002

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tion, and drying achieved an 89.5% succinic acid yield from substrate and 99% purity [8]. However, a commercial-scale biorefinery should instead recover valuable and volatile pyruvic, acetic, and formic acid by-products rather than eliminate them at 60°C and pH 4 with vacuum distillation [16]. In contrast, a nanofiltration process achieved sharp and non-destructive separation of succinate from a quaternary mixture containing lactate as opposed to pyruvate co-product but was not integrated with other purification steps [17].

Electrodialysis has been effectively used to concentrate and acidify succinic acid and other organic acids due to its environmental benignity, scalability, and ability to achieve high purity [18-27]. For instance, de-salting electrodialysis removed impurities and achieved a suitably concentrated, but undersaturated (< 25% weight) succinate solution for one process [22]. This was then converted into a supersaturated succinic acid solution where ionized succinic acid was converted into undissociated succinic acid by passing it through a water-splitting bipolar electrodialysis unit, from which an alkali NaOH stream was recycled to neutralize produced acids [22]. Conventional electrodialysis was similarly integrated to a feed containing concentrated organic salt sodium gluconate to a bipolar membrane as a way to increase stability and limit a decrease in current efficiency and dramatic increase in energy consumption that frequently results at a high organic salts conversion rate in bipolar membranes due to salt depletion in feed compartments and organic acids diffusion [25]. Integration resulted in an apparent current efficiency higher than 100%, low energy consumption, and a predicted process cost of $0.31 kg⁻¹, which was less than the $0.39 kg⁻¹ for the bipolar membrane [25]. Another process involving a succinic acid fermentation by E.coli strain ATCC202021 used first nanofiltration and then desalting electrodialysis to further concentrate and purify succinate salts and remove small and large molecular weight nonionic or weakly ionic compounds like sugars [26]. Severe membrane fouling was here alleviated by cleaning-in-place, reducing protein content in the fermentation broth, and raising its pH prior to microfiltration to denature the majority of proteins [26]. A mono-polar electrodialysis unit was also integrated with a continuous cell recycle fermentor for the production of succinic acid by A. succinigenes to continuously remove succinate and acetate from the permeate and recycle an organic acids-depleted solution back to the fermentor [19]. Compared to the cell recycle fermenter, this resulted in a five-fold increase in succinate concentration to 83 g/L at a high average succinate yield of 1.35 mol/mol and a slightly lower volumetric productivity of 10.4 g/L·h⁻¹ [19].

Nonetheless, a comparison between the technical feasibility of electrodialysis and that of other downstream methods must consider various factors like the cost of membrane and electrical energy consumption [8, 13, 18]. This may depend on purity levels and concentration profile, which in turn depends on water transport, the co-ion leakages [8, 13, 18]. This may depend on purity levels and concentration profile, which in turn depends on water transport, the co-ion leakages [8, 13, 18].

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J Bioprocess Biotechniq Bioprocessing ISSN:2155-9821 JBPBT, an open access journal
derived kinetics to the finite volume method of Computational Fluid Dynamics (CFD).

CFD involves numerical solution of conservation equations for mass, momentum and energy in a flow geometry of interest, together with additional subsidiary sets of equations reflecting the considered problem [35]. Flow optimization via this tool represents significant potential savings in time and resources and increased profitability for a low profit margin, bio-commodity succinic acid process [35] by providing more data than physical trials and reducing the need for numerous and expensive experiments with prototype fermentors and probes. This is the first reported process simulation for industrial-scale bio-succinic acid production.

Method

Microsoft Excel v. 2007 software was used for calculations associated with process mass and energy balances, unit simulation via variable changes, and cost and sensitivity analysis. CFD numerical procedure was conducted with commercial code FLUENT (v.6.3.26)[36]. The simulated biorefinery process is shown (Figure 1). Description of major process streams are listed (Table 1). The feedstock was corn stover containing approximately 40–45% cellulose, 30–35% hemicellulose, and 10–20% lignin [11]. The biorefinery was located in Iowa, a state accounting for 19% of total U.S. corn production having infrastructure to fulfill biorefinery requirement for co-production of corn-based ethanol. Capacity of 2,500 tons (wet basis) of corn stover/day was selected according to a National Renewable Energy Laboratory (NREL) model where raw material was collected within a 50 km radius [37]. This was the basis for the mass and energy balances and flow rates to simulate the succinic acid process units ranging from lignin microfiltration to crystallization. Unlike for plants devoted solely to ethanol fuel production, the generalized energy balance did not aim to show the extent that corn stover was converted into fuel energy since acid products were not fuels. Instead, energy losses and stream energy content were estimated:

\[ E_{\text{stover}} = E_{\text{electricity}} + E_{\text{ethanol}} + E_{\text{acetic acid}} + E_{\text{formic acid}} + E_{\text{succinic acid}} + E_{\text{steam/hot water}} \]  

Energy content was determined by multiplying mass flux by the corresponding High Heating Values (HHV) of 16, 29.7, 21.1, and 32.1 MJ/kg for corn stover, ethanol, lignin, and for each of the carboxylic acid products, respectively [38]. Electricity requirement was determined from estimates of electrical motor power consumption (i.e. for fermentor and crystallizer agitator), control systems, etc. Thermal energy requirement was determined from individual unit energy balances.

Figure 1: General flow diagram for succinic acid biorefinery.
Lignin-generated steam flow rate was calculated from lignin HHV, a boiler thermal efficiency of 0.65, specific enthalpy of steam at pre- 
hydrolysis conditions, and recovered lignin flow rate. For microfiltration, all insoluble lignin was retained, and the amount of glucose sub-
strate partitioned to the retentate and permeate was 5% and 95% by mass, respectively. Retentate lignin concentration was specified based on a 
reported level 300g/L of soluble lignin ultra-filtered in a pulp and mill plant [39]. To avoid rapid membrane caking or fouling, recircula-
tion rate of 6m/s was used for the baseline process but also varied for 
simulation, and specified inner diameter and length dimensions of the 
tubular module ensured turbulent Reynolds number. Assuming 40μm diameter spherical and insoluble lignin particles, inertia-lift theory [40] was used to calculate constant critical permeate flux representing 66% of the steady-state permeate flux [41] as follows:

\[ J_c = \frac{0.024 \rho_p r^3 \gamma_w}{\mu_p} \]  

(2)

where \( J_c \) is critical permeate flux (m/s), \( \rho_p \) is permeate density (kg/m³), \( \mu_p \) is permeate viscosity (Pa·s), \( r \) is lignin particle radius (m), and \( \gamma_w \) is tubular wall shear rate (s⁻¹). Microfiltration membrane area requirement was the ratio of mass balance-derived permeate flow rate to critical flux. Microfiltration power consumption was calculated [42]:

\[ P_{micro-1} = 0.04 \rho \eta_p A_{micro-1} U_{micro-1} \rho_p \]  

(3)

where \( P_{micro-1} \) is pump power consumption (J/s), \( U_{micro-1} \) is recirculation rate (m/s), \( \eta_p \) is pump efficiency (Dimensionless), \( A_{micro-1} \) is the area requirement (m²), and Re is Reynolds Number (Dimensionless) calculated as follows:

\[ Re = \frac{U_{micro-1} d_{micro-1} \rho_p}{\mu_p} \]  

(4)

Where \( d_{micro-1} \) is tube inner diameter (m). The microfiltration reten-
tate was then centrifuged to further de-water and concentrate its lignin 
before boiler combustion. A Sigma Factor Σ specifying disk-type cen-
trifuge area requirement was calculated [40]

### Fermentation

The centrifuged and de-lignified retentate liquid stream containing 
glucose was then combined with microfiltration permeate, sterilized 
and cooled in external heat exchanger, and introduced to the continu-
ous fermentor for succinic acid and co-production of lactic acid, ace-
tic acid, and formic acid. The baseline process used the available batch 
kINETIC parameters of M. succiniciproducens MBEL55E [6], a gram-
negative capnophbic bacterium isolated from bovine rumen [32]. 
Succinic acid is metabolically both an intermediate of the reductive TCA cycle and fermentative end product for this and other anaerobic and 
faculative microorganisms [32]. Some other strains [3] have reportedly 
higher succinic acid yields and titers than M. succiniciproducens (Table 2). 
Some even have the flexibility of C5 and C6 sugar uptake [11] and 
Simultaneous Sacharification and Fermentation (SSF) [43]. However, 
their parameters were either unreported or less usable because yield 
and production terms were convoluted into single terms [33]. Nonethe-
less, the effect of substituting in an A. succinogenes succinic acid pro-
ductivity term on overall succinic acid yield was simulated.

An algorithm depicting the CFD-coupled model to predict the 
effect of impeller speed and inlet temperature on fermentor cooling 
jacket heat transfer area requirement is illustrated (Figure 2). To ini-
tially determine fermentor dimensions for such CFD simulation, an 
idealized Continuously Stirred Tank Reactor (CSTR) at steady-state

| Major Process Stream ID | Description |
|------------------------|-------------|
| 1                      | Corn Stover Feedstock (Dry Basis) |
| 2                      | Corn Stover Feedstock Water Moisture Content |
| 3                      | Losses |
| 4                      | Supplemented Water |
| 5                      | Shredded Corn Stover |
| 6                      | Sulfuric Acid |
| 7                      | Steam |
| 8                      | Pre-treated Stover 1 |
| 9                      | Steam |
| 10                     | Pre-treated Stover 2 |
| 11                     | Supplemented Water |
| 12                     | Liquid Hemicellulose Fraction to Ethanol Plant |
| 13                     | Solids Cellulose Fraction to Succinic Acid Plant |
| 14                     | Calcium Hydroxide |
| 15                     | Supplemented Water |
| 16                     | Cellulose Fraction to Sacharification |
| 17                     | Hydrosolayte |
| 18                     | Lignin Microfiltration Retentate |
| 19                     | Concentrated Lignin to Steam and Power Generation |
| 20                     | Centrifuged Retentate Flowthrough |
| 21                     | Lignin Microfiltration Permeate |
| 22                     | Combined Permeate Feed to Fermentation |
| 23                     | Fermentation Product Streams (Cells, succinate, acetate, formate, and lactate) |
| 24                     | Cell Microfiltration Stage#1 Permeate |
| 25                     | Cell Microfiltration Stage#2 Retentate |
| 26                     | Cell Microfiltration Stage#1 Permeate |
| 27                     | Cell Microfiltration Stage#2 Retentate |
| 28                     | Combined Permeate Feed to Adsorption and Desorption |
| 29                     | Recovered Glucose Sugars |
| 30                     | Regenerating Hot Water Solution |
| 31                     | Nanofiltration Feed |
| 32                     | Nanofiltration Permeate |
| 33                     | Nanofiltration Retentate |
| 34                     | Hot Water Regeneration Solution |
| 35                     | Lactic Acid Flowthrough for Further Processing |
| 36                     | Stripped Lactic Acid Eluant |
| 37                     | Vented Water Vapor |
| 38                     | Mother Liquor from Circulating Magma for Further processing |
| 39                     | Succinic Acid Crystal |

Table 1: Description of major process flow streams.

Upstream processes including lignin microfiltration and cen-
trification

Upstream processes ranging from raw material corn stover feed 
handling to sacharification resembled those of a previous corn-based 
ethanol biorefinery [37], with the following major modifications and 
simplifying assumptions: First, pre-hydrolysis, the most thermal energy-
consuming plant process, involved 1.2% diluted sulfuric acid and 
pressurized steam at 245°C, and 13.6 bar instead of ammonia fiber ex-
pansion (AFEX) to enable separation of liquid hemicellulose streams 
composed primarily of pentoses for ethanol fermentation and solid 
celulose streams composed primarily of hexoses for glucose-based 
succinic acid fermentation. Second, the process included single-stage 
cross-flow tubular microfiltration units and centrifuge to remove and 
recover insoluble lignin from hydrolysate for combustion in a boiler 
and extra biorefinery steam and electricity.

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Table 2: Yields, reaction rates, and titers for C. glutamicum, A. succinogenes, and M. succiniciproducens.

| Microorganisms       | Y (g/g DCW) | qm (g/g DCW/h) | r_{max} (g/l/h) | Titer (g) | Residence-Time (h) |
|----------------------|-------------|----------------|-----------------|-----------|--------------------|
| C. glutamicum        | 0.92        | 0.06           | 3.17            | 146       | 46                 |
| A. succinogenes      | 0.82        | N.D.           | 1.36            | 105.8     | 78                 |
| M. succiniciproducens| 0.76        | 0.72           | 1.80            | 52.4      | 30                 |

with equivalent inlet and outlet flow rates was assumed. The fermentor was assumed to be cylindrical, free of headspace and internals, and sparged at the bottom by pure CO2 gas from a clean, filtered, and recycled exhaust waste stream integrated from biorefinery ethanol fermentors. Steady-state liquid-phase mass balances for the component cell biomass, substrate, and carboxylic acid products using the available batch kinetic parameters of M. succiniciproducens MBEL55E [6] were therefore developed:

Viable cell liquid-phase mass balance:

\[
dX \frac{dt}{dt} = 0 = \frac{F(X_s - X_c)}{V_l} + \mu X_c - k_d X_c
\]  

where is steady-state cell biomass concentration (kg DCW/m3), is initial feed cell biomass concentration (kg DCW/m3), is specific death rate (s^{-1}), is inlet/outlet volumetric flow rate (m^3/s), is fermentor liquid volume (m^3), and is specific growth rate (s^{-1}). Omitting substrate and product inhibition terms [6] and assuming Monod kinetics to avoid multiple non-washout steady-states [34], was further expressed as:

\[
\mu = \frac{\mu_{max} S_c}{K_S + S_c}
\]

where \(\mu_{max}\) is maximum specific growth rate (s^{-1}), is glucose substrate half-saturation constant (kg/m^3), and \(S_c\) is steady-state glucose substrate concentration (kg/m^3). Because feed was previously sterilized, \(X_c = 0\) kg/m^3. The recycle of cells back to the fermentor after downstream microfiltration recovery was for simplicity not simulated. A shear-dependent death rate term coupled with CFD simulation parameters was included as follows [44]:

\[
k_d = \frac{CN_{impeller}d_{impeller}^3}{V_{1.25}^2V_{7.575}}^{3.75}
\]

where \(N_{impeller}\) is rotational impeller speed (rps), \(d_{impeller}\) is equivalent diameter for rodococcal M. succiniciproducens (m), \(D_{impeller}\) is impeller diameter (m), is dynamic viscosity (m^2/s), \(V_l\) is fermentor liquid volume (m^3), and \(c\) is cell-dependent death rate constant (m^3/s). However, \(k_d\) is 0, as M. succiniciproducens, unlike animal cells, likely had a very small death rate constant since E.coli were reportedly damaged only at shear rates exceeding 1250 Pa [45].

Carboxylic acids product liquid-phase mass balances:

\[
\frac{dP_A}{dt} = 0 = \alpha_{A_{ss}} \mu X_c + \beta_{A_{ss}} X_s - \frac{F(P_{A_{ss}})}{V_{L_{ss}}}
\]

\[
\frac{dP_A}{dt} = 0 = \alpha_{A_{ss}} \mu X_c + \beta_{A_{ss}} X_s - \frac{F(P_{A_{ss}})}{V_{L_{ss}}}
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\]

\[
\frac{dP_A}{dt} = 0 = \alpha_{A_{ss}} \mu X_c + \beta_{A_{ss}} X_s - \frac{F(P_{A_{ss}})}{V_{L_{ss}}}
\]

Glucose substrate liquid-phase mass balance:

\[
\frac{dX_s}{dt} = \frac{F(S_s - S_c)}{V_l} + \mu X_c \frac{X_s}{\gamma_s} + \frac{K_S}{\gamma_s} \left( \frac{X_c}{\gamma_c} \right) - \frac{P_{A_{ss}} \gamma_A}{\gamma_A} X_s - m X_s
\]

where \(S_s\) is initial glucose substrate feed concentration (kg/m^3), \(m\) is glucose substrate maintenance term (kg/kg), \(Y_{L_{ss}}\) is yield coefficient of biomass from glucose substrate (kg/kg), \(Y_{A_{ss}}\) and \(Y_{L_{ss}}\) are yield coefficients for succinic acid, acetic acid, lactic acid, and formic acid, respectively (kg/kg).
The steady-states of Equation 14-20 were then plotted against dilution rate. Graphically determined optimal dilution rate corresponding to maximum steady-state volumetric productivity was used to obtain the steady-state outlet liquid-phase biomass, glucose, and carboxylic acid product concentrations. Optimal dilution rate was also obtainable by setting the derivative of steady-state volumetric productivity with respect to dilution rate to 0. The fermentor liquid volume specifying conditions were applied on all walls. The wall temperature was set at the fermentation broth temperature 39°C [6]. The convergence criteria required that the scaled residuals decrease to $10^{-5}$ for each conservative equation. For gas-liquid two-phase flow where Re>10,000, mixing time was estimated as follows [44]:

$$t_s = \frac{6}{N_0 \cdot \rho \cdot \omega}$$

Aerated power consumption $P_{impeller}$ was then calculated [44]:

$$P_{impeller} = 0.10 \cdot F_g^{0.15} \cdot N_{impeller}^{2.4} \cdot \rho_f^{0.2} \cdot \frac{g \cdot H_{impeller} \cdot V_l}{\alpha_{impeller}}$$

where $F_g$ is volumetric CO$_2$ gas flow rate (m$^3$/s), $g$ is gravitational constant (m/s$^2$), and $H_{impeller}$ is height of impeller blade (m). The rate $F_g$ was obtained from $V_l$ and the 0.25 vvm of pure CO$_2$ reportedly sparged in $M$. succiniciproducens MBEL55E fermentation [6]. A superficial CO$_2$ gas velocity $V_g$ (m/s) was obtained from $F_g$ and $D_o$ and a volumetric gas-liquid mass transfer coefficient $k_a$ (s$^{-1}$) was calculated from an empirical correlation for non-coalescing (dirty) dispersions as follows [34]:

$$k_a = 0.002 \cdot \left( \frac{P_{impeller}}{V_l} \right)^{0.7} \cdot V_l^{0.2}$$

Using the CFD-derived $k_a$, the steady-state CO$_2$ liquid-phase concentration exiting the fermentor [CO$_2$]$_l$ (kg/m$^3$) was then solved from the following steady-state mass balance:

$$\frac{d[CO_2]_l}{dt} = 0 = F_g ([CO_2]_g - [CO_2]_l) + K_a \cdot V_g \cdot \frac{y \cdot H[CO_2]_g}{P} - r_{CO_2} V_l$$

where [CO$_2$]$_l$ is inlet CO$_2$ concentration (kg/m$^3$), $y$ is CO$_2$ mass fraction in inlet gas sparging stream, $H$ is Henry's Law constant (Pa kg CO$_2$/m$^3$), $P$ is total pressure (Pa), $r_{CO_2}$ is volumetric rate of consumption of CO$_2$ by reaction in the liquid phase (kg/s), and $K_a$ is overall gas phase mass transfer coefficient (kgPa$^{-1}$s$^{-1}$). The Kga was approximated with $k_a$ assumed negligible:

$$1 = \frac{1}{K_a} = \frac{1}{k_a} + \frac{H}{k_a}$$

It was assumed that there was no axial or time-dependence on the gas phase composition of the bubble since pure CO$_2$ was assumed sparged and $y=1$. Total pressure accounted for atmospheric and fermentor height-dependent hydrostatic pressure. CO$_2$ is incorporated in the PEP carboxylation pathway [32], and a reported 1:1 ratio of moles of CO$_2$ fixed to moles of succinic acid produced [6] was used for calculation of $r_{CO_2}$. Metabolic production of CO$_2$ by $M$. succiniciproducens was not modeled [6]. The Henry's Law constant was adjusted for ionic...
strength of fermentation broth using Bunsen coefficients [32]. The inlet liquid-phase concentration \([\text{CO}_2]\) was 0 kg/m³.

Flow rates and solved \([\text{CO}_2]\) concentration and inlet gas-phase concentration \([\text{CO}_2]\) were then used to calculate steady-state gas-phase CO2 concentration \([\text{CO}_2]\), exiting the fermentor at the top (kg/m³) from a total CO2 fermentor mass balance. The mass fraction of water vapor also exiting the top was estimated from ratio of water vapor pressure estimated with the Antoine equation [49] at atmospheric pressure and 39°C to total atmospheric pressure. This and the exiting CO2 gas mass flow rate \(F_{\text{CO}_2,\text{out}}\) (kg/s) were then used to obtain a mass flow rate of exiting water vapor \(F_{\text{water,\text{out}}}\) (kg/s). With gas and liquid-phase mass flow rates now specified, a fermentor energy balance provided the heat removed term using the agitator power consumption and exiting CO2 and water vapor enthalpy terms obtained from CFD simulation:

\[
Q_{\text{removed}} = \eta_{\text{impeller}} P_{\text{impeller}} + \sum F_i h_i + \sum F_{\text{out}} h_{\text{out}}
\]

where \(Q_{\text{removed}}\) is rate of heat to be removed (J/s), \(\eta_{\text{impeller}}\) is gearbox efficiency, \(F_i\) and \(F_{\text{out}}\) are inlet and outlet mass flow rates of components i, respectively (kg/s), \(h_i\) and \(h_{\text{out}}\) are inlet and outlet mass enthalpy of components i, respectively (J/kg). With exception of terms for water vapor involving a phase change and \(M.\ succiniciproducens\) cells, component enthalpy terms were calculated as follows:

\[
H_i = H_i^0(T_i^0) + \frac{1}{T_i} C_p dT
\]

where \(H_i^0(T_i^0)\) is heat of combustion for component i (J/kg) at reference temperature \(T_i^0 = 25°C\), \(T_i\) is fermentation broth temperature of 39°C for outlet streams and either the baseline 40°C or simulated 42°C for inlet liquid streams, and \(C_p\) is heat capacity of component i (J/kg°C). Water vapor mass enthalpy was similarly calculated but by also adding an enthalthemic enthalpy of vaporization for water vapor (J/kg). Heat of combustion mass enthalpy for \(M.\ succiniciproducens\) cells biomass on dry-weight, 8% ash-basis was calculated by the Dulong equation [34]:

\[
H_i^0 = 8.076C + 34.462(H - O)\frac{Q}{8}
\]

where C, H, and O represent the experimentally-determined weight fractions of carbon, hydrogen, and oxygen, respectively, for \(M.\ succiniciproducens\) cells from its elemental composition CH1.736O0.367N0.240 [6]. Assuming cooling water with inlet and outlet temperatures of 25°C and 39°C across a length of 0.0254 m, a high cooling water mass flow rate was obtained from \(Q_{\text{removed}}\) temperature difference, and water heat capacity. Fermentor cooling jacket heat transfer area requirement was therefore calculated:

\[
A_{\text{heat}} = \frac{Q_{\text{removed}}}{U(T_i - T_w)}
\]

where \(U\) is overall heat transfer coefficient (W/m²°C), \(T_i\) is average cooling water temperature of 30°C, and \(T_w\) is fermentation broth temperature of 39°C. Like the previous overall mass transfer coefficient \(K_{\text{a}}\), overall heat transfer coefficient was approximated as a sum of resistances in series as follows:

\[
\frac{1}{U} = \frac{1}{h_f} + \frac{1}{h_{FD}} + \frac{\Delta x}{h_C} + \frac{1}{h_L} + \frac{1}{h_{CD}}
\]

where \(h_f\) is heat transfer coefficient for the fermentation broth (W/m²°C), \(h_{FD}\) is heat transfer coefficient (a.k.a. dirt factor) from fermentation broth fouling deposits (W/m²°C), \(k_i\) is thermal conductivity of the fermentor wall stainless steel (W/m°C), \(\Delta x\) is fermentor wall thickness (m), \(h_L\) is cooling water heat transfer coefficient (W/m²°C), and \(h_{CD}\) is cooling water fouling deposits heat transfer coefficient (W/m²°C). The fermentation broth heat transfer coefficient \(h_i\) depended directly on impeller speed and diameter specified for CFD simulation as follows [34]:

\[
\frac{h_i}{k_i} = 0.42 \left( \frac{D_{\text{impeller}}/N_{\text{impeller}} \rho_f}{\mu_f} \right)^{0.24} \left( \frac{C_{\text{cell}} \mu_f}{k_f} \right)^{0.13} \left( \frac{\mu_f}{k_f} \right)^{0.14}
\]

where \(\mu_f\) is wall viscosity (kg/s/m), and \(k_i\) is fermentation broth thermal conductivity (W/m°C). Effect of impeller speed and inlet temperature on heat transfer area was therefore simulated.

Cell microfiltration

A two-stage cross-flow tubular microfiltration unit, whereby the retentate of the first stage became the feed of the second stage, then removed and recovered all cells from the broth exiting the fermentor containing succinate, acetate, formate, lactate, and unconsumed glucose. The intended recycle of cells back to the fermentor for simplicity was not simulated. Final cell retentate concentration was limited to 100 kg/m3 because this corresponded to an exponential increase in viscosity and a non-Newtonian transition of a lactic acid fermentation broth increasing pump energy consumption [50].

\[
J_{\text{micro-2}} = 1.31 \left( \frac{D_{\text{cell}}}{L_{\text{micro-2}}} \right)^{1/3} \left( \frac{C_{\text{cell}}}{C_{\text{cell}} - 1} \right)^{1/3}
\]

where \(D_{\text{cell}}\) is particle diffusion coefficient of \(M.\ succiniciproducens\) cells in succinic acid fermentation broth (m²/s), \(L_{\text{micro-2}}\) is tube length (m), \(\gamma\) is shear rate (s⁻¹), \(C_{\text{cell}}\) is gel polarization volume fraction, and \(C_{\text{cell}}\) is bulk cell volume fraction. Effect of single-stage on area and power requirements, calculated as before, was simulated and compared to two-stage baseline process.

Adsorption and desorption

A granulated activated carbon (GAC) counter-current-moving-bed adsorber then removed 98% of glucose from microfiltration permeate to further purify the products. Intended recycle of glucose back to the fermentor for simplicity was not simulated. Only 2.5% lactate and 1% succinate was lost in the sorption process. GAC sorbent was selected for its low cost and future derivation from biochar via pyrolysis of recovered lignin. Column height was estimated from the product of NTU (Number of Transfer Units) and HTU (Height of Transfer Units). NTU was calculated by integrating area from a plot of the single-component glucose equilibrium curve and of the mass balance-derived operating line [53]. The adsorption equilibrium curve was generated from Langmuir single-component glucose-GAC equilibria isotherm data [54]:

\[
q_{\text{glu}} = q_{\text{m,glu}} \frac{bC_{\text{glu}}}{1 + bC_{\text{glu}}}
\]

where \(q_{\text{m,glu}}\) is glucose concentration in GAC sorbent phase (mol glucose/kg GAC sorbent), \(q_{\text{m,glu}}\) is maximum sorbent capacity (mol glucose/kg GAC sorbent), \(C_{\text{glu}}\) is glucose concentration in liquid phase (mol glucose/m³ feed solution). HTU was estimated as follows [53]:

\[
HTU = \frac{V_{\text{adsorber}}}{K_{\text{adsorber}} a_{\text{t}}}
\]

where \(K_{\text{adsorber}}\) is overall mass transfer coefficient (m/s), \(V_{\text{adsorber}}\) is industry-acceptable adsorber hydraulic loading rate based on selected...
column diameter (m/s), and \( a_i \) is particle interfacial area/volume ratio (m\(^3\)) calculated as follows:

\[
\frac{a_i}{d_i} = \frac{6(1 - \varepsilon)}{d_i}
\]

where \( \varepsilon \) is bed porosity or void fraction (dimensionless) and \( d_i \) is GAC particle diameter (m), which for the baseline process was 800\( \mu \)m but was also simulated at 600\( \mu \)m. Overall mass transfer coefficient \( K_{\text{adsorber}} \) was estimated as follows [55]:

\[
K_{\text{adsorber}} = \frac{1}{k_{\text{film}}} + \frac{1}{k_i}
\]

where \( k_{\text{film}} \) is film-mass transfer coefficient (m/s) and \( k_i \) is intra-particle mass transfer coefficient (m/s). The \( k_{\text{film}} \) and \( k_i \) and associated effective and Knudsen diffusivities were estimated from empirical correlations [55]. Adsorber column pressure drop for pump power consumption was estimated with the Ergun equation [56]. For a desorber column, it was assumed that regenerant had 0% glucose entering. A 96% regeneration yield in the desorber was assumed using 90°C hot water for a 2nd regeneration. Column loading was estimated as follows [59]:

\[
\frac{\text{LUB}}{L_t} = \left(1 - \frac{k_i}{K_{\text{adsorber}}}\right)\frac{d_i}{L_t}
\]

where \( L_t \) is length of small-scale column (m), \( t_b \) is breakthrough time for succinic acid (s), \( t_s \) is service time (s), \( q_{\text{in}} \) is ratio of feed succinate liquid-phase concentration to Dowex sorbent succinate solid-phase concentration in equilibrium, and \( \varepsilon \) is bed porosity or void fraction (dimensionless). Area reduction factor correlation for hollow fibers and turbulent flow regime [58]. Area and power requirement was calculated as before.

**Ion exchange**

Nanofiltration retentate then entered one of two fixed-bed ion-exchanger columns containing weak anion exchange Dowex resin to both acidify and purify the undissociated (protonated) succinic acid from lactic acid via its greater hydrophobicity and unique divalent charge [31]. Column loading of the binary lactate and succinate mixture occurred at pH=4 above the pKa of lactic acid and below the pKa1 of succinic acid [31]. While one column was loaded, a second was regenerated with three bed volumes of 90°C water [59]. Loading and regeneration times were equal for steady-state operation. Sorption temperature exceeded 55°C to prevent crystallization of the highly concentrated succinic acid, although its adsorption efficiency on Amberlite resin is reportedly reduced at higher temperatures [60]. Ion exchange column height was the sum of SBH (Stochiometric Bed Height) [61] and LUB (Length of Unused Bed) [40]:

\[
\text{SBH} = \frac{v_{\text{in}} t_s}{(1 - \varepsilon) (q_{\text{in}} - c_o)}
\]

**Crystallization**

Ion exchanger eluant then entered an idealized continuous, circulating magma, stirred-tank, cooling-type MMSMR (Mixed Solution Mixed Product Removal) crystallizer to supersaturate only anhydrous 2- succinic acid from solution at pH=2 and 4°C [16]. Yield was obtained [62]:

\[
Y_{\text{cry}} = S_{\text{cry}} R_0 \left[ C_{\text{in-cry}} - C_{\text{in-cry}} \left(1 + V_d - V_s\right)\right]
\]

where \( Y_{\text{cry}} \) is maximum yield rate of crystal produced (kg/s), \( S_{\text{cry}} \) is weight of original free solvent water (kg/s), \( V_s \) is added dihent (kg/kg original free solvent water), \( V_d \) is solvent loss from evaporation (kg/kg original free solvent water), \( C_{\text{in-cry}} \) is initial concentration of succinic acid crystal in feed (kg anhydrous succinic acid/kg free solvent water), \( C_{\text{in-cry}} \) is final concentration assumed to be solubility at 4°C and pH=2 of succinic acid crystal in saturated mother liquor (kg anhydrous succinic acid/kg free solvent water), \( R_0 \) is ratio of molecular weights of hydrate and anhydrous salts. About 2% of the water in the feed was assumed evaporated. Crystal growth was size-dependent, and nucleation was mediated by both primary and secondary mechanisms from crystal-crystallizer impeller or wall collisions [63]. To estimate crystallizer volume, experimentally-derived batch kinetic expressions for succinic acid nucleation and growth rates as functions of supersaturations were available in literature [30]:

\[
J_{\text{nano}} = k_{\text{nano}} \ln \frac{C_{\text{in-cry}}}{C_{\text{in-cry}}}
\]

where \( k_{\text{nano}} \) is succinate mass transfer coefficient (m/s), \( C_{\text{in-cry}} \) is gel polarization concentration (kg/m\(^3\)), and \( C_{\text{in-cry}} \) is bulk feed concentration of succinate (kg/m\(^3\)). The \( C_{\text{in-cry}} \) was obtained by first plotting steady-state permeate flux as a function of trans-membrane pressure for reported succinate concentrations [17]. Natural logarithm of sodium succinate concentration was then plotted against these fluxes to yield a straight line equation where the x-intercept corresponding to \( J_{\text{nano}} = 0 \) at \( C_{\text{in-cry}} = 1 \) represented the \( C_{\text{in-cry}} \) of interest. The \( k_{\text{nano}} \) was determined from a linear regression.
However, we combined these into a more useful relative-kinetic expression:

\[ B = k_B n^{b_{\text{cry-impeller}}} G^{s} M_T^{b} \]  

(48)

where \( B \) is crystal nucleation rate(s\(^{-1}\)), \( G \) is crystal growth rate(s\(^{-1}\)), \( N \) is impeller speed (rps), \( M_T \) is magma density (kg succinic acid crystal/m\(^3\) mother liquor), and \( k_B, k_s, b, s, j, h, v, z \) are dimensionless coefficients and exponents. Assuming a power-volume ratio \( \varepsilon \) proportional to impeller speed as \( \varepsilon = P/V \sim N^3 \), by substitution crystallizer residence time was then estimated [63]:

![Figure 3: Changes in major stream flow rates throughout process.](image-url)
where $\tau$ is residence time (s), $L_m$ is median crystal size (m), $\varepsilon$ is power-volume ratio, $k_v$ is succinic acid crystal rhombic shape factor [30,64], $\rho_c$ is succinic acid crystal density (kg/m$^3$). Because $j=1$, crystal size and residence time were not functions of magma density. Also, because the growth to nucleation ratio-1 and $g_j$, crystal size was a function of residence time. The crystallizer did not include fines removal or crystal size classification. However, a 550 μm median crystal size was assumed and corresponded to a low 17.8% by weight adherence of residual mother liquor [63] that later affects filter cake porosity and reduce downstream rotary drum filter liquid washing costs. As for fermentor, crystallizer magma volume was estimated from volumetric flow rate and residence time.

**Economic analysis**

The biorefinery was considered an attractive investment only if recovery of investment period was less than 5 years. All costs were indexed for year 2010. No financial costs were included. Operating costs, investments and their adjustments by capital costs estimated from the materials of construction, etc. for sized units of operation from an ethanol biorefinery were used from literature [37]. Fixed costs were adjusted to include shift operators, shift supervisors, and yard employees for the operation of the downstream processes. The current variable cost of $60U.S./t of corn stover included harvesting, storage, transportation, and handling costs. A 10% per year depreciation rate for fixed-capital equipment with no salvage value was assumed. Sensitivity analysis was done to determine production costs when corn stover prices were $60/t and increased to $80 and $100/t, assuming a succinic acid yield of 1) that obtained in our baseline simulated process (Scenario A), 2) 15% (Scenario B), and 3) 19% (Scenario C). Current and future product market selling prices of $1/kg, $1/kg, $0.20/kg, $0.30/kg, and $40/MW/ hr for succinic acid, acetic acid, formic acid, and ethanol, and generated electricity, respectively, were used to determine annual revenues [65]. Because the targeted product was succinic acid, contributions to total production cost were assumed 60%, 5%, 5%, and 30% for succinic acid, acetic acid, formic acid, and ethanol, respectively.

**Results and Discussion**

An overall yield of 12.9% succinic acid, 10% ethanol, 5.4% acetic acid, 5.3% formic acid, and 0.5% lactic acid from corn stover feedstock was estimated after crystallization for the baseline process (Figure 3). The major process mass flow rates, temperatures, and pressures are depicted (Table 3). For 88542 kg/hr of corn stover feedstock, 11453 kg/hr succinic acid crystal was produced. Estimated area or volume requirements for the downstream units of operation are shown (Table 4).

\[
L_m = 3.67 \left( \frac{e^{-\frac{1}{6k_v^2}}}{M_p} \right)^{\frac{L_m^2}{k_v \rho_c \sigma}}
\]

where $\tau$ is residence time (s), $L_m$ is median crystal size (m), $\varepsilon$ is power-volume ratio, $k_v$ is succinic acid crystal rhombic shape factor [30,64], $\rho_c$ is succinic acid crystal density (kg/m$^3$). Because $j=1$, crystal size and residence time were not functions of magma density. Also, because the growth to nucleation ratio-1 and $g_j$, crystal size was a function of residence time. The crystallizer did not include fines removal or crystal size classification. However, a 550 μm median crystal size was assumed and corresponded to a low 17.8% by weight adherence of residual mother liquor [63] that later affects filter cake porosity and reduce downstream rotary drum filter liquid washing costs. As for fermentor, crystallizer magma volume was estimated from volumetric flow rate and residence time.

Using the available baseline kinetic terms of *M. succiniciproducens* for fermentation resulted in an overall succinic acid 12.9% yield that was less than the 18.65% yield from dried biomass from *C. glutamicum* [5] having unreported kinetic model parameters. However, replacing the *M. succiniciproducens* succinic acid productivity term $\alpha_a=1.169$ (kg/kg) with the $\alpha_a=3.60$ (kg/kg) reported for *A. succinogenes*, overall succinic yield nearly doubled to 25%, exceeding even the *C. glutamicum* yield. Such 25% yield using a term not of *C. glutamicum* but of the less productive *A. succinogenes* suggests improvements in both fermentation and our novel downstream recovery and purification are responsible. An optimal dilution rate of 1.20 hr$^{-1}$ corresponding to maximum *M. succiniciproducens* volumetric succinic acid productivity of 69.23 kg m$^{-3}$hr$^{-1}$ was predicted graphically (Figure 5) and compared well with the reported maximum *M. succiniciproducens* specific growth rate of 1.12hr$^{-1}$ at a dissolved CO$_2$ concentration of 23.3mM [32].This optimal dilution rate then provided a baseline fermentor liquid volume of 178.29m$^3$, liquid height of 12.69 m, and diameter of 4.23m as CFD inputs.

The extent that cooling jacket heat transfer area was linearly reduced by increasing $N_{imp}$/day from 10pm to 200rpm at both 40°C and 4°C. Simulation of microfiltration of insoluble lignin showed that area requirement decreased and pump power consumption increased with increasing recirculation rate (Figure 4). The baseline 6m/s recirculation rate consumed 123.325kW and resulted in a permeate flux of 0.0048 m/s.

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42°C inlet temperatures were simulated (Figure 6). At inlet \( T_2 \) of 40°C, at 200rpm, CFD predicted the average liquid speed of 3.01 m/s, \( P_{impeller} \) of 433391 Watts, \( k_a \) of 0.230 s\(^{-1}\), \( [CO_2] \) of 34.9 mM, and of 19.4 m\(^2\), \( P_{impeller} \) while at 100 rpm, CFD predicted an average liquid speed of 1.50 m/s, of 54575.3 Watts, \( k_a \) of 0.052 s\(^{-1}\), \( [CO_2] \) of 33.32 mM, and of 55.4 m\(^2\). The \( A_{heat} \) appears to linearly decrease with \( N_{impeller} \) with a regression coefficient of \( r^2=0.9896 \) as follows:

\[
A_{heat} = -0.4291N_{impeller} + 103.47
\] (50)

The predicted \( [CO_2] \) values at these conditions are within the same order of magnitude as the reported 23.3 mM when sparging with pure CO\(_2\) at partial pressure of 101.4 kPa (y=1) in a 2.2L liquid volume fermentor at 39°C agitated at 200 rpm [32]. Assuming instead an inlet \( T_2 \) of 42°C and minimal \( N_0 \) of 10 rpm, a higher heat term \( Q_{removed} \) resulted, and CFD predicted an \( A_{heat} \) of 211.7 m\(^2\) exceeding the available fermentor surface area of 168.6m\(^2\). Another external heat exchanger or more efficient spiral-wound cooling coils are therefore necessary for cooling at these impeller and inlet temperature conditions.

The CFD fermentor flow fields simulated at 10rpm, 100rpm, and 200 rpm are visually presented (Figure 7). There is a more pronounced increase in average velocity from 10-100 rpm than from 100-200 rpm. At 200 rpm, using instead a graphical power number correlation for power consumption, heat transfer area increases with impeller diameter up to an asymptotic value of 48m\(^2\) corresponding to the impeller diameter of 2m (Figure 8). The CFD fermentor flow field simulated at 200rpm for both baseline 178m\(^3\) and a 78m\(^3\) fermentor are visually presented (Figure 9). Maximum velocity of 16.9 m/s and 10.4 m/s is predicted for the large and small fermentor, respectively. A 3:1 height to diameter ratio was specified for our process, but future CFD simulations can instead predict hydrodynamic changes from varying fermentor height. At minimum, additional hydrostatic head from increased liquid height would impact the gas-liquid CO\(_2\) mass transfer of rising bubble flow.

The CFD fermentor flow fields simulated at 200rpm for the smaller 78m\(^3\) fermentor employing either the uniform impeller spacing [46] for the baseline process or a previously described alternate spacing [47] are visually presented (Figure 10). Evidently, the alternate spacing resulted in a higher maximum liquid velocity of 7.92 m/s and homogeneity and much less localized mixing, approaching more the assumed CSTR of the baseline process. Using the baseline 200 rpm and uniform impeller spacing, mixing time \( t_m \) was estimated to be 60.67 s for the 178 m\(^3\) fermentor. With greater computational power and resources available, multi-phase CFD fermentor simulations involving sparged CO\(_2\) gas and liquid can help process engineers optimize flow conditions and scale-up. In addition, mixing time can be used to schedule feeding of MgCO\(_3\) solution to both neutralize inhibitory carboxylic acid products and provide a more soluble and storable carbon source than CO\(_2\) gas in the fermentor [32].

Although the recycle of cells back to the fermentor after downstream microfiltration recovery was for simplicity not simulated, it is essential to note the potential outcomes if it were. The fermentation industry has long recognized the benefits of cell recycle using membranes or even expanded-bed adsorbers for increasing cell density and volumetric productivity in fermentations, and its mathematical depiction can include such things as a recycle ratio in the mass balances [66, 67]. In one study,
densities by virtue of the concurrent supply of both pH neutralizer and...the ratio Cg/Co, it was possible to have an intermediary bulk...m² and 68.80 kW for the two-stages of our baseline process. Because...compared with those at 0.1 h⁻¹ dilution rate [67]. Cell concentration in-
crease with dilution rate, even though it often oscillated before settling...of this current work, as these are expected to positively impact biosuc-
nic acid volumetric productivity increased five-fold to 6.63 g L⁻¹h⁻¹ at a
dilution rate of 0.5 h⁻¹ [67]. At high dilution rate, contamination by a lactic acid producer and severe membrane fouling were observed
[67]. M. succiniciproducens MBEL55E in this cell-recycle fermentor also
achieved a cell concentration and succinic acid productivity at the
dilution rate of 0.3 h⁻¹ that were at least 3 and 2.3 times higher, respectively, compared with those at 0.1 h⁻¹ dilution rate [67]. Cell concentration in-
crease with dilution rate, even though it often oscillated before settling
to a constant value [67]. Future studies to simulate the effect of such
cell recycle, in addition to glucose recycle, and compare productivity
gains obtained by either acid neutralization or electrolysis removal of inhibitory acid levels, should be further done to augment the scope of this current work, as these are expected to positively impact biosuc-
nic acid production.

Simulation of cell microfiltration with tubes of 0.75m length and 0.007m inner diameter resulted in a total area requirement and power consumption of 876 m² and 78.80 kW for single-stage and a lower 765 m² and 68.80 kW for the two-stages of our baseline process. Because permeate flux was predicted using gel polarization theory and was a function of the ratio Cg/Cc, it was possible to have an intermediary bulk feed cell concentration Cc from the first stage that differed from that of the second stage and resulted in different permeate fluxes for each stage [53].

A primary aim of this work was to simulate a large-scale, continu-
ous succinic acid biorefinery process. Advantages of membrane sepa-
ration like microfiltration include the ability to operate without phase change, at near ambient temperatures, with relatively low energy con-
sumption. Cross-flow microfiltration for macromolecular insoluble lignin and cells where feed flows parallel to the membrane surface was assumed more suitable for a continuous process than the relatively simpler dead-end filtration configuration requiring lower capital and maintenance costs [69], where the feed contacts the membrane surface at a perpendicular angle. This was primarily due to the intended high

Figure 10: CFD liquid velocity flow patterns at alternating and fixed axial im-
peller spacing for 78m³ fermentor.

Figure 11: Adsorption equilibrium curve and operating line for glucose re-
moval.

The M. succiniciproducens MBEL55E being fermented in the base-
line simulated process is a rod-shaped bacteria [1]. It is again interest-
ing to note that the morphology of this and other fermented succinic acid-producing anaerobes like A. succinogenes can also become more spherical and less productive for succinic acid due to high inhibitory glucose substrate concentrations above 80 g/L [70], which exceeded the calculated 10.89 g/L steady-state glucose concentration of this work. Rod-like bacterial morphology, unlike that of yeast cell layers, has in turn also influenced cake resistance differently in both dead-end and cross-flow filtration [71].

Activated carbon adsorption was previously used in downstream succinic acid recovery and purification processes [8, 26]. Simulation of the GAC adsorption column (Figure 11) resulted in an overall mass transfer coefficient of 5.29×10⁻⁴ m/s and pressure drop of 59 Pa/m for the baseline 841µm GAC particle diameter and a coefficient of 7.33×10⁻⁴ m/s and pressure drop of 90 Pa/m for a 600µm particle diameter. Evi-
dently, greater mass transfer efficiency must be balanced with higher pump power consumption costs.

The resulting nanofiltration retentate concentrations for succinate and lactate were 197.77 and 10.85g/L, respectively, while their permeate concentrations were 3.83 and 4.12g/L, respectively. A graphical method was used to predict gel-polarization concentration for the nanofiltration unit of the baseline process (Figure 12). For this, only three data points corresponding to succinate concentrations of 0.1, 0.2, and 0.3M were available from the literature to relate permeate flux with trans-
membrane pressure [17] but a reasonably high R² value of 0.9397 was still obtained from these. A gel-polarization concentration value of 303.2 kg/m³ succinate using the relatively simple gel-polarization mod-
el that assumes a steady-state permeate flux to be both independent of transmembrane pressure but dependent on solute concentration was calculated and then used to predict a steady-state flux of 1.42×10⁻⁴ m/s which was the same order magnitude but lower than the experimentally observed 4.44×10⁻⁴ m/s corresponding to 95% succinate rejection [17] that resulted in a very high area requirement.

Membrane nanofiltration performance depends on the complex in-
teration of many factors, and various models have been developed to try to predict actual phenomena but do not always perfectly succeed, as the results in this study also indicate [40,42,72,73]. For instance, molecular weight, molecular size (length and width), acid dissociation constant, hydrophobicity and hydrophilicity, and diffusion coefficient were identified as key solute parameters primarily affecting solute rejection [73]. Also, molecular weight cut-off, pore size, surface charge (measured as zeta potential), hydrophobicity and hydrophilicity (measured as contact angle), and surface morphology (measured as roughness) were identified as key membrane properties primarily affecting rejection [73]. Furthermore, solute rejection was affected by feed composition, like ionic strength, pH, hardness, and organic matter [73]. Another study evaluated the effects of pH, salt concentration, and temperature on the lactate flux and rejection when using a FILMTECTM NF-200B membrane nanofiltration of concentrated organic/inorganic mixtures of salt (up to 17% (w/v)) and lactic acid (2% (w/v)). Salt rejection was low, and lactate rejection was highest at neutral pH, decreasing with temperature and salt concentration for all evaluated solutions [27]. The measured flux and rejection values indicated that skin shrinkage in concentrated salt solutions and membrane sorption of lactate influences nanofiltration beyond the typical effects of charge, solute size and osmotic difference between the retentate and permeate streams [27].

According to the literature from which the high 95% succinate rejection values for simulation were derived, divalent anions of succinate in monovalent anion solutions could also dramatically decrease the rejection of the monovalent anions of formate, lactate, and acetate in the transport through nanofiltration membranes [17]. In this previous work, flux changed with concentration even at identical pressure, and rejection of succinate by NF45 membrane for different concentrations was plotted versus transmembrane pressures and permeate [17]. The rejection of succinate by NF45 membrane nanofiltration for different concentrations was plotted versus transmembrane pressures and permeate [17]. The typically observed decrease of a solute’s rejection with its concentration likely due to the increased screening of membrane surface charge by counterions like sodium was not observed in the cited study because even the lowest 0.1 M concentration of Na+ tested was probably already high enough to fully screen the membrane surface charge [17]. Clearly, the current biorefinery simulation work can be improved with more comprehensive and intensive evaluation of all significant factors affecting succinate rejection in nanofiltration. Operating conditions should as a result be further optimized to exploit this technology enabling non-destructive separation of succinate from other co-products in real-life industrial processes.

Capacity, low-cost regenerability, and specificity for succinate when acidifying and purifying it were factored into the selection of Dowex MWA-1 ion exchange resin and will also be considered in more comprehensive future economic studies. Nonetheless, it was before noted that a final concentration exceeding 100 g of succinic acid/L was likely economically feasible if achieved with resins that included XUS-40285 and XFS-40422 that were similarly manufactured by Dow® [59], and, in this work, a concentration of 222.87 g of succinic acid/L was predicted. As previously mentioned, an ion exchange resin like Amberlite IR-120 that was similarly used to acidify organic salts but that, in contrast, required HCl or H2SO4 regeneration, was also viewed as economically favorable to electrodialysis in some instances [18]. As for the fermentor, future multi-phase CFD simulation of crystallizer involving solid succinic acid crystal and liquid mother liquor can be done to assess the effect of impeller speeds on complex crystal nucleation and growth phenomena.

The general biorefinery energy balance is shown (Table 5). Approximately 15938 kg/h of lignin was recovered via microfiltration to fuel a boiler to generate steam and electricity, and 47.9% of the corn-stover feedstock (42412 kg/hr) was not converted into products. Lignin-generated steam msteam was estimated at 69410 kg/hr. However, to meet the biorefinery requirement of 154324 kg/hr of steam [37], first the steam pressure and temperature were increased by assuming instead that a commercial bubbling fluidized-bed boiler produced up to 160000 kg/h of steam at 15 MPa and T=450ºC with hsteam=3157 kJ/kg. Second, 42% of the biomass lost in the process was assumed recovered to provide the 17863 kg/h needed to fuel this new boiler. Since the new assumed steam conditions exceeded pre-hydrolisi requirements, the steam energy content was used to produce extra electricity in a steam turbine-generator system. Assuming a total efficiency of 52%, corresponding to 65% efficiency of turbine and 80% efficiency for generator when steam pressure and temperature drop to 1.36 MPa and 245 ºC, respectively, the generated power capacity was 4.2 MW, and electricity production was 36847 MWh/year. Total biorefinery power consumption, includ-

| Feedstock/Product          | Energy Content (MJ/h) | % of Total |
|----------------------------|-----------------------|------------|
| Dry corn-stover biomass    | 1416667               | 100        |
| Electricity                | 15120                 | 1.1        |
| Ethanol                    | 141667                | 10         |
| Lactic Acid                | 13161                 | 0.9        |
| Acetic Acid                | 153021                | 10.8       |
| Formic Acid                | 149147                | 10.6       |
| Succinic Acid              | 367641                | 26         |
| Steam+ Hot Water           | 511142                | 36         |
| Losses                     | 65173                 | 4.6        |

Table 5: General energy balance for succinic acid biorefinery process.

| Description of Analyzed Economic Parameter | US $ |
|-------------------------------------------|------|
| Total Project Investment (installed equipment and indirect costs) | 2.93E+08 |
| Annual Fixed Operating Costs (i.e. labor, overhead) | 11504720 |
| Annual Variable Operating Costs (i.e. feedstock, cooling water, etc.) | 55756068 |
| Annual Depreciation costs | 34367862 |
| Annual Revenues (Assumes product and lignin-electricity selling prices and yields) | 1.75E+08 |
| Annual Income | 73207273 |
| Return on Investment Period | 4.00 |

Table 6: Summary of Biorefinery Economic Analysis.
ing that estimated from CFD for the fermentor, was estimated as 8561 MWh/year. The difference between energy generated and consumed (27847 MWh/year) was therefore exported to the grid for $1131420/ year of revenues.

By integrating costs and capital investments literature data for ethanol bioferries [37] with feedstock costs, product pricing, and the predicted product yields and steam generation of the baseline simulated succinic acid bioferrie process, the rough estimates of costs, revenues, and income for the baseline succinic acid bioprocess were obtained and are shown (Table 6). Corn stover raw material represented the highest variable operating cost. Assuming a $1 U.S./kg succinic acid selling price for scenarios involving our 12.9% baseline yield, 15%, and 19%, the effect of increasing corn stover costs on ROI period is summarized (Figure 13). The succinic bioferrie was therefore profitable and attractive with an ROI period of 5 years or less only if succinic acid selling exceeded $1.6/kg.

Conclusion

A novel industrial-scale bioferrie succinic acid process was described and integrated pre-treatment and hydrolysis with lignin removal and recovery to provide on-site steam and electricity generation, glucose removal and recovery, and non-destructive nanofiltration succinate separation. A multi-unit process model was developed for important units of operation to enable future optimization. For the fermentor, Computational Fluid Dynamics (CFD) through its coupling to the kinetics, mass and energy balances was demonstrated to be a valuable and useful tool for scale-up. The succinic acid bioferrie was considered profitable and attractive only if the selling price of the succinic acid exceeded $1.6/kg. This work represents the first reported industrial-scale process design model for biochemically-derived succinic acid.

Acknowledgment

The work was funded by the Washington State University.

Nomenclature

| Symbol | Description |
|--------|-------------|
| $I_p$ | critical permeate flux, m/s |
| $p_r$ | permeate density, kg/m$^3$ |
| $v_p$ | permeate viscosity, Pa·s$^{-1}$ |
| $r$ | lignin particle radius, m |
| $Y_s$ | tubular wall shear rate, s$^{-1}$ |
| $D_{imp}$ | impeller diameter, m |
| $N_{imp}$ | rotational impeller speed, rps |
| $y$ | CO$_2$ mass fraction |
| $d_{eq}$ | equivalent cell diameter, m |
| $P_{limp}$ | pump power consumption, J/s |
| $V_i$ | dynamic viscosity, m$^2$/s |
| $u_{rec}$ | recirculation rate, m/s |
| $\eta_{p}$ | pump efficiency |
| $M$ | impeller torque, N·m |
| $d_{in}$ | tube inner diameter, m |
| $\mu$ | specific growth rate, s$^{-1}$ |
| $\Sigma$ | centrifuge Sigma factor, m$^2$ |
| $\alpha_{SA}$ | growth-associated productivity term for succinic acid, kg/kg |
| $f$ | inlet/outlet volumetric flow rate, m$^3$/s |
| $\alpha_{AA}$ | growth-associated productivity term for acetic acid, kg/kg |
| $X_a$ | steady-state biomass concentration (kg DCW/m$^3$) |
| $\alpha_{FA}$ | growth-associated productivity term for formic acid, kg/kg |
| $\beta_{SA}$ | non-growth associated productivity terms for succinic acid, kg/kg |
| $\beta_{AA}$ | non-growth associated productivity terms for acetic acid, kg/kg |
| $\beta_{FA}$ | non-growth associated productivity terms for formic acid, kg/kg |
| $K_S$ | glucose substrate half-saturation constant, kg/m$^3$ |
| $S_0$ | glucose substrate feed concentration, kg/m$^3$ |
| $S_{ss}$ | steady-state glucose substrate concentration, kg/m$^3$ |
| $P_{imp}$ | power number |
| $Y_{bi}$ | yield coefficient of biomass from glucose substrate, kg/kg |
| $N_p$ | power number |
| $Y_{sa}$ | yield coefficient of succinic acid from glucose substrate, kg/kg |
| $Y_{ss}$ | steady-state glucose substrate concentration, kg/m$^3$ |
| $Y_{SA}$ | yield coefficient of succinic acid from glucose substrate, kg/kg |
| $Y_{LA}$ | yield coefficient of lactic acid from glucose substrate, kg/kg |
| $Y_{FA}$ | yield coefficient of formic acid from glucose substrate, kg/kg |
| $F_0$ | volumetric CO$_2$ flow rate, m$^3$/s |
| $D_d$ | dilution rate, s$^{-1}$ |
| $g$ | gravitational constant, m/s$^2$ |
| $H_{imp}$ | height of impeller blade, m |
| $N_0$ | minimum impeller speed, rps |
| $k_a$ | volumetric gas-liquid mass transfer coefficient, s$^{-1}$ |
| $\sigma$ | surface tension, dyn/cm |
| $v_g$ | superficial CO$_2$ gas velocity, m/s |
| $\rho_f$ | fermentation broth density, kg/m$^3$ |
| $I_{w}$ | inlet mass flow rates of components i, kg/s |
| $P_{a}$ | aerated power consumption, J/s |
| $F_i$ | outlet mass flow rates of components i, kg/s |

Figure 13: Periods of return of investment for succinic acid selling price of $1 U.S./kg.
| Parameter | Definition |
|-----------|------------|
| $[\text{CO}_2]$ | inlet CO$_2$ concentration, kg/m$^3$ |
| $H$ | Henry’s Law constant, Pa kg CO$_2$/m$^3$ |
| $P$ | total pressure, Pa |
| $r_{CO_2}$ | rate of consumption of CO$_2$, kg/s |
| $K_{a,d}$ | overall gas phase mass transfer coefficient, kg/ Pa*s |
| $k_{a,d}$ | local gas phase mass transfer coefficient, kg/ Pa*s |
| $[\text{CO}_2]$ | inlet liquid-phase concentration, kg/m$^3$ |
| $[\text{CO}_3]$ | steady-state gas-phase CO$_2$ concentration exiting fermentor, kg/m$^3$ |
| $F_{CO_2-ext}$ | exiting CO$_2$ mass flow rate, kg/s |
| $F_{water-inlet}$ | exiting water vapor mass flow rate, kg/s |
| $Q_{inlet}$ | rate of heat to be removed, J/s |
| $U$ | overall heat transfer coefficient, W/m$^2$-°C |
| $C_T$ | average cooling water temperature, °C |
| $T_s$ | fermentation broth temperature, °C |
| $h_s$ | heat transfer coefficient for the fermentation broth, W/m$^2$-°C |
| $R_i$ | ratio of molecular weights of hydrate and anhydrous salts |
| $N_{cry}$ | crystalizer impeller speed (rpm) |
| $M_i$ | magma density, kg succinic acid crystal/m$^3$ |
| $k_c$ | Crystallizer coefficient |
| $k_s$ | Crystallizer coefficient |
| $L_{m}$ | median crystal size, m |
| $\tau$ | Crystallizer residence time (s) |
| $\Delta c$ | supersaturation, kg/m$^3$ |
| $k_{ps}$ | film-mass transfer coefficient, m/s |
| $v_{an}$ | ion-exchanger hydraulic loading rate, m/s |
| $k_i$ | intra-particle mass transfer coefficient, m/s |
| $q_{s} / c_s$ | ratio of feed succinate liquid-phase concentration to Dowex sorbent succinate solid phase-concentration in equilibrium |
| $k_{ads}$ | succinate mass transfer coefficient, m/s |
| $I_{t}$ | service time(s) |
| $C_{p, succ}$ | Succinate gel polarization concentration, kg/m$^3$ |
| $S_{ow}$ | weight of original free solvent water, kg/s |
| $J_{ads}$ | nanofiltration steady-state permeate flux, m/s |
| $V_{s}$ | added diluted, kg/kg original free solvent water |
| $R_i$ | ratio of molecular weights of hydrate and anhydrous salts |
| $M_i$ | magma density, kg succinic acid crystal/m$^3$ |
| $k_c$ | Crystallizer coefficient |
| $k_s$ | Crystallizer coefficient |
| $L_{m}$ | median crystal size, m |
| $\tau$ | Crystallizer residence time (s) |
| $\epsilon$ | power-volume ratio |
| $\rho_i$ | succinic acid crystal density, kg/m$^3$ |

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