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Embedding Aspen Custom Modeller for Bioethanol Fermentation into the Aspen Plus Flowsheet Simulator

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Commercial processes used to produce first generation biofuels are mature. In this study, a kinetic model using the equation-oriented process modelling tool Aspen Custom Modeller (ACM) was embedded into the process simulation environment of Aspen Plus and used to simulate industrial bioreactors with cell recycle for bioethanol production. To embed a native module in a process simulation environment, the legacy codes written in ACM were treated as a black box and integrated into the component-based framework. The compliance of ACM to Aspen Plus allows for proper integration of the reactor simulator developed for the fermentation process for bioethanol production using kinetic models. The aim of this research is to improve the ability to use custom kinetic models of fermentation processes, developed in equation-oriented modelling tools, within a sequential modular flowsheet simulator. The results obtained showed the accuracy of the selected kinetic model in ACM with less than 1% difference to industrial data, while a stoichiometric model showed approximately 9% difference to the industrial data. The simulation shows that ACM integrated into Aspen Plus allows for complex biological processes to be predicted accurately in terms of biomass growth, ethanol production and sugar consumption.

1. Introduction

Simulation provides a powerful tool to support the design of industrial processes and is now accepted as a critical step (Rhodes, 1996). Simulation tools for chemical process design can be divided into two categories, namely sequential modular (or block oriented) flowsheet simulators and equation-oriented process modelling tools (Schopfer et al., 2004). Sequential modular flowsheet simulator (SMFS) environments (e.g. Aspen Plus, Aspen HYSYS, and PRO/II) are widely used by process engineers owing to their ease of use and robustness in handling large-scale process simulation problems (e.g. large number of unit operations, process streams and chemical components) (Gani et al., 2012). However, most SMFSs are limited in type and number of process unit operations models and are restricted to continuous steady-state processes (Dimian et al., 2014). The equation-oriented environments (e.g. gPROMS and ACM) can be used for steady-state and dynamic process simulation and optimization, as well as for parameter estimation and experimental design (Nawaz, 2015) . Equation-oriented process modelling tools offer the opportunity to develop custom process unit operation models without the need to develop numerical solution methods for the model equations (Gani et al., 2012). Therefore, it would be beneficial to combine these two simulation environments. The use of a custom process unit operation model, developed using equation-oriented modelling tools combined in a SMFS, requires interfacing between the different software programmes. In the early 1990s, the idea of an open interface for integration data between process simulation software of various origins was put forward by academic institutions and industry. Several CAPE-OPEN (Computer Aided Process Engineering) projects were initiated to develop standards and to explore the possibilities for open interfaces for integration of process unit operations, thermodynamic and physical property packages, and numerical solvers between the various process simulation tools (COLaN, 2016). ACM can be used to develop custom process unit operation models which are not available in the Aspen Plus model library (Brinkmann et al., 2003). After development,

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the custom model can be used as a user model block embedded inside a sequential modular flowsheet simulator (Dimian et al., 2014). For consistent flowsheet simulation and optimization, the use of a custom model in Aspen Plus requires interfacing with equation-oriented modelling tools (Nikolić, 2016). Testing the status and performance of the software interoperability, as well as examining the custom model performance in Aspen Plus with experimental and, specifically, industrial results for full-scale process design would be essential. Hence, this paper describes the development of the customised kinetic model, its interfacing with Aspen Plus and the validation with experimental and industrial data for bioethanol production. The current practice is for simulating a unit operation present in a process flowsheet, in which the required kinetic model of bioethanol production from sugarcane, considering ethanol inhibition, substrate inhibition and substrate limitation, does not exist in the model library. To allow a deeper understanding of the impacts of inserting kinetic models for the fermentation process into the sequential modular flowsheet simulator Aspen Plus, simulations of bioethanol fermentation process were executed at a small scale and industrial plant scale. A schematic picture of the unit model interface in Aspen Tech (ACM and Aspen Plus) is shown in Figure 1.

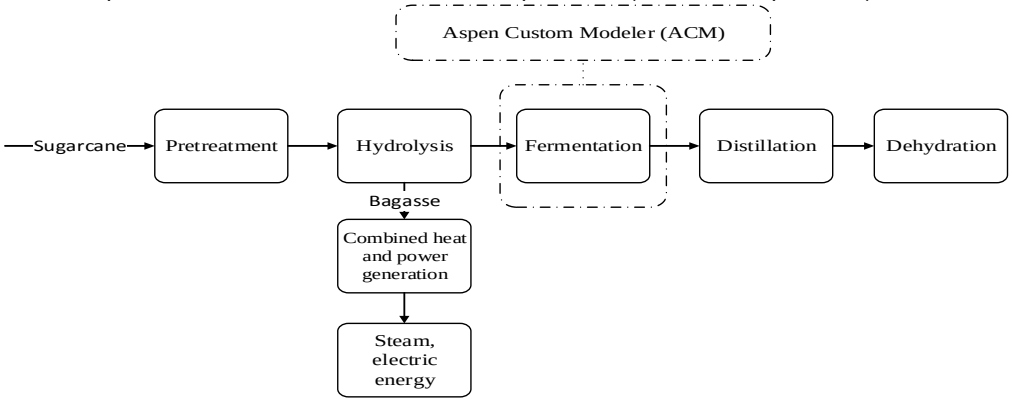

Figure 1: The custom model block (ACM) of a process unit operation in a sequential modular flowsheet simulator (Aspen Plus) for bioethanol production process from sugarcane (Dias et al., 2010)

2. Materials and Methods

2.1 Experimental work for validation

2.1.1 Microbial strains, culture storage and growth media

The strain of *Z. mobilis* ZM4 (ATCC 31821) was used throughout the study. For short-term storage, all cultures were stored in the solid rich medium (RM) (Goodman et al., 1982) containing per litre: 20 g glucose, 10 g yeast extract, 2 g KH_2PO_4, 15 g agar, 1000 ml DI water. Agar plates were stored at 4 °C. For long-term storage, the cultures were suspended in sterile 40% (v/v) glycerol and stored in 1.5 mL volumes at -60 °C. For this, equal amounts of the bacterial culture and 80% glycerol were mixed. The cell-glycerol mixture was kept at room temperature for half an hour prior to freezing.

2.1.2 Inoculum preparation and fermentation studies

Z. mobilis ZM4 (ATCC 31821) was subcultured in fresh inoculum media (10 g L^{-1} yeast extract, 1 g L^{-1} $MgCl_2$, 1 g L^{-1} $(NH_4)_2SO_4$, 1 g L^{-1} KH_2PO_4, with 44 g L^{-1} glucose) twice before being inoculated into the fermentor. For all cultivations, the yeast extract and inorganic salts (YEIS) solution were autoclaved separately from glucose. Inocula were incubated for 24 h at 30 °C in 250 mL conical flasks containing 50 mL medium in a shaker incubator at a speed of 120 rpm. Initial biomass of 2.1 g L^{-1} was used to inoculate the fermentor. Initial glucose concentration and initial ethanol concentration were 48.8 g L^{-1} and 0.001 g L^{-1} respectively. Experiments were conducted in a 7 L BioFlo 110 New Brunswick reactor with a working volume of 5 L in CSTR at an agitation rate of 200 rpm and 30 °C. The pH was controlled at 6.0 using 1 M NaOH.

2.1.3 Analytical procedures

Dry cell mass from 2 ml samples was determined gravimetrically. The optical density was determined at 660 nm spectrophotometrically (Gensys 10S UV-VIS) and kept at around 0.3 OD by dilution in continuous process. The fermentation culture was analysed for glucose and ethanol concentrations as a function of time, using HPLC (Aminex column HPX-87H (300 × 7.8 mm) (Bio- Rad, Ion exclusion column), operated at 65 °C with filtered (0.45 µm) and degassed 5 mM sulphuric acid as mobile phase at 0.3 ml min^{-1}, refractive index detector). Standards containing analytical grade components were used to confirm calibration accuracy. Samples and standards were filtered with a 0.22 µm syringe filter.

2.2 Computational methods

2.2.1 Model framework

The custom kinetic model for the fermentation process for bioethanol production was developed in ACM (Ver. 9.0) and embedded in Aspen Plus (Ver. 9.0). The model included equations for vapour-liquid equilibrium (VLE) Eq(1), mass balance Eq(2) and energy balance Eq(3) (e.g. molecular weight, thermodynamic phase equilibria, kinetic equation). VLE equation (modified Raoult's law):

$$P_{tot}\,Y = L_{mole\ fraction}\,\gamma\ P_{vap} \tag{1}$$

Mass balance:

$$Z\,F + r_{rate}\,R_{vol} = Y\,V + L_{mole\ fraction}\,L_{molar\ flow} \tag{2}$$

Energy balance:

$$H_{in}\,F + Q = L_{molar\ flow}\,H_L + V\,H_V \tag{3}$$

where P_{tot} is total vapour pressure (unit pressure), Y is vapour mole fraction (dimensionless), $L_{mole\ fraction}$ is liquid mole fraction (dimensionless), γ is activity coefficient (dimensionless), P_{vap} is vapour pressure of the pure component (unit pressure), Z is inlet mole fraction (dimensionless) , F is feed molar flow (mole/unit time), r_{rate} is reaction rate (mass /unit volume/unit time), R_{vol} is reactor volume (unit volume), V is vapour molar flow (mole/unit time), $L_{molar\ flow}$ is liquid molar flow (mole/unit time), H_{in} is feed enthalpy (energy unit/mole/unit time), Q is heat (unit energy/unit time), H_L is liquid enthalpy (energy unit/mole/unit time) and H_V is vapour enthalpy (energy unit/mole/unit time).

2.2.2 Kinetic models

The kinetic model in this paper incorporates substrate limitation, substrate inhibition, and product inhibition functions, which are based on modified Monod expressions for glucose conversion using *Zymomonas mobilis* ZM4 (Lee and Rogers, 1983; Leksawasdi et al., 2001). The terms are explained in Table 1.

Specific biomass growth rate: $C_{glu} \leq 100$ g L^{-1}

$$\mu_{glu} = \left(\frac{\mu_{m,glu} C_{glu}}{K_{x,glu}' + C_{glu}}\right)\left(1 - \frac{P - P_{ix,glu}}{P_{m,x,glu} - P_{ix,glu}}\right) \tag{4a}$$

Specific biomass growth rate: $C_{glu} > 100$ g L^{-1}

$$\mu_{glu} = \left(\frac{\mu_{m,glu} C_{glu}}{K_{x,glu}' + C_{glu}}\right)\left(1 - \frac{P - P_{ix,glu}}{P_{m,x,glu} - P_{ix,glu}}\right)\left(\frac{K_{ix,glu}}{K_{ix,glu}' + C_{glu}}\right) \tag{4b}$$

Biomass growth rate:

$$r_x = \mu_{glu}\,C_x \tag{5}$$

Specific glucose uptake rate:

$$q_{glu} = \left(\frac{q_{m,glu} C_{glu}}{K_{s,glu}' + C_{glu}}\right)\left(1 - \frac{P - P_{is,glu}}{P_{m,s,glu} - P_{ix,glu}}\right)\left(\frac{K_{is,glu}}{K_{is,glu}' + C_{glu}}\right) \tag{6}$$

Substrate conversion rate:

$$r_{glu} = q_{glu}\,C_x \tag{7}$$

Specific ethanol production rate:

$$v_{glu} = q_{glu}\,Y_{sp,glu} \tag{8}$$

Ethanol production rate:

$$r_e = v_{glu}\,C_x \tag{9}$$

2.2.3 Kinetic constants

The kinetic parameters are given in Table 1 for *Z. mobilis* ZM4 (Lee and Rogers, 1983).

Table 1: Kinetics of Z. mobilis ZM4 *(Lee and Rogers, 1983)*

Constant	Description	Value
$\mu_{max,glu}$	Maximum specific growth rate in glucose (h^{-1})	0.5
$K_{x,glu}$	Glucose limitation constant for biomass production rate (g L^{-1})	0.5
$P_{max,x,glu}$	Maximum ethanol concentration in glucose above which cells do not grow (g L^{-1})	86
$K_{ix,glu}$	Glucose inhibition constant for biomass production rate (g L^{-1})	200-220
$P_{ix,glu}$	Minimum ethanol concentration above which cells production is affected negatively when grown in glucose (g L^{-1})	22
$q_{max,glu}$	Maximum specific glucose utilization rate (h^{-1})	5.0
$K_{s,glu}$	Glucose limitation constant for substrate uptake rate (g L^{-1})	0.5
$P_{max,s,glu}$	Maximum ethanol concentration in glucose above which there is no substrate uptake (g L^{-1})	127
$K_{is,glu}$	Glucose inhibition constant for substrate uptake rate (g L^{-1})	500-2000
$P_{is,glu}$	Minimum ethanol concentration above which glucose consumption is affected negatively (g L^{-1})	55
$Y_{sp,glu}$	Ethanol yield constant from glucose (g-product/g-glucose)	0.48
μ_{glu}, q_{glu} and v_{glu}	Specific growth rate on glucose, specific glucose utilization rate and specific rate of product formation change with time (g L^{-1})	
C_{glu}, C_x and P	Glucose concentration, biomass concentration and ethanol concentration change with time (g L^{-1})	

2.2.4 Stoichiometric model

The ethanol production, biomass growth, sugar consumption, water and carbon dioxide production rates were calculated by Eqs(10-13) that were sourced from data provided in the Aspen simulation of Brazilian Bioethanol Science and Technology Laboratory (CTBE) to describe a typical industrial unit (Bonomi et al., 2011). The by-products (glycerol, and acetic acid) were calculated by Eqs(12-13), thereby reflecting by-product formation in the real-world processes.

Glucose conversion via complete oxidation Eq(10) and for biomass formation Eq(11):

$C_6H_{12}O_6 \rightarrow 2\ C_2H_6O + 2\ CO_2$, fractional conversion: 90% of glucose (mole) (10)

$3.3\ C_6H_{12}O_6 + 2.8\ NH_4OH + 2.1\ CO_2 \rightarrow CH_3COOH + 6.9\ H_2O + 19.6\ CH_{1.8}O_{0.9}N_{0.145}$, fractional conversion: 100% of NH_4OH (mole) (11)

Glucose conversion to by-products: glycerol Eq(12) and acetic acid Eq(13): (12)

$0.6\ C_6H_{12}O_6 + 0.5\ H_2O \rightarrow 0.5\ CO_2 + C_3H_8O_3$, fractional conversion: 52.09% of glucose (mole)

$C_6H_{12}O_6 \rightarrow 3\ CH_3COOH$, fractional conversion: 1.315% of glucose (mole) (13)

2.2.5 Mass balance

The mass balance over the CSTR, including the biomass growth rate (r_x), substrate uptake rate (r_{glu}), and ethanol formation rate (r_e) are given in Eqs(14-16).

$$r_x = D.(C_{x0} - C_x) \quad (14)$$

$$r_{glu} = D.(C_{glu0} - C_{glu}) \quad (15)$$

$$r_e = D.(P_0 - P) \quad (16)$$

where D is the dilution rate, C_{x0} is the initial biomass concentration, C_{glu0} is initial glucose concentration, P_0 is the initial ethanol concentration, C_x is the biomass concentration, C_{glu} is the glucose concentration and P represents the ethanol concentration.

2.2.6 Process of interfacing

The same versions of process simulation software for the development of the work processes were used in order to prevent issues of backward compatibility and to retain consistency in the property database version. The procedures and issues are divided into cases that have to do with physical property interfacing and with unit model interfacing.

3. Results and discussion

3.1 Comparing kinetic and stoichiometric models with literature experimental data and the experimental data from this study

The results of the kinetic model developed in ACM and from the stoichiometric model in Aspen Plus in comparison to the experimental result of this study under anaerobic continuous stirred tank reactor using *Z. mobilis* (0.07 h^{-1}) for bioethanol fermentation from 48.8 g L^{-1} of glucose are shown in Figure 2. The kinetic

model showed better agreement with the experimental data than the stoichiometric model (Figure 2). The ethanol, biomass and residual glucose concentrations from this study were 22.97, 2.94 and 0.0 g L^{-1} respectively compared to 24.34, 7.95, 0.10 g L^{-1} from the kinetic model developed in ACM and embedded in Aspen Plus, and 22.45, 9.79, 4.88 g L^{-1} from stoichiometric model in Aspen Plus. The calculated regression coefficient (R^2) between the kinetic model and the experiment of the study is 0.778 whereas between stoichiometric model and the experiment of the study is 0.415. Hence, the better agreement was found between the kinetic model and the experimental data.

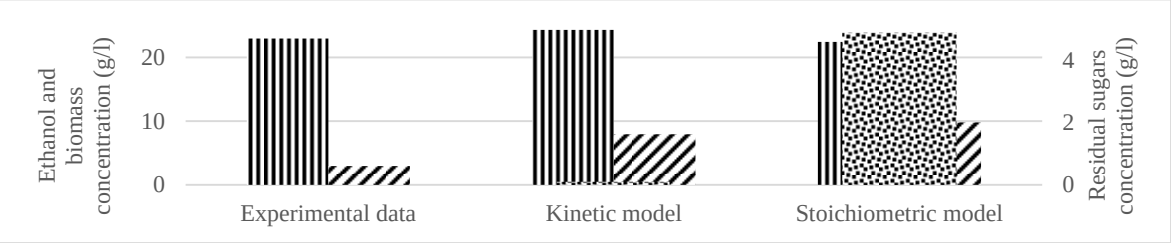

Figure 2: Comparison of the kinetic and stoichiometric model with experimental data from this study. (|||) represents ethanol concentration, (///) biomass concentration and (⁝⁝⁝) residual sugars concentration

In another example, the predictions of the kinetic model in ACM and stoichiometric model in Aspen Plus were compared to the experimental results of Lee et al. (1980) using *Zymomonas mobilis* for bioethanol production from glucose at feed concentration of 170 g L^{-1} (Figure 3). The results show that the kinetic models gave better agreement than the stoichiometric model with the experimental results for concentrations of ethanol and biomass produced, and glucose substrate consumed across dilution rates using a feed substrate concentration of 170 g.L^{-1}. The dilution rate, an important factor in CSTRs, played no role when the stoichiometric model was used and resulted in constant ethanol (78.25 g L^{-1}), biomass (11.06 g L^{-1}) and substrate concentrations (170 g L^{-1}), as shown in Figure 3.

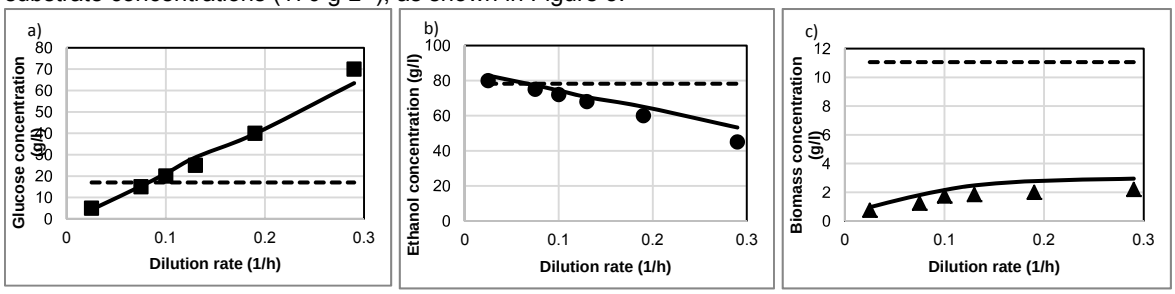

Figure 3: Ethanol production from 170 g L^{-1} glucose using Z. mobilis (Lee et al., 1980). *a) (■) represents experimental glucose concentration, (---) glucose concentration using stoichiometric model, (—) glucose concentration using kinetic model; b) (●) represents the experimental ethanol concentration, (---) ethanol concentration using stoichiometric model, (—) ethanol concentration using kinetic model; c) (▲) represents the experimental biomass concentration, (---) biomass concentration using stoichiometric model, and (—) biomass concentration using kinetic model*

3.2 Comparing kinetic and stoichiometric models with industrial data

Ethanol production, substrate consumption, by-product production, and microbial growth from glucose during fermentation were predicted using ACM for the kinetic model and Aspen Plus for the stoichiometric model. These predictions were compared to the industrial data provided by CTBE (Bonomi et al., 2011). The conversions for the stoichiometric model were calculated based on industrial data from a typical industrial unit (Bonomi et al., 2011). The mass fraction ratio of acetic acid over ethanol in industry in Brazil is 3.6 wt%. Kinetic modelling in ACM embedded in Aspen Plus predicted 3.2 wt% while the stoichiometric model in Aspen Plus predicted 3.1 wt%. The ratio of glycerol to ethanol in the industry was reported to be 6.33 wt%, lower than the prediction of 6.9 wt% using the kinetic model and 6.6 wt% using the stoichiometric model. The typical residual sugar to ethanol ratio in the Brazalian industry was 0.25 wt%, comparable to the ACM kinetic model prediction (0.3 wt%). The stoichiometric model under-estimated this value at 0.13 wt%. Biomass to ethanol production ratio in the industry was 5.85 wt%. This was predicted as 4.64 wt% when the kinetic model was used, but over-predicted at 14.5 wt% by the stoichiometric model. Overall, the differences in results between industrial data and kinetic model were less than 1 wt% in each case, indicating that the kinetic model

developed using ACM embedded into the Aspen Plus framework is an acceptable tool as a simulator of industrial data. In contrast, the industrial data were not well predicted by stoichiometric conversions across all components. In particular, the biomass over ethanol fraction was out of range. The stoichiometric equations were inter-dependent; hence the sensitivity of the conversions affected each component more readily. A small variation in the conversion led to large misinterpretation of the final outputs.

4. Conclusion

Stoichiometric models can be implemented in sequentially modular simulators with less information and effort. However, stoichiometric models do not represent continuous experimental data sufficiently because of uncertainty in the estimation of reaction conversions and the absence of kinetic information to reflect the impact of dilution rates on CSTR performance. In this study, it was shown that kinetic models developed in ACM and embedded in Aspen Plus represented experimental and industrial data accurately. Since it is not possible to develop complex kinetic models of microbial systems in Aspen Plus, these models were developed using an equation-oriented approach. The custom kinetic model, developed in ACM, served as a case study to test the current status of software interfaces and custom model performance in Aspen Plus. However, the interfacing between ACM and Aspen Plus was challenging, hence implementations of proper estimations, additional scripts and assumptions were required to maximise proper integration between the two platforms. The complexity of estimating biomass formation remains a key issue in modelling in general. Consideration of including additional parameters such as by-product inhibition and limitation, and maximum biomass concentrations in the kinetic model could be considered. However, predicting the behaviour of biological factors such as cell-to-cell interaction, cell sizes and the cell's intracellular metabolic state are less accessible in kinetic models as these remain relatively unknown in mechanism for growth regulation.

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