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An Integrated Biorefinery Framework for the Coproduction of Biofuels and Chemicals: Experimental Analysis, Detailed Modelling, Optimization and Life Cycle Analysis

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In this work, a novel integrated biorefinery framework is introduced. A 'cradle to grave' analysis is developed by adding novel steps into a basic biodiesel process involving the valorization of waste streams to value-added chemicals. Insights are given towards a new bioconversion route of glycerol to succinic acid. An unstructured model of batch experiments at different conditions is constructed. Experimental results at the bench scale are used to estimate kinetic parameters and to validate model predictions. The developed model is used in optimization studies to compute the best initial conditions for batch as well as the optimal feeding profiles for fed-batch processes to maximize succinic acid productivity. Finally, the above process is incorporated into a biorefinery scheme. Simulation and optimization in conjunction with life cycle analysis (LCA) is performed to simultaneously improve its sustainability and its economics.

1. Introduction

The vast majority of today's global energy supply comes from fossil fuels like petroleum, natural gas and coal. As population levels and prosperity increase, the global energy demand also rises (Smil, 2005). However, from the excessive use of fossil fuels, a number of issues emerge. The most important is the fast rate at which these resources are being depleted so the immediate development of new technologies exploring alternative energy sources is needed. Also, fossil fuels are the main cause for the climate change (Jaccard, 2005). In the next decades, the world has to deal with two major problems concerning energy use and supply: first to ensure its supply meets the growing demand and second to reduce the environmental impact of global warming caused by gaseous emissions from fossil fuels (Smil, 2005). Alternative ways of producing energy based on renewables, which seem to reach the two targets of supplying energy at the required rates simultaneously reducing environmental damage by decreasing green house gas emissions (Jaccard, 2005) need to be constructed.

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Petroleum products, such as petrol, kerosene and diesel, currently dominate the transport fuels market, which has grown dramatically due to the increasing number of cars, air travel and freight transport (Worldwatch Inst., 2007). Biofuels, i.e. fuels derived from biomass are an alternative to fossil fuels. Recently, their production and use has increased significantly (Worldwatch Inst., 2007). Unfortunately, first generation biofuels still cost more than petroleum fuels and their production is competitive only due to governments' policies involving tax breaks, subsidies and directives targeting the reduction of petroleum dependence such as the European directive 2003 on biofuels (Worldwatch Inst., 2007). Although, total bioethanol production seems to triumph over biodiesel in Brazil and USA, the latter has been developed significantly in EU countries in the last decade. In fact the EU has become the world leader in production and consumption of biodiesel (European Board of Biodiesel, 2010). Biodiesel is produced from vegetable oils and animal fats through transesterification, a simple chemical process, which also generates glycerol (containing impurities) by 10% (w/w) as a waste stream (Thompson and He, 2006). The crude glycerol stream is the major bottleneck in the biodiesel process. Small- and medium-scale producers prefer to pay for its disposal rather than to refine and sell it, as this is too costly (Thompson and He, 2006). On the other hand, biodiesel glycerol purification results in its oversupply that glycerol markets cannot absorb (Johnson and Taconi, 2007). Hence, new methods should be developed to valorize the vast amounts of glycerol glut. Here we consider glycerol not as waste stream but as a co-product and a key renewable feedstock for biorefineries co-generating added-value chemicals that are, up to now, petroleum-based. We consider a new bioconversion route of glycerol to succinic acid (SA) by using the bacterium *Actinobacillus succinogenes*. According to the US department of Energy SA, a carbon dicarboxylic acid, is one of the top value-added chemicals, as a key building block for deriving both commodity and specialty chemicals (Werpy and Petersen, 2004). An unstructured model of batch fermentation is developed considering both substrate and product inhibition. Estimation of kinetic parameters as well as model validation is achieved through comparisons with experimental results. Optimization studies are used to obtain the best initial conditions and feeding profiles for batch and fed-batch processes to maximize yield, productivity and/or final SA concentration. An integrated biorefinery framework is constructed by adding the SA bio-route to a biodiesel process (Figure 1), which starts from rapeseed feed and includes oil extraction, transesterification with KOH catalyst followed by separation units to purify the biodiesel and (partially) the glycerol similar to the process described by Apostolakou (2009). Integrated simulations are performed, employing Aspen Plus/ Custom Modeler. Optimization and LCA of the overall process are then used to simultaneously compute optimal parameters for economics and sustainability.

2. Materials and Methods

2.1 Inoculum preparation, cultivation conditions and analytical methods

Actinobacillus succinogenes (ATCC 55617) was obtained from the American type culture collection and it was preserved in cryopreservation vials in -70^{o}C. Preculture of the strain, cultivation conditions and analytical methods for the analysis of cell growth, substrate and products concentrations were described previously (Vlysidis et al., 2009).

2.2 Model studies for the batch & fed-batch systems

A modified Monod model was used to describe the growth kinetics considering both substrate and product inhibition. The equations describing the batch process as well as the parameter estimation methods were described previously (Vlysidis et al., 2009). Parameters were estimated through least squares fitting between estimated and experimental values and results are shown in Tab. 1. The model of the batch system was modified to introduce the dilution rate, D=F(t)/V accounting for the continuous feed.

Table 1 Optimization Parameters of the unstructured model

Parameter	Units	Values	Description	Bounds
μ_{max}	h^{-1}	0.12	Maximum specific growth rate	0.06-0.25
K_S	g/l	2.896	Substrate saturation constant	0.5-8
K_I	g/l	15.36	Substrate inhibition constant	10-80
$n_{S.A.}$	-	1.074	Linearity of the P_{SA} inhibition	0.3-1.4
$a_{S.A.}$	g-P_{SA}/g-X	9.864	Growth association constant of P_{SA}	1.2-10.4
$b_{S.A.}$	g-P_{SA}/g-X h	0.001	Non-growth constant of P_{SA}	0.001-1.2
$a_{F.A.}$	g-P_{FA}/g-X	0.428	Growth association constant of P_{FA}	0.1-2.4
$b_{F.A.}$	g-P_{FA}/g-X h	0.002	Non-growth constant of P_{FA}	0.001-1.2
$a_{A.A.}$	g-P_{AA}/g-X	0.753	Growth association constant of P_{AA}	0.1-2.4
$b_{A.A.}$	g-P_{AA}/g-X h	0.001	Non-growth constant of P_{AA}	0.001-1.2
Y_X	g-X/g-S	0.130	Stoichiometric Yield of Cells to S	0.01-0.8
Y_{SA}	g-P_{SA}/g-S	2.790	Stoichiometric Yield of P_{SA} to S	0.1-4.5
m_s	g-S/g-X h	0.001	Specific maintenance coefficient	0.001-0.1

Here F(t) is the feed flow rate and V the working volume of the fermenter. Cell (X), substrate (S) and product/by-products concentration (P_i) evolution is described by Equations 1-5. The feeding profile was discretized in 5 piece-wise constant segments.

$$dX/dt = (\mu - D)\cdot X \quad (1)$$

$$\frac{dS}{dt} = -\frac{1}{Y_X}\frac{dX}{dt} - m_s X - \frac{1}{Y_{SA}}\frac{dP}{dt} + D\cdot(S_f - S) \quad (2)$$

$$\frac{dP_i}{dt} = \alpha_i \frac{dX}{dt} + \beta_i X - D\cdot P_i \quad (3)$$

$$dV/dt = F(t) \quad (4)$$

$$\text{where} \quad \mu = \mu_{max}\cdot\left(\frac{S}{S + K_S + (S^2/K_I)}\right)\prod_{i=1}^{m}\left(1 - \frac{P_i}{P_i^*}\right)^{\eta} \quad (5)$$

2.3 Optimization of batch and fed batch systems

The objective for both batch and fed-batch optimization was to maximize SA productivity. For the batch system the degrees of freedom are the initial conditions (cell and glycerol concentration X_o, S_o) (Eq.6) while in the fed-batch system, we also consider the feeding rates for the different time periods ($F_{(t)}$), the feeding concentration (S_f), the incubation time (t_f) and the initial working volume (V_o) (Eq.7) (Wang and Cheng, 1999). The optimization procedure used here employing simulated annealing

and successive quadratic programming was described in (Vlysidis et al., 2009). In this work, all parameters were constrained within bounds imposed by system limitations.

$$\max_{S_o, T_o} \quad J = P_{SA}(t_f)/t_f \qquad (6) \qquad\qquad \max_{S_0, X_0, F(t), S_f, V_0, t_f} \quad J = P_{SA}(t_f)/t_f \qquad (7)$$

2.4 Overall simulation and optimization runs

The above model was combined with an optimized biodiesel process to construct an integrated biorefinery for the co-production of fuels and chemicals (Figure 1). Simulations were implemented in Aspen Plus and fermenter kinetics were built in Aspen Custom Modeler using values obtained from batch experiments. Overall optimization was performed using simulated annealing focusing on maximizing the overall biorefinery profit (Eq.8) and minimizing emissions by changing two crucial process parameters: the water flow rate, W_{fr} (kmol/h) and the cycle time of the fermenter, t_f (h).

$$\max_{t_f, W_{fr}} \quad \text{Profit} = \text{VP} - \text{CR} - \text{EC} - \text{CP} \qquad (8)$$

Here, VP is the product value, CR the raw materials cost, EC the energy cost and CP the capital cost. Emissions are calculated by using the energy requirements of the system combined with emissions factors giving the mass of CO_2 released/KWh of energy used.

3. Results and Discussion

3.1 Batch experiments and simulations

Results from the batch experiments and model predictions are illustrated in Figure 2. Model predictions fit well with experimental results using a wide range of initial conditions. The glycerol(S) -succinic acid (SA) system demonstrates high yields, which can reach up to 0.9 g-SA/g-S, even in high initial glycerol concentrations (>40g-S/L). Another important positive aspect is the low formation of by-products (formic and acetic acid) with respect to SA production that can play a crucial role simplifying the downstream process by reducing energy requirements for SA purification. The only disadvantage seems to be the low productivity of the desired product, which is usually the most important factor when developing an industrial scale bio-process. Therefore, we performed optimization studies for batch and fed-batch fermentations by using the kinetics obtained from batch experiments in order to further enhance the productivity.

3.2 Optimization of batch and fed-batch processes

As mentioned above, increasing process productivity is vital for the industrialization of SA. Figure 3 illustrates the increase in productivity from optimizing the batch and fed-batch processes. In the optimal batch process productivity is increased by 21 % and by 39% in the optimal fed-batch process resulting in a value of 0.44 g-SA/l/h.

3.3 Simulation and optimization of an overall biorefinery

The optimized SA fermentation process was attached to the glycerol by-product stream of an overall biorefinery process of biodiesel production from oilseeds (Figure 1). Simulation, optimization and LCA of the integrated biorefinery using kinetics obtained from the batch and fed-batch models were performed. Three cases were studied: (i) Disposing, (ii) purifying crude glycerol and (iii) producing SA. The objective was to maximize profit and to minimize emissions based on correlations and values found in

the literature (Apostolakou et al., 2009) and (Turton et al., 2009). As it can be seen in Tab. 2 producing SA gives the largest profit, with no significant emission increases, verifying that this is a viable integrated option.

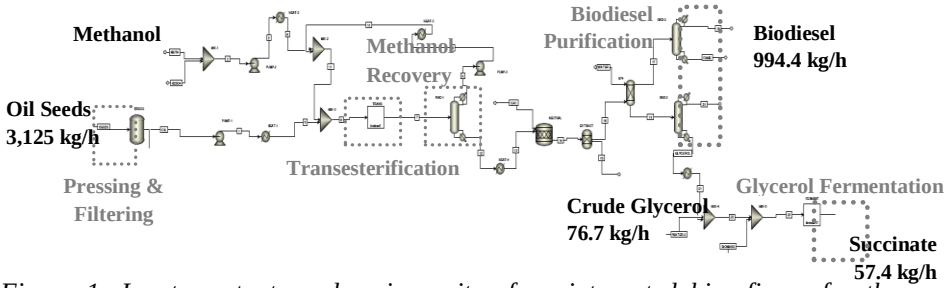

Figure 1: Inputs, outputs and major units of an integrated biorefinery for the co-production of biodiesel and succinic acid simulated in Aspen Plus

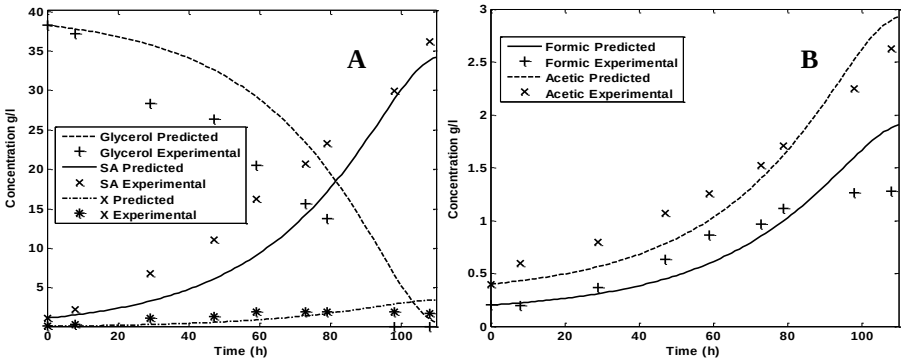

Figure 2: Experimental and simulation data of: A) succinic acid (SA), biomass (X) and glycerol (S) and B) by-products formic and acetic acid concentrations

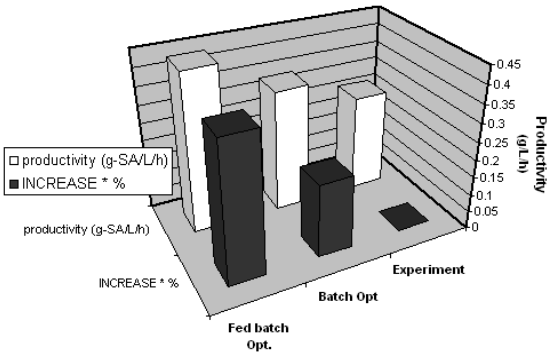

Figure 3: Optimal productivities for batch and fed-batch processes

4. Discussion and Conclusions

This work gives an interesting insight on the concepts of future biorefineries. Sustainable development of the biodiesel industry is made possible by valorizing waste

streams through the production of value-added chemicals, making them competitive with petroleum refineries. New bio-routes, like the succinic acid production from glycerol, need to be studied to provide to integrated biorefineries the flexibility to switch their production lines according to market demands. We have demonstrated that the profitability of an integrated biorefinery was increased by 38 % when the glycerol waste stream was converted to succinic acid and just by 6.5 % when crude glycerol was purified. The succinic acid bioprocess can be further improved by creating better biocatalysts. Metabolic modeling is a useful tool to indicate pathways to be supported or suppressed, by overexpression or knock-out of genes, respectively, as well as to provide the theoretical maximum of the bacterium. Finally, existing biorefinery frameworks should be complemented with additional units including downstream processing which has a significant effect on the total energy consumption of bioprocesses.

Table 2 Results from the optimization studies for different biodiesel schemes on the optimum: W_{fr}=100 kmol/h and $t_{fermenter}$= 100 h, for a total capacity of 25,000 t/y

Biodiesel Process	Profit (€/t feed)	Emissions (kg-CO_2/t feed)
Crude glycerol (80 %)	85.77	0.151
Purified glycerol (95 %)	91.73	0.155
SA co-production	138.33	0.152

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