MASS INTEGRATION APPLIED TO SUGARCANE BIOREFINERY USING THE MODIFIED FLEXIBLE TOLERANCE METHOD

A. M. LIMA¹, F. F. FURLAN¹, A. J. G. CRUZ¹,² and W. H. KWONG¹,²

¹PPGEQ-UFSCar, Federal University of São Carlos, Department of Chemical Engineering
²Federal University of São Carlos, Department of Chemical Engineering
Contact e-mail: alice.medeirosdelima@gmail.com

ABSTRACT – This paper presents the application of mass integration methodology to a sugarcane biorefinery, using a modified flexible tolerance method (MFTM) for optimization. For environmental reasons, the targets for mass integration were water, emissions of carbon dioxide from the fermentation process, and vinasse. The MFTM presented good performance in optimization of the process configuration, with reductions of 29, 28, and 33% in the costs of fresh water supply, wastewater treatment, and vinasse fertirrigation (including the costs associated with vinasse concentration), respectively. In addition, emissions of CO₂ were avoided using algae farm technology for ethanol production, resulting in benefits to the environment as well as economic advantages including carbon credits and additional ethanol production.

1. INTRODUCTION

The production of ethanol from lignocellulosic materials has been extensively studied because it increases the amount of ethanol that can be produced from the same crop area, hence helping to meet the growing demand for biofuel. Environmental issues and the rise in petroleum costs have also stimulated research into the production of alternative fuels from renewable raw materials. Two options have been evaluated for fuel production from lignocellulosic raw materials, namely the use of dedicated crops, such as willow and elephant grass, and full utilization of the biomass derived from other processes, such as wastes from agricultural (wheat straw, sugarcane bagasse, and corn stover) and forestry sources.

Due to the large-scale production of ethanol from sugarcane in Brazil, sugarcane bagasse is one of the most suitable materials available for second-generation ethanol production, despite competition with the use of this material for energy production. However, the processes (biochemical and/or thermochemical) are not yet available for large-scale production, due to the high costs of enzymes and catalysts, low productivity, low profit margins, and difficulty in scaling up the hydrolysis step.

Mass integration methodology can be used to determine the minimum consumption of materials and utilities (solvents, water, etc.), minimum discharge of wastes, minimum purchase of fresh raw materials, minimum production of undesirable by-products, and maximum outputs of desirable products. The mass targets that need to be considered in the case of a sugarcane biorefinery include the minimum purchase of fresh water, the minimum expense with wastewater treatment, the minimum expense with vinasse fertirrigation, and recovery of carbon dioxide at the lowest cost and with the highest profit in terms of products.
The aim of the present work was to apply mass integration methodology to a sugarcane biorefinery, using a modified flexible tolerance method for the optimization task.

2. METHODOLOGY

The process adopted in this case study was developed by Furlan et al. (2013), who used EMSO software (Environment for Modeling, Simulation and Optimization) to perform the simulations. Simulation of the first-generation plant included the processes of cleaning, milling, physical and chemical treatment, concentration, fermentation, distillation, and cogeneration. The processes considered in the second-generation plant included the weak acid pretreatment, enzymatic hydrolysis, and fermentation of the resulting sugars. Figure 1(a) shows the process flowsheet for the sugarcane biorefinery. A complete process description can be found in Furlan et al. (2013).

In this case study, the targets for process integration included water, the carbon dioxide produced during fermentation, and the vinasse. The process was described by a source-interception-sink configuration, where the interception device was discretized, as proposed by El-Halwagi (2012). The objective was to minimize the costs associated with fresh water, wastewater treatment, fertirrigation using vinasse, the vinasse interception device, and the CO₂ recovery interception device, and to maximize the profits associated with the products obtained from the CO₂ recovery process.
2.1. Water network

The water network included direct recycle of streams containing water free from impurities. The source-sink superstructure developed for water reuse is illustrated in Figure 1(b). The configuration included eight direct recycle sources (including the water available from vinasse concentration) and six process sinks. The unrecycled water streams were fed into the wastewater treatment system. The sources and sinks of water are listed in Figure 1(b), in accordance with the flow diagram shown in Figure 1(a).

2.2. Vinasse network

Vinasse is widely employed as a fertilizer due to its high contents of salts (mainly of potassium, calcium, and magnesium) and organic matter. Concentration of vinasse is usually performed using a multiple-effect evaporator, and the best results have been obtained using the falling film evaporator (Rocha, 2009). The number of effects can vary from 4 to 7, but 4 or 5 effects are generally used (Freire and Cortez, 2000, *apud* Rocha, 2009). The application of vinasse can have substantial economic benefits, compared to the use of traditional fertilizers (Rocha, 2009; Carvalho, 2010). However, the financial gain varies as a function of vinasse Brix; at Brix levels greater than 25-30%, the volume of concentrated vinasse does not decrease significantly, which means that the concentration of vinasse beyond 25-30% Brix does not result in further economic gains when vinasse is transported by road.

In this study, an evaporation plant with five effects was adopted, with the falling film evaporator for all effects. The vinasse concentration was fixed at 25% Brix, the total pressure drop was 1.2 bar, and the initial vinasse Brix was 4.5%. The outlet pressure \( P_n \) of each effect was determined as indicated in Equation 1 (Castro and Andrade, 2007), where \( N \) is the total number of effects, and \( P_0 \) and \( P_f \) are the initial and final pressures. The boiling point elevation \( \text{BPE} \), in °C) was calculated according to Equation 2, where \( x_{\text{brix}\_\text{out}} \) is the Brix mass fraction at the exit of the evaporation effect (Araujo, 2007).

\[
P_n = \frac{P_{n-1} - (P_0 - P_f)}{11 - (n - 1) \frac{11 - 9}{N - 1}}
\]

\[
\text{BPE} = \frac{2x_{\text{brix}\_\text{out}}}{1-x_{\text{brix}\_\text{out}}}
\]

The overall heat transfer coefficient \( U \), in kJ/h.m².K) was determined as shown in Equation 3 (Rein, 2007), where \( T_s \) is the temperature (in °C) of the heating steam in the calandria, \( n_r \) is the steam enthalpy at evaporator pressure, and \( k \) is the Dessin coefficient.

\[
U = k (100 - x_{\text{brix}\_\text{out}}) T_s (T_s - 54) H P_n
\]
\[ Q = UA \left( T_{s,n} - T_{0,n} \right) \] (4)

The mass flowrates and temperatures in the evaporator effects were determined using mass and energy balances, and the vapor properties were evaluated using steam tables. In order to minimize the costs associated with fertirrigation, analysis was made of the degree of concentration using different proportions of the total vinasse mass flow. These fractions ranged from 18% to 100%, and the area of each effect was calculated for each mass flow of vinasse. The costs of the evaporation system were evaluated using Capcost software (Turton, 1998) and other calculations were performed using electronic spreadsheets.

![Figure 2](image)

**Figure 2**: (a) Evaporation system with 5 effects; (b) Source-interceptor-sink superstructure for vinasse concentration and CO\(_2\) recovery; (c) Optimized superstructure for the sugarcane biorefinery.

### 2.3. Carbon dioxide recovery

The capture of CO\(_2\) from ethanol fermentation is simple, and due to the high purity, the only processes required are dehydration and compression. The cost of capture (including dehydration and compression) from ethanol facilities was reported to be in the range 6-12 USD/tCO\(_2\) (Xu *et al*., 2010). The CO\(_2\) obtained from capture can be marketed for use by the CO\(_2\) industry.

The production of NaHCO\(_3\) was evaluated using the soda method, where caustic soda is used as the reagent (NaOH + CO\(_2\) → NaHCO\(_3\)). The purity of NaHCO\(_3\) obtained from this process is greater than obtained using the carbonate method. An analysis of the economics of this system was provided by Cunha *et al.* (2009), considering the reactor, centrifugation of the product, drying, and fine particle separation in a cyclone.
The production of biodiesel and ethanol from algae analyzed in this work employed the SAT process developed by SEE ALGAE Technology (SAT, 2012). This process can produce biodiesel and algal protein from algae, or ethanol from genetically modified algae. The photobioreactor uses CO₂ and solar energy to activate the photosynthesis of the microalgae. Algae farms do not compete for arable land with crops intended for human consumption. Furthermore, algae are the most efficient plants in the world, with growth rates that far outstrip those of traditional crops. Evaluation of the productivity and economic performance of the process was based on data reported by SAT (2012), and the mass fraction of CO₂ delivered to this system needed to be greater than 25% of the total mass. The profit derived from carbon credits was also included, since emissions to the atmosphere were avoided using the proposed procedure. The objective of carbon dioxide recovery was to maximize the profit margin, since a variety of products can be obtained from the different processes analyzed.

Table 1 - Summary of costs, prices of products, and specific production of CO₂ recovery processes.

| Process                        | Cost (USD/t) | Reference       |
|--------------------------------|--------------|-----------------|
| Fresh water inputs             | 0.018        | JornalCana (2011) |
| Wastewater treatment           | 0.0025       | PECEGE (2012)   |
| Vinasse evaporation            |              | This work       |
| Vinasse fertirrigation          | 3.06         | CERES (2013)    |
| CO₂ capture                    | 9.14         | Xu et al. (2010) |
| NaHCO₃ soda method             |              | This work       |
| Algae farm - biodiesel         | 0.25         | This work       |
| Algae farm - ethanol           | 0.25         | This work       |

| Products                      | Price (USD/t) | SP (t product/tCO₂) | Reference   |
|--------------------------------|---------------|---------------------|-------------|
| Carbon credits                | 7.73          | -                   | Investing.com (2012) |
| CO₂                            | 315.79        | SP₂ = 1.0           | Santos et al. (2012) |
| NaHCO₃                         | 200.00        | SP₂ = 1.91          | Qingdao (2014) |
| Biodiesel                      | 1.513.22      | SP₄ = 0.22          | ANP (2012)   |
| Algal protein                  | 473.08        | SP₄ = 0.25          | SAT (2012)   |
| Ethanol                        | 1.603.64      | SP₅ = 0.35          | PECEGE (2012) |

Cₜₚ: cost of process u; Xᵣ: vinasse fraction sent to concentration; XᵣC: fraction of CO₂ in NaHCO₃ production; Xᵣc: fraction of CO₂ in algae farm for biodiesel production; Xᵣc: fraction of CO₂ in algae farm for ethanol production; Pₜₚ: price of product from process u; SPₜₚ: specific production of process u

2.4. Economic estimation

The fixed capital investment (FCI) for the CO₂ recovery process was estimated using the six-tenths rule to correct for the production scale. The FCI of the vinasse concentration plant was calculated using the Capcost software, based on the area of the evaporators, the operating pressure, and the construction material (stainless steel). The working capital investment (WCI) was set to 15% of the FCI (Silla, 2003). The annualized fixed cost (AFC = WCI + FCI) was corrected using the CEPCI cost index for the year 2012. The annualized operational cost (AOC) was estimated using the empirical correlations described by Silla (2003). All estimates were made for the year 2012, considering an interest rate of 10%, a service life of
10 years, and 210 days of operation annually. The total annualized cost \( TAC = AFC + AOC \) was normalized on a per kg basis by dividing the \( TAC \) by the annual quantity of mass to be processed (El-Halwagi, 2012).

2.5. Optimization

The optimization of the source-interception-sink superstructure was performed using the modified flexible tolerance method (MFTM) implemented in Python, as described by Lima et al. (2014). Since CO\(_2\) recovery was independent of water and vinasse, two optimization problems were immediately resolved. The optimization functions are described in Equations 5 and 6. The equality constraints were composed of mass balances around each source, interception device, and sink, together with cost functions; the inequality constraints were the limits and bounds of each variable.

\[
\text{Minimize } TAC = C_{Fr} F_{Fr} + C_{waste} G_{waste} + C_{V}(X_{V}) W_{V} X_{V} + C_{Fert} G_{Fert}
\]

\[
\text{Minimize } TAC = \sum_{u=2}^{5} C_{waste}(X_{u,C}) W_{c} X_{u,C} - \sum_{v=2}^{5} W_{c} X_{v,C} P_{u} SP_{u} - W_{c} P_{creditC}
\]

where: \( C_{Fr} \) = cost of fresh water, \( F_{Fr} \) = flow rate of fresh water inputs, \( C_{waste} \) = cost of wastewater treatment, \( G_{waste} \) = flow rate of wastewater sent for treatment, \( C_{V}(X_{V}) \) = cost of vinasse concentration, \( W_{V} \) = vinasse flow rate, \( X_{V} \) = vinasse fraction sent to concentration, \( C_{Fert} \) = cost of fertirrigation, \( G_{Fert} \) = flow rate of vinasse for fertirrigation, \( C_{u}(X_{u,C}) \) = cost of CO\(_2\) recovery in process \( u \), \( W_{c} \) = flow rate of CO\(_2\), \( X_{u,C} \) = fraction of CO\(_2\) in process \( u \), \( P_{u} \) = price of product obtained from process \( u \), \( SP_{u} \) = specific production \( (t_{product}/t_{CO2}) \), \( P_{creditC} \) = price of carbon credits.

3. RESULTS AND DISCUSSION

The costs, production rates, and prices adopted and calculated in this work are shown in Table 1. The solution of this problem using a nonlinear optimization method was possible because the modeling and costing of the interceptors was performed outside the optimization formulation and transformed into a presynthesis task, with discretization of the interceptors. After transformation of the equality constraints using the explicit substitution method, the water and vinasse problem (Equation 5) had 16 variables and 51 inequality constraints. The solution obtained using the MFTM was reached after 1981 function evaluations and 1312 iterations. After transformation of the equality constraints (using the explicit substitution method), the CO\(_2\) recovery problem (Equation 6) had 3 variables and 8 inequality constraints, and the solution using the MFTM was reached after 20 function evaluations and 10 iterations. The optimized diagram is shown in Figure 2(c).

The results obtained using mass integration are summarized in Table 2. The main features were reductions of 29, 28, and 33% in the costs of fresh water inputs, wastewater treatment, and vinasse fertirrigation (including the costs associated with vinasse concentration),
respectively. Moreover, CO₂ emissions were avoided using the algae farm technology for ethanol production, which provided both environmental benefits and economic advantages including carbon credits and a 32% increase in ethanol production.

Table 2 - Optimization results for the sugarcane biorefinery.

|                         | Current process | Optimized process |
|-------------------------|-----------------|-------------------|
| Cost of fresh water (USD/y) | 187,436.01      | 132,536.05        |
| Cost of wastewater treatment (USD/y) | 23,260.81     | 16,609.74         |
| Fresh water inputs (t/y)          | 10,621,374.02   | 7,363,113.92      |
| Wastewater generation (t/y)        | 9,456,025.51    | 6,643,895.34      |
| Cost of fertirrigation with vinasse (USD/y) | 14,257,542.86  | 9,537,666.334     |
| Vinasse for fertirrigation (t/y)   | 2,794,478.4     | 2,382,013.388     |
| CO₂ emissions (t/y)              | 212,452.52      | 0                 |
| Carbon credits (USD/y)           | -               | 1,642,255.51      |
| Cost of CO₂ interception (USD/y)  | -               | 27,695,268.79     |
| Profit due to ethanol from algae (USD/y) | -              | 119,243,896.10   |
| Ethanol production from algae (t/y) | -               | 74,358.27         |

4. CONCLUSIONS

The results of this work indicate that environmental and economic benefits can be obtained by applying mass integration methodology to a biorefinery concept. The inclusion of a presynthesis task involving the modeling, costing, and discretization of the interceptors was essential in order to be able to apply the modified flexible tolerance method, because this avoided both nonconvexity of the objective function and bilinearity of several constraints present in the mixed-integer nonlinear program formulation. The use of mass integration enabled a reduction of more than 30% in the costs associated with fresh water inputs and wastewater treatment, compared with the current process, and 14% of the vinasse volume was used for fertirrigation (with the same composition in terms of nutrients). In addition, the CO₂ could be recovered using algae farm technology for ethanol production.

These findings are not intended to be definitive or exhaustive, since the simulated process adopted for integration contained a number of simplifications, compared to a real process, and some of the technologies analyzed are protected by patents, so process information was limited to that provided by the manufacturers. Nonetheless, the results provide an indication of an economically viable way of achieving substantial advances in terms of water consumption and pollution reduction.

5. ACKNOWLEDGMENTS

The authors thank CNPq and CAPES for financial support.

6. REFERENCES

ANP, Agência Nacional do Petróleo, Gás Natural e Biocombustíveis . Resumo dos leilões na fase da mistura obrigatória - 2012, 2012.

ARAUJO, E. C. C. *Evaporadores*. EdUFSCar, SP, Brazil, 2007.
CARVALHO, T. C. Redução do volume de vinhaça através do processo de evaporação. Master’s thesis (in Portuguese), State University of São Paulo (UNESP), Faculty of Mechanical Engineering, 2010.

CASTRO, S. B.; ANDRADE, S. A. C. Tecnologia do Açúcar . Editora Universitária UFPE, PE, Brazil, 2007.

CERES, Inteligência Financeira. Estudo de viabilidade técnica e econômica de um grupo selecionado de tecnologias inovadoras relacionadas à cadeia sucroenergética. Relatório técnico, MDIC, 2013.

CUNHA, L. C.; POIANI, L. M.; GUBULIN, J. C. Análise das viabilidades técnica e econômica para produção de bicarbonato de sódio a partir de dióxido de carbono residual de processos fermentativos. In: VI Congresso de Meio Ambiente da AUGM , São Carlos, 2009.

EL-HALWAGI, M. M. Sustainable Design Through Process Integration. Butterworth-Heinemann, 2012.

FURLAN, F. F.; FILHO, R. T.; PINTO, F. H. P. B.; COSTA, C. B. B.; CRUZ, A. J. G.; GIORDANO, R. L. C.; GIORDANO, R. C. Bioelectricity versus bioethanol from sugarcane bagasse: is it worth being flexible? Biotechnol. Biofuels, 6(1), 1-12, 2013.

Investing.com. Crédito carbono, 2012.

JornalCana. Cobrança pelo uso da água ganha impulso em regiões de usinas, 2011.

LIMA, A. M.; CRUZ, A. J. G.; KWONG, W. H. Constrained nonlinear optimization using modified flexible tolerance method: Application in mass integration. Braz. J. Chem. Eng. (submitted), 2014.

PECEGE. Custos de produção de cana-de-açúcar, açúcar e etanol no Brasil: Fechamento da safra 2011/2012. Relatório técnico, ESALQ, Piracicaba, 2012.

QINGDAO Sonf Chemical Company Limited. Sodium bicarbonate. 2014.

REIN, P. Cane Sugar Engineering. Verlag Dr. Albert Bartens KG, Berlin, Germany, 2007.

ROCHA, M. H. Uso da análise do ciclo de vida para comparação do desempenho ambiental de quatro alternativas para tratamento da vinhaça. Master’s thesis (in Portuguese), Federal University of Itajubá, Institute of Mechanical Engineering, 2009.

SANTOS, D.; REBELATO, M.; RODRIGUES, A. Análise da viabilidade econômica de uma planta para captura de CO₂ na indústria alcooleira. Revista Gestão e Tecnologia, 12, 64-88, 2012.

SAT, SEE ALGAE Technology GmbH. Commercial infrastructure for production of algae-based compounds. 2012.

SILLA, H. Chemical Process Engineering: Design and Economics. Taylor & Francis, 2003.

TURTON, R. Capcost software. 1998.

XU, Y.; ISOM, L.; HANNA, M. A. Adding value to carbon dioxide from ethanol fermentations. Bioresour. Technol., 101, 3311-3319, 2010.