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Energy Integration of Bioethanol Production Process Topology from Microalgae Biomass: Evaluation of SSCF, SSF, Acid Hydrolysis and Product Purification Alternatives

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An increasing interest exists in the use of ethanol as substitute of fossil fuels which can be obtained from renewable resources, microalgae are a promising source for third generation bioethanol due to the high percentage of carbohydrates/polysaccharides presents in some species and thin cellulose walls. Ethanol can be produced from either microalgae biomass before lipid extraction or from microalgae cake after cell disruption and oil extraction. Second option gives the interesting possibility of producing both biodiesel and ethanol from the same biomass.
Energy analysis can be used for evaluation of the performance and efficiency of a process based on the first law of thermodynamics. In this work, third generation bioethanol production process was evaluated using the methodology of energy integration with the software Aspen Plus, the microalgae genera used was *Chlorella* sp. and technologies evaluated were Simultaneous Saccharification and Co-fermentation SSCF, Simultaneous Saccharification and Fermentation SSF, and Separate Saccharification and Fermentation using acid hydrolysis (SHF).
Results shows that technology of Simultaneous Saccharification and Co-fermentation SSCF (route 1) presents the highest bioethanol yield 24.1 %, and the lowest energy requirements after energy integration. Separated hydrolysis and fermentation SHF (route 3) presents the lowest efficiency, ΔT_{min} was defined in 9 °C for SSCF, 4 °C for SSF, and 8.5 °C for SHF, the use of molecular sieves technology for bioethanol dehydration represents lower energy requirements respect to extractive distillation.

1. Introduction

An increasing interest exists in the use of ethanol as substitute of fossil fuels which can be obtained from renewable resources. CO_2 from combustion reaction is fixed by biomass in growing stage. Mature technologies for bioethanol production from biomass are based on sugars fermentation which are obtained from industrial processing of feedstocks with high percentage of sugars or cellulose, most of them are important for human and animal diet, for this reason new possibilities of bioethanol production are been evaluated in order to avoid problems related with competition of feedstocks with food and feed and use of land.

1.1 Microalgae biomass

Microalgae is an energy source that potentially can offer considerable amounts of fuel from small crop areas and and high photosyntetic efficiency, which further helps in the mitigation of global warming; its culturing tolerates high concentrations of CO_2 (Iancu et al., 2012), and decreases the amount of nitrogen oxides released into the atmosphere. Microalgae biomass is been evaluated mostly for biodiesel production (Wibul et al., 2012).
Although technologies por microalgae biomass proccesing are being improved, biodiesel-from-microalgae production chain is still away of sustainability by several factors, in energy terms, comparison of energy

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demands for microalgal biodiesel production shows that energy required in all stages of production process is more than energy produced by third generation biodiesel.
In this sense, results of studies related to bioprospecting, exploitation and production of microalgae biomass made by research centers and several researchers worldwide, concludes that production of biodiesel from microalgae can be economically viable if total biomass components are used for obtaining biofuels and high value products, and the concept of biorefinery is incorporated. As in an oil refinery, a biorefinery uses all biomass components for obtaining several biofuels and high value products (Khan et al., 2009).

1.2 Bioethanol from microalgae

Microalgae has a wide variety of components which can be extracted and/or converted in biofuels and high value products (González-Delgado and Kafarov, 2012), most of microalgae species contains some common components such cellulose, proteins, lignin, pectins as polyuronic acids, arabinans and glactans, hemicelluloses as xylans and arabinoglactans and other carbohydrates, most of the polymers located in the microalgal cell wall can be converted in monomers through an acid, alkaline or enzymatic reactions (Chong Fu et al., 2010).
Ethanol can be produced from microalgae biomass with high percentage of cellulosic material, fermentable sugars can be produced from microalgae through hydrolysis of harvested biomass (Gonzalez and Kafarov, 2010). Bioethanol from microalgae biomass can be produced before lipid extraction or from microalgae cake after cell disruption and oil extraction. Second option gives the interesting possibility of producing both biodiesel and ethanol from the same biomass (González-Delgado and Kafarov, 2011).

1.3 Energy Integration

Energy analysis can be used for evaluation of the performance and efficiency of a process based on the first law of thermodynamics. Energy integration is a technique for process design which looks for minimization of the energy consumption and maximization of the heat recovery.
Analysis starts with the mass and energy balance for the process, simulation tools can be used for achieving this stage. After that, targets for energy Integration are identified and network is designed. Utility levels that are supplied to the process that is evaluated or designed, can be part of a centralized utility system. Energy integration provides a well-structured methodology for energy saving in cooling and heating, from the basic mass and energy balance to the total utility system.

1.4 Aim of the work

The main contribution of this work, is the computer-aided evaluation and optimization from the energy point of view, of three alternatives for microalgal bioethanol production using the methodology of energy integration. Software used was Aspen Plus (V7.1, Aspen Technology, Inc., Burlington, USA, 2008), the microalgae genera used was *Chlorella sp.* and technologies evaluated were Simultaneous Saccharification and Co-fermentation SSCF (route 1), Simultaneous Saccharification and Fermentation SSF (route 2), and Separate Saccharification and Fermentation using acid hydrolysis SHF (route 3).

2. Description of technologycal systems

2.1 Simultaneous Saccharification and Co-fermentation SSCF (route 1)

In Simultaneous Saccharification and Co-fermentation pathway, a hydrolysis step reduces cellulose and hemicelluloses to hexoses and pentoses, which simultaneously are fermented using *Zimomonas mobilis* and *Saccharomyces cerevisiae*. It is reported that the production rate does not have a high impact on enzymatic hydrolysis because its concentrations are low, but presence of alcohol inhibits specific growth rate and accelerates cell degradation (Spatari et al., 2010).

2.2 Simultaneous Saccharification and Fermentation SSF (route 2)

Simultaneous saccharification and fermentation (SSF) pathway has been experimentally studied for bioethanol production from lignocellulosic material. This pathway performs the stage of hydrolysis copuled to fermentation stage, this variation allows to decrease the final product inhibition, however, is difficult to find the operating conditions for efficient performing of microorganisms involved in both stages. This technique is one of the most promising because only one reactor is used for hydrolysis and fermentation, improving the conversion of sugars to ethanol, the key of SSF process is the fast ethanol production from glucose (Ojeda et al., 2011).

2.3 Separated hydrolysis and fermentation SHF (route 3)

Acid hydrolysis was used as identified experimentally as convenient alternative for reducing sugars production from microalgae (González-Delgado and Kafarov, 2012), althought literature also reports high

reducing sugars yields from microalgae using another alternatives for hydrolysis (Galatro and Verruschi, 2012), sugars obtained are mainly glucose, xylose and cellubiose.
When this route is performed, hydrolysis and fermentation steps occurs in different reactors optimizing operating conditions for each reaction, best operating conditions found by authors in unpublished research works and literature were used for simulation of pathway, for evaluation of this route, acid hydrolysis was chosen first stage of bioethanol production chain.

3. Simulation of pathways

Figure 1 shows important stages of simulation of three routes evaluated for energy integration, at the top of figure is shown the fermentation stage of SSCF route, where cellulase and recombinant *Zymomonas mobilis* are used in REACTOR 3 (red lines) for hydrolysis and pentoses and hexoses fermentation in a multifunctional unit, reaction temperature was set on 41 °C.
At the medium of Figure 1 is shown the simulation of SSF fermentation, which does not require the addition of cellulase, however, hydrolysis must be performed in a separate unit, fermentation is performed in REACTOR 4 (red lines), and temperature was set on 32°C for efficient hexoses fermentation. At the bottom of Figure 1 is shown enzymatic hydrolysis stage for route 3, where reaction is performed in REACTOR3 (red lines) using cellulase at 48 °C.

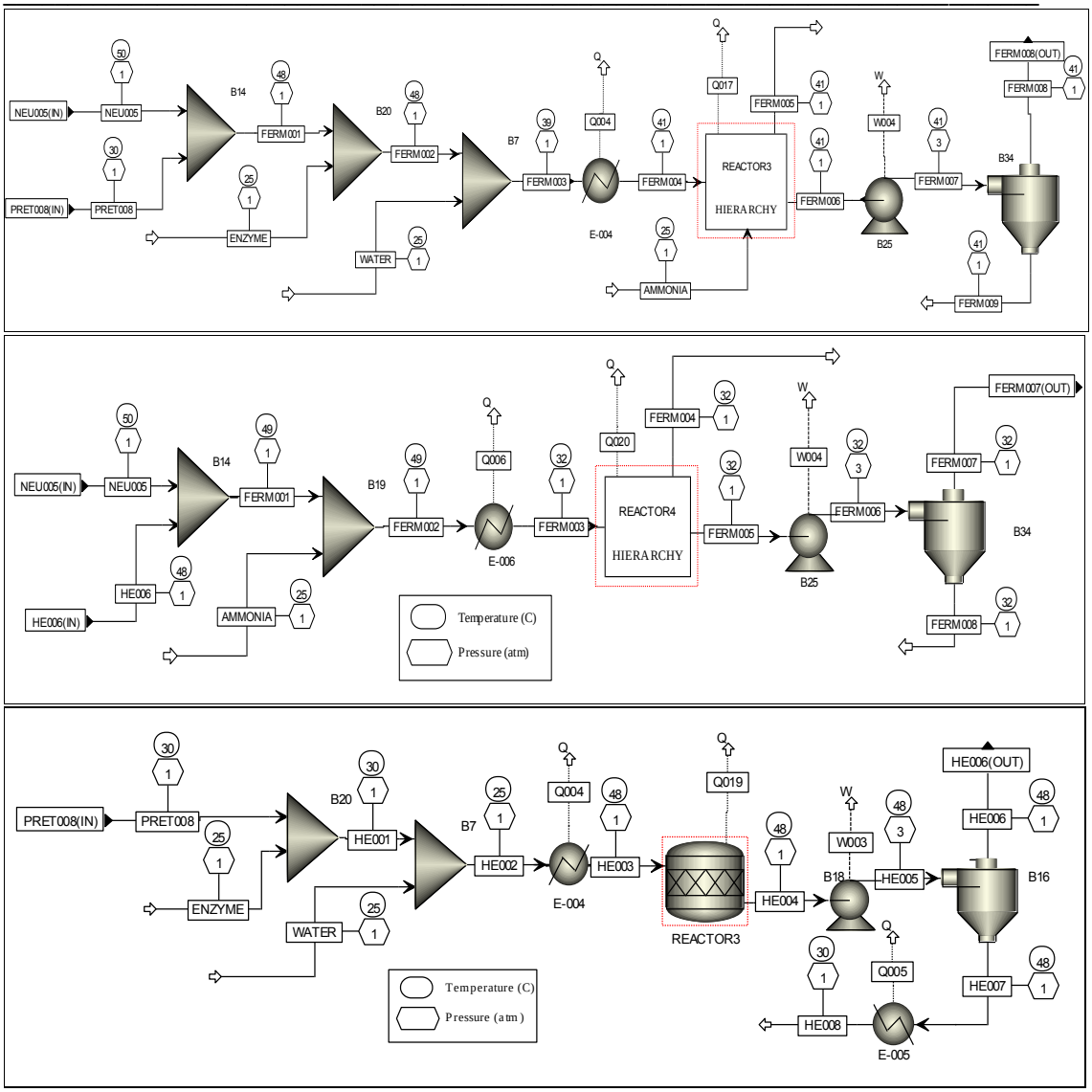

Figure 1: Simulation of routes evaluated for microalgal bioethanol production SSCF (upper), SSF (medium) and SHF (lower)

For microalgal bioethanol production a commercial industrial process simulation software (Aspen Plus V7.1, Aspen Technology, Inc., Burlington, USA, 2008) was used, properties of components were estimated using the NRTL (Non-Random Two Liquid) thermodynamic model, Table 1 shows the flows of algal biomass and bioethanol specifications of output streams for main steps in each route obtained from process simulation.

Table 1: Compositions of output streams for routes evaluated

Route		Stages		
SSCF			Fermentation	Separation
	Total mass flow (kg/s)		56.66	2.26
	Bioethanol flow (kg/s)		2.74	2.23
SSF		Fermentation (Pentoses)	Fermentation (Hexoses)	Separation
	Total mass flow (kg/s)	73.85	7.78	2.0
	Bioethanol flow (kg/s)	0.758	0.327	1.9
SHF		Hydrolysis	Fermentation	Separation
	Total mass flow (kg/s)	92.69	94.25	1.69
	Bioethanol flow (kg/s)	0	1.32	1.67

4. Results

According to simulation, SSCF technology (route 1) shows the highest efficiency of microalgal ethanol production for the routes evaluated (24.1 %), in addition, acid hydrolysis shows lower efficiencies in terms of reducing sugars production in comparison to obtained data from enzymatic hydrolysis, this can be explained by the selectivity of enzymes in comparison to acid hydrolysis reaction which presents low efficiencies in cellulose hydrolysis.

Table 2: Comparison of microalgal bioethanol production routes using energy integration.

	SSCF		SSF		SHF	
	Base Case	Energy Integration	Base Case	Energy Integration	Base Case	Energy Integration
Heat Exchangers	12	22	19	38	14	26
Total Area (m2)	34,700	26,285	49,059	9,950	35,505	9,078
Heating Service (GJ/h)	14.6	2.3	548	503	923	700
Cooling Service (GJ/h)	630	617.1	576	531	832	609

4.1 Energy integration

Table 2 shows energy integration results for routes evaluated, SSF route requires 14,000 kW more in heating services than SSCF technology, this difference is caused by the higher amount of separation units in SSF route and the need of additional stages of fermentation products purification. Taking into account energy requirements and bioethanol yield, SSCF technology is more convenient in a large-scale microalgal bioethanol production.

As the route with highest bioethanol yield and lower energy requirements, SSCF route was assessed in energy integration section using as molecular sieves as extractive distillation for bioethanol purification. Composite curves obtained for each route are show in Figure 2, using these curves the ΔT_{min} was defined in 9 °C for SSCF, 4 °C for SSF, and 8.5 °C for SHF.

4.2 Comparison of bioethanol dehydration alternatives for SSCF route

Extractive distillation was compared to molecular sieves as alternatives for microalgal bioethanol purification from the energetic point of view (Table 3), difference between energy requirements were calculated in 12.4 GJ/h y 215.3 GJ/h for heating and cooling services respectively, being more convenient the use of molecular sieves for large scale microalgal bioethanol purification.

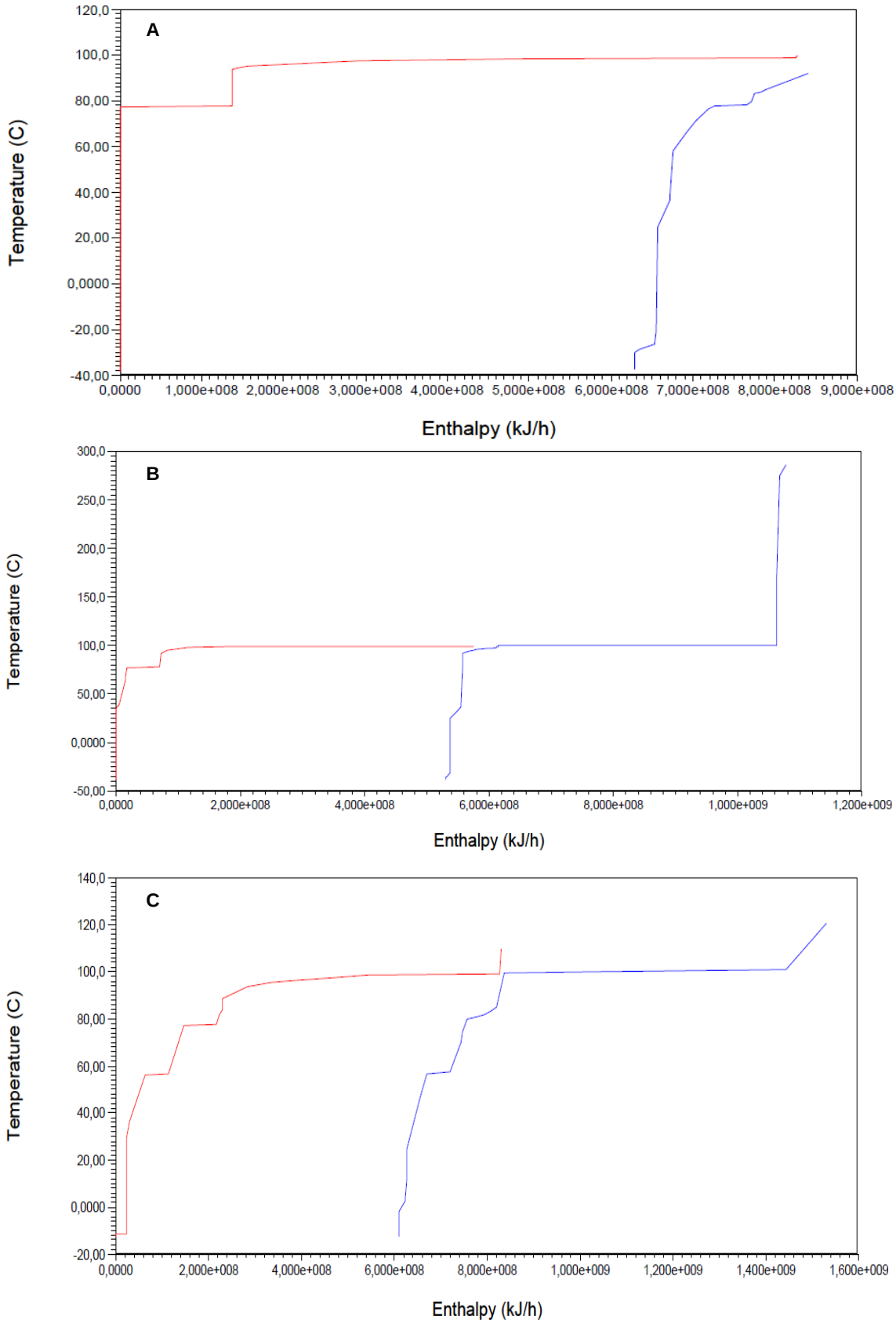

Figure 2: Composite curves of microalgal bioethanol production routes: A: SSCF, B: SSF, C: SHF.

Table 3: Compositions of output streams for routes evaluated

	Extractive distillation	Molecular sieves
Total Area (m^2)	34,700	18,285
Heating Service (GJ/h)	14.7	2.2
Cooling Service(GJ/h)	629.7	414.4

5. Conclusions

Three alternatives for microalgal bioethanol production from residual biomass were evaluated from the energetic point of view, and energy integration methodology was applied to each alternative in order to optimize the routes proposed. Technology of Simultaneous Saccharification and Co-fermentation SSCF (route 1) shows the highest bioethanol yield 24.1 % and lowest energy requirements after energy integration.

Separated hydrolysis and fermentation SHF (route 3) presents the lowest efficiency, ΔT_{min} was defined in 9°C for SSCF, 4 °C for SSF, and 8.5 °C for SHF. Finally, it could be established that the use of molecular sieves technology for bioethanol dehydration in the last part of the process represents lower energy requirements respect to extractive distillation with glycerol.

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References

Chong Fu C., Chieh Hung T., Yi Chen J., Hung Su C., Teng Wu W., 2010. Hydrolysis of microalgae cell walls for production of reducing sugar and lipid extraction, Bioresource Technology, 101, 8750-8754.

Galatro D., Verruschi E., 2012. Simulation of a hydrogen production process from algae, Chemical Engineering Transactions, 27, 373-378, DOI: 10.3303/CET1227063.

González A., Kafarov V., 2010. Design of a multifunctional reactor for third generation biofuels production, Chemical Engineering Transactions, 21, 1297-1302, DOI: 10.3303/CET1021217.

González-Delgado A.D., Kafarov V., 2011. Microalgae Based Biorefinery: Issues to Consider, CT&F – Cienc. Tecnol. Futuro, 4, 47-60.

González-Delgado A.D., Kafarov V., 2012. Microalgae based biorefinery: Evaluation of several routes for joint production of biodiesel, chlorophylls, phycobiliproteins, crude oil and reducing sugars, Chemical Engineering Transactions, 29, 607-612, DOI: 10.3303/CET1229102.

Iancu P., Pleşu V., Velea, S. 2012. Flue gas CO_2 capture by microalgae in photobioreactor: A sustainable technology, Chemical Engineering Transactions, 29, 799-804, DOI: 10.3303/CET1229134.

Khan S., Rashmi, Hussain M., Prasad S., Banerjee C., 2009. Prospects of biodiesel production from microalgae in India. Renew. Sustain. Energ. Rev., 13, 2361–2372.

Ojeda K., Sánchez E., El-Halwagi M., Kafarov V., 2011. Exergy analysis and process integration of bioethanol production from acid pre-treated biomass: Comparison of SHF, SSF and SSCF pathways, Chemical Engineering Journal, 176, 195-201.

Spatari S., Bagley D., MacLean H., 2010. Life cycle evaluation of emerging lignocellulosic ethanol conversion technologies, Bioresource Technology, 101, 654–667.

Wibul P., Malakul P., Pavasant P., Kangvansaichol K., Papong S., 2012. Life cycle assessment of biodiesel production from microalgae in Thailand: Energy efficiency and global warming impact reduction, Chemical Engineering Transactions, 29, 1183-1188, DOI: 10.3303/CET1229198.