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Exergy analysis of enzymatic hydrolysis reactors for transformation of lignocellulosic biomass to bioethanol

K. Ojeda, V. Kafarov*

Research Center for the Sustainable Development of Industry and Energy, Department of Chemical Engineering, Industrial University of Santander, Bucaramanga, Colombia

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ABSTRACT

The fast development of the world's bioethanol industry initiated debates on "food versus fuel" and the industry's environmental impact. Lignocellulosic biomass does not compete with food crops because it utilizes waste resources; however, the processing of a renewable energy source usually involves the consumption of non-renewable resources. To justify the production of second generation biofuels it is necessary to confirm that the energy produced from the lignocellulosic biomass is greater than the energy consumed in the ethanol production. The exergy analysis provides a unified and effective tool for the evaluation of the global process efficiency. This methodology requires an analysis of each stage of the production process. In this work, the stage of enzymatic hydrolysis was chosen as a case study because it is a decisive step in production process performance. The exergy analysis concept has been applied to evaluate two types of enzymatic hydrolysis reactors of lignocellulosic biomass for the production process of second generation bioethanol fuels from renewable resources, with the support of ASPEN-HYSYS® and other software developed by the authors.

1. Introduction

Ethanol can be produced using agricultural feedstock such as starch and sugar, or lignocellulosic biomass. The fast development of the world's bioethanol industry initiated debates on "food versus fuel" and the industry's environmental impact. According to Hayes [1], the production of biofuels through second generation technologies disputes many food versus fuel and socio-economic concerns since they use waste resources and, hence, do not compete with food crops. Land unsuitable for food production can instead be utilized for lignocellulosic energy crops. One of the largest potential feedstock for ethanol is lignocellulosic biomass, specifically agricultural residues (e.g., sugar cane bagasse, crop straws, and corn stover), herbaceous crops (e.g., alfalfa, switchgrass), forestry wastes, wood (hardwoods, softwoods), wastepaper, and municipal waste.

Other point to be considered in biofuels production is "energy consumption versus energy production." The processing of a renewable energy source usually involves the consumption of non-renewable resource (NRRs). When the exergy content of a NRR is altered through an irreversible process, the environment is also considered altered. Hence, much research [2–4] has been undertaken on the exergy accounting of NRR consumption in order to measure the environmental impact of many manufacturing processes. The intensive exploitation of a renewable energy source may also generate excessive wastes due to insufficient recycle systems. Some work and NRRs must be consumed to treat these wastes in order to prevent environmental damage.

In accordance with Dincer and Rosen [5], sustainable development requires sustainable energy resources and the efficient use of such residues. In this work, a decisive step in production process performance; that of enzymatic hydrolysis was chosen as a case study. Hence, Continuous Stirred-Tank Reactor (CSTR) and Plug-Flow Reactor (PFR) were evaluated as two types of enzymatic hydrolysis reactors of lignocellulosic biomass for the production process of second generation bioethanol fuels using the exergy analysis method. Exergy methods are important since they are useful tools for improving the efficiency of a production system.

2. Energy consumption in ethanol production process versus energy content in second generation bioethanol produced from lignocellulosic biomass

The biofuels production process starts with the farming of biomass (corn, sugarcane, lignocellulosic biomass, etc). Chemicals are used to help biomass growth; lime is used for soil pH adjustment. Energy and raw materials are consumed in all fertilizer and pesticide production processes. Machinery consumes diesel fuel, exemplifying the high energy consumption of farming. The biomass is transferred to a manufacturing plant, where it then could be

* Corresponding author at: Research Center for Sustainable Development of Industry and Energy, Department of Chemical Engineering, Industrial University of Santander, K 27 Cll 9, Bucaramanga, Colombia. Tel.: +57 7 6344000x2603.
E-mail addresses: cisyc@uis.edu.co, kafarov@uis.edu.co, vkafarov@gmail.com, vkafarov@yahoo.com (V. Kafarov).

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Nomenclature

E_T	total enzyme concentration (g/kg)
E_B	bound enzyme concentration (g/kg)
E_F	free enzyme concentration (g/kg)
E_{1B}	bound concentration of CBH and EG (g/kg)
E_{2B}	bound concentration of β-glucosidase (g/kg)
E_{2F}	concentration of β-glucosidase in solution (g/kg)
E_{max}	maximum mass of enzyme that can adsorb onto a unit mass of substrate (g protein/g cellulose)
G	glucose concentration (g/kg)
G_2	cellobiose concentration (g/kg)
K_{ad}	dissociation constant for enzyme adsorption/desorption reaction (g protein/g cellulose)
k_{ir}	reaction rate constants (kg/g h)
K_{ilG}	inhibition constants for glucose (g/kg)
K_{ilG_2}	inhibition constants for cellobiose (g/kg)
K_{ilX}	inhibition constants for xylose (g/kg)
K_{3M}	substrate (cellobiose) saturation constants (g/kg)
r_i	reaction rate (g/kg h)
R	universal gas constant (cal/mol K)
R_s	substrate reactivity
S	substrate concentration (g/kg)
T	temperature (K)
X	xylose concentration (g/kg)
α	Adjustment factor
$\dot{M}$	mass flow of substrate (g/h)
$\dot{m}_T$	total mass flow (kg/h)
ρ_m	density of mixture (kg/m^3)
m_T	reaction mass (kg)
$\dot{G}$	mass flow of glucose (g/h)
X_M	substrate conversion
V	volume (m^3)

transformed into biofuel. Electricity and fossil fuels are consumed during the conversion of the biomass into ethanol [5].

The global energy consumption in ethanol production from lignocellulosic residues, like bagasse, is lower than that of non-residual energy crops because the residual biomass from existing sugar industry is used. As such the energy consumption for all farming stages of sugar cane is assumed by the traditional sugar production chain. According to Cardona and Sánchez [6], the bioethanol production process from lignocellulosic biomass requires steam, electricity, and a cooling water supply. Thermal energy in the form of steam is the primary energy used in this process. Overall, production of fuel ethanol from lignocellulosic biomass includes five main steps: biomass pretreatment, cellulose hydrolysis, fermentation of hexoses, separation, effluent treatment, and, depending upon the feedstock, gathering, which may have an additional cost (Fig. 1). Furthermore, the pentoses released during the pretreatment step can be detoxified and fermented. According to Claassen et al. [7], one of the main problems in bioethanol production from lignocellulosics is that *S. cerevisiae* can ferment only certain mono- and disaccharides like glucose, fructose, maltose and sucrose. This microorganism is not able to assimilate cellulose and hemicellulose directly. In addition, pentoses obtained during hemicellulose hydrolysis (mainly xylose) cannot be assimilated by this yeast. Pentose fermentation, when it is carried out, is accomplished in an independent unit. The need for separate fermentations is due to the fact that pentose utilizing microorganisms ferment pentoses and hexoses slower than microorganisms that only assimilate hexoses. Moreover, the former microorganisms are more sensitive to the inhibitors and to the produced ethanol; for this reason, the hemicellulose hydrolyzate resulting from pretreatment should be detoxified [6]. The sequential configuration employed to obtain cellulosic ethanol includes the hydrolysis of a solid fraction of pretreated lignocellulosic that contains cellulose easily accessible to acids or enzymes. Once the hydrolysis has been completed, the resulting cellulose hydrolyzate is fermented and converted into ethanol [8].

The pure bioethanol produced can be used as fuel or as inputs in other chemical processes. Like all biofuels, ethanol produces work, CO_2, and other combustion products. It represents an energy production that can be quantified (Fig. 2).

To justify the production of second generation biofuels it is necessary to confirm that the energy produced from the lignocellulosic biomass is greater than the energy consumed in the ethanol production. The exergetic method provides a unified and effective tool to evaluate the biofuel process efficiency. This methodology requires an analysis of each stage of the production process. In this work, the reaction stage was selected as a case study because it is decisive step of production process performance. The exergy analysis concept has been applied to evaluate two types of enzymatic hydrolysis reactors of lignocellulosic biomass for the production process of second generation bioethanol fuels from renewable resources.

3. Exergy analysis—formulations

The concept of exergy provides an estimate of the minimum theoretical resource requirement (requirement for energy and material) of a process [9]. The energy and exergy balances for a flow process in a system during a finite time interval may be written as

$$\text{Energy input} - \text{energy output} = \text{energy accumulation} \quad (1)$$

$$\text{Exergy input} - \text{exergy output} - \text{exergy consumption} = \text{exergy accumulation} \quad (2)$$

According to Wall [10], the exergy E of a system may be written as

$$E = S(T - T_0) - V(p - p_0) + \sum_i n_i(\mu_i - \mu_{i0}) \quad (3)$$

where the extensive parameters are entropy S, volume V, and number of moles of substance i n_i, and the intensive parameters are temperature T, pressure p, and chemical potential of substance i μ_i for the system. The subscript o describes the state when thermodynamic equilibrium with the reference environment is established.

The exergy of a flow can be written as

$$E = H - H_0 - T_0(S - S_0) + \sum_i \mu_{i0}(n_i - n_{i0}) \quad (4)$$

where H is the enthalpy.

The energy and exergy efficiencies are generally defined as

$$\eta = \frac{\text{energy in products}}{\text{total energy input}} \quad (5)$$

$$\eta_e = \frac{\text{exergy in products}}{\text{total exergy input}} \quad (6)$$

The standard exergy of many compounds can be found in the literature [11,12]. When not available, the chemical exergy content of any pure substance can be computed by the approximate Eq. (7)

$$B_{ch} = \Delta G_{Fo} + \sum_i N_i b_i \quad (7)$$

where ΔG_{Fo} signifies the standard Gibbs free energy of formation of the substance [J/kg]; b_i, chemical exergy of the ith pure element of the substance [J/kg]; and N_i, molar fraction of the ith pure element of the compound.

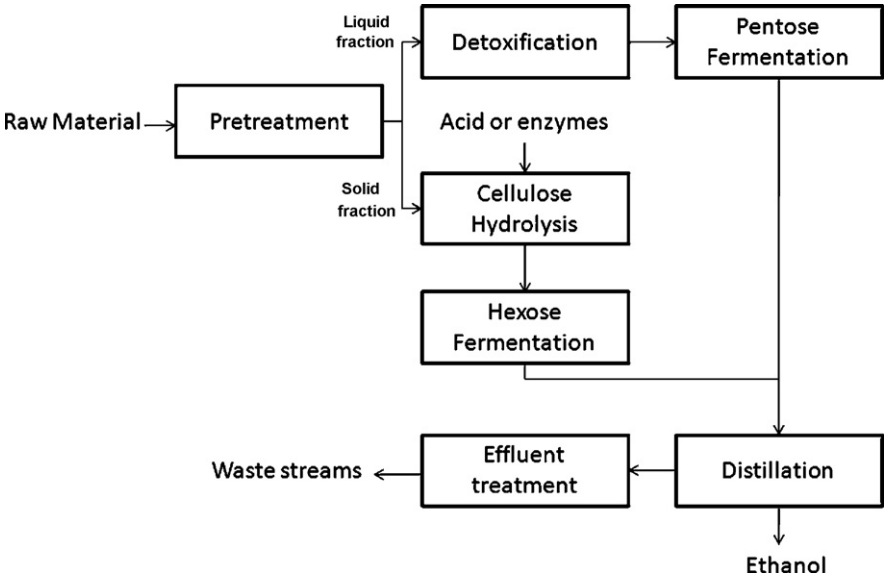

Fig. 1. General diagram of bioethanol production from lignocellulosic biomass.

The Gibbs free energy of formation is available for most chemical compounds in standard reference sources for a large number of chemicals. If not available, it is determined by methodologies as the Van Krevelen–Chermin equation [13]

$$\Delta G_{Fo} = A + BT \tag{8}$$

where T, temperature [K]; ΔG_{Fo} [kcal]; $A{\cdot}B$, functional groups contributions.

The chemical exergy of mixtures is defined as the sum of the chemical exergy of substances forming the mixture plus the exergy loss due to the mixing of the substances [14]

$$B_{chmixture} = \sum_i N_i b_i + RT_0 y_i \ \ln y_i \tag{9}$$

where b_i, chemical exergy of the ith substance [J/kg]; N_i, molar fraction of the ith substance; R, gas law constant [J/kg K]; T_0, temperature [K]; y_i, mole fraction of the ith substance.

According to Sorin et al. [15] it is possible to compute the exergy contents of all in-coming and out-going streams to and from a system and to establish an overall exergy balance over any system. The total exergy input of a real system is always higher than its exergy output, because a certain amount of exergy is irreversibly destroyed within the system. This exergy, generally referred to as the internal exergy losses, is directly linked to the thermodynamic irreversibilities in the system.

As reported by Talens et al. [14], Exergy Flow Analysis provides a way for process assessment that can be used as a tool for identifying material wastes and energy loss, detecting areas needing technological improvements by calculating the exergetic efficiency. Exergy is also a useful indicator for measuring material potential reactivity and quality, comparing different production processes of product substitutes that are especially useful in comparing renewable sources of energy.

4. Exergy analysis of enzymatic hydrolysis reactors

4.1. Kinetic model

Several theoretical and empirical models have been proposed to depict enzymatic hydrolysis of lignocellulose [16–22]. In this

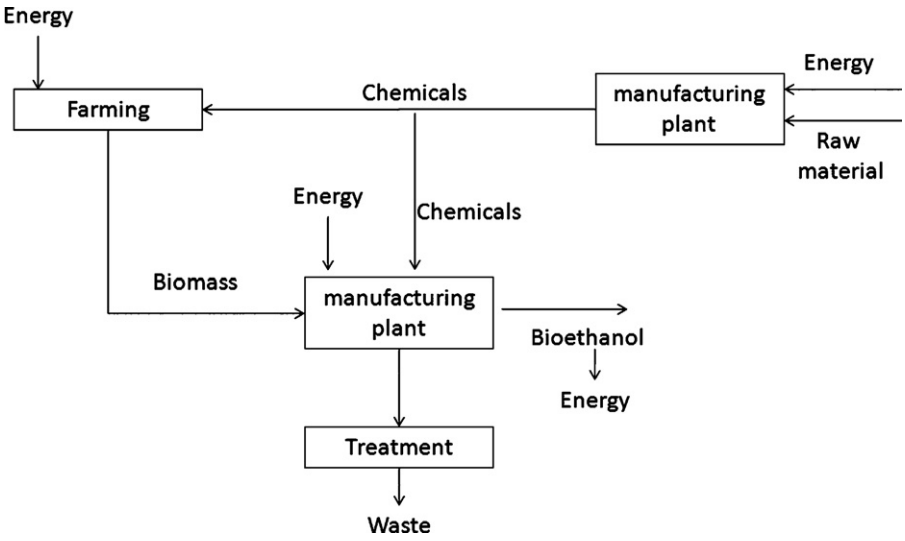

Fig. 2. Global energy consumption in the second generation bioethanol production process.

work, the kinetic model proposed by Kadam et al. [23] was selected because it considers all assumptions of the above mentioned models in addition to inhibition by xylose, a major sugar in hemicellulose-derived hydrolyzates. The model performed well in predicting cellulose hydrolysis trends at experimental conditions both inside and outside the design space used for parameter estimation [23].

Kadam et al. [23] modeled three hydrolysis reactions: two heterogeneous reactions for cellulose breakdown to cellobiose and glucose and one homogeneous reaction for hydrolyzing cellobiose to glucose. The following sugar products of cellulose hydrolysis were assumed to competitively inhibit the enzymatic hydrolysis reactions: cellobiose, glucose, and xylose, the dominant sugar prevalent in most hemicellulose hydrolyzates.

Cellulose hydrolysis is effected via a synergistic action of endo-β-1,4-glucanase (EG), exo-β-1,4-cellobiohydrolase (CBH), exo-β-1,4-glucan glucohydrolase, and β-glucosidase. The first three enzymes produce cellobiose and glucose; additionally, cellobiose is hydrolyzed to glucose by the action of β-glucosidase. Both sugars cause end-product inhibition. However, cellobiose is a much stronger inhibitor than glucose [23].

$$\text{Cellulose} \xrightarrow{r_1} \text{cellobiose}$$

$$\text{Cellulose} \xrightarrow{r_2} \text{glucose}$$

$$\text{Cellobiose} \xrightarrow{r_3} \text{glucose}$$

Enzyme adsorption:

$$\text{Langmuir isotherm } E_{iB} = \frac{E_{i\max} K_{iad} E_{iF} S}{1 + K_{iad} E_{iF}} \tag{10}$$

Cellulose-to-cellobiose reaction with competitive glucose, cellobiose and xylose inhibition:

$$r_1 = \frac{k_{1r} E_{1B} R_S S}{1 + (G_2/K_{1/G_2}) + (G/K_{1/G}) + (X/K_{1/X})} \tag{11}$$

Cellulose-to-glucose reaction with competitive glucose, cellobiose and xylose inhibition:

$$r_2 = \frac{k_{2r}(E_{1B} + E_{2B}) R_S S}{1 + (G_2/K_{2/G_2}) + (G/K_{2/G}) + (X/K_{2/X})} \tag{12}$$

Cellobiose-to-glucose reaction with competitive glucose and xylose inhibition:

$$r_3 = \frac{k_{3r} E_{2F} G_2}{K_{3M}(1 + (G/K_{3/G}) + (X/K_{3/X})) + G_2} \tag{13}$$

These rate equations assume that (1) enzyme adsorption follows a Langmuir-type isotherm with the first order reactions (r_1 and r_2) occurring on the cellulose surface, (2) the cellulose matrix is uniform in terms of its susceptibility to enzymatic attack, (3) enzyme activity remains constant, and (4) conversion of cellobiose to glucose occurs in solution and follows classical Michaelis–Menten kinetics [23].

4.2. Reactor model

Continuous Stirred-Tank Reactor (CSTR) and Plug-Flow Reactor (PFR) were chosen for having been considered reference models for industrial processes. An analysis of the efficiency of exergy in these two types of reactors using lignocellulosic biomass as raw material for second generation of biofuels production was made by the assistance of ASPEN-HYSYS® and software developed by the authors.

In this work a process of enzymatic hydrolysis on 1 ton/h of bagasse generated in conventional sugar production with typical chemical composition (w/w): cellulose 47.5%, hemicellulose 20%, lignin 32.5%, was simulated [24,25]. Properties such as: critical temperature, volume and pressure; acentric factor; I.G. heat of formation@ 298.15 K; vapour pressure; heat of vaporization; among others for cellulose, xylose and glucose components were obtained from [26]. The NRTL model for the calculation of the activity coefficients for the liquid phase and equation of state SRK for the vapour phase were chosen. Lignocellulosic biomass was pretreated using the organosolv process (solution (v/v) with ethanol 65%, NaOH 2.5% and water) after this process the liquid phase containing dissolved lignin in organosolv solution is recovered. Xylose and glucose were used in this simulation for representation of pentoses and hexoses. The cellulose removed in the delignification step is diluted with water in a hydrolysis reactor to obtain 4% (w/w) solids concentration. So for both types of enzymatic hydrolysis reactors the inputs of 6 ton/h of the obtained solution, with same reactor volume (7 m^3) were considered. The output solution composition for example, for temperature in reactor 50 °C, for PFR was (w/w): glucose 3.71%, unreacted cellulose 0.4%, xylose 0.13%, moisture 95.7%, and for CSTR was (w/w): glucose 3.24%, un-reacted cellulose 0.88%, xylose 0.13%, moisture 95.7.

4.2.1. CSTR (Continuous Stirred-Tank Reactor)

Assumptions:

- Lignocellulosic biomass pretreated with organosolv process.
- Enzymes: *Trichoderma reesei cellulases*.
- Cellobiose conversion 100%.
- In terms of inhibition capacity, xylose was used as the surrogate for both pentoses (xylose and arabinose) and glucose was used as the surrogate for all hexoses (glucose, galactose, and mannose). Xylose, glucose and cellobiose competitively inhibit the enzymatic hydrolysis reactions.
- Steady-state reaction conditions are prevalent.

Mass balances

$$\text{Cellulose}: \dot{M}_o - \dot{M} = m_T(r_1 + r_2) \tag{14}$$

$$\text{Cellobiose}: \alpha r_1 = r_3 \tag{15}$$

$$\text{Glucose}: \dot{G} = m_T(r_2 + r_3) \tag{16}$$

$$\text{Energy balance}: \dot{m}_T(h_o - h_s) + \Delta\dot{H} + \dot{Q} = 0 \tag{17}$$

4.2.2. PFR (Plug-Flow Reactor)

Assumptions:

- There is a steady-state operation (i.e., no change with time in the system).
- Plug flow.
- Enzymes: *Trichoderma reesei cellulases*.
- Cellobiose conversion 100%.
- In terms of inhibition capacity, xylose was used as the surrogate for both pentoses (xylose and arabinose) and glucose was used as the surrogate for all hexoses (glucose, galactose, and mannose). Xylose, glucose and cellobiose competitively inhibit the enzymatic hydrolysis reactions.
- The system operates isothermally (i.e., the rate constant does not change with L).

Mass balances
Cellulose:

$$\dot{M} = \dot{M} + d\dot{M} + \rho_m(-r_1 - r_2)dV \tag{18}$$

$$d\dot{M} = d[\dot{M}o(1 - X_M)] = -\dot{M}dX_M \tag{19}$$

$$\int_0^{X_M} \frac{dX_M}{(r_1 + r_2)} = \frac{\rho_m V}{\dot{M}o} \tag{20}$$

Glucose:

$$-\int_0^{X_M} \frac{dX_M}{(r_2 + r_3)} = \frac{\rho_m V}{\dot{M}o} \tag{21}$$

Sugar and substrate concentrations are expressed as g/kg, i.e., grams of entity per kilogram of total system mass.

4.3. Results and discussion

Chemical exergy of the components was calculated by means of the Gibbs Free Energy of Formation of the Substance based on the Van Krevelen–Chermin equation [13]. With this information, the exergy flows—both exergy consumed and produced by the process—were calculated.

The comparison of exergetic efficiency between CSTR and PFR is shown in Fig. 3. Exergy efficiencies between 64.27 and 68.12% for the CSTR and between 65.21 and 72.06% for the PFR were obtained. The analyzed reactors presented an increase in exergy efficiencies during the change of temperature operation from 40 to 50 °C, the operating range of cellulase enzymes. However, temperatures higher than 50 °C decreased the exergy efficiency. This is explained by the fact that the temperature optimum for the enzyme is near 50 °C, and the enzyme slowly inactivated at higher temperatures [16]. CSTR shows a characteristic sigmoidal curve in the 40–50 °C temperature interval. This behaviour was also noticed when the mechanism of the reaction changes with temperature [13] for instance, a change in the rate-controlling step. In the lower temperature interval the global velocity process is controlled by the biochemical reaction. But in the higher temperature interval diffusion has a greater influence on the controlling velocity factor. As is well known the PFR can be considered as a sequence of CSTR. In this way, the highest exergy efficiency for PFR and the lowest exergy efficiency for CSTR were obtained.

Fig. 4 shows the consumed exergy and the produced utilizable exergy in CSTR and PFR, respectively. The results show superior values of exergy flows for PFR. The system presents internal and external exergy losses that decreases the produced utilizable exergy. The influence of the temperature of the reactor on the exergy losses in CSTR and PFR is shown in Fig. 5. The exergy losses decrease with the increase in temperature of the reactor, but rise at higher temperatures (>50 °C).

According to Sorin et al. [15], in a chemical reactor only part of the utilizable exergy is produced by the system in the accomplishment of all the physicochemical phenomena which take place

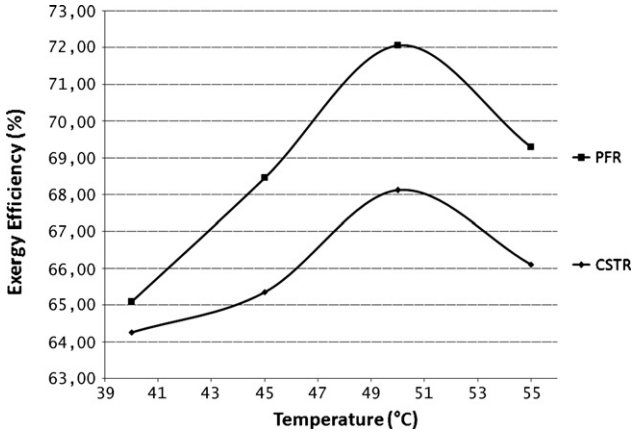

Fig. 3. Comparison of exergetic efficiency between Continuous Stirred-Tank Reactor (CSTR) and Plug-Flow Reactor (PFR).

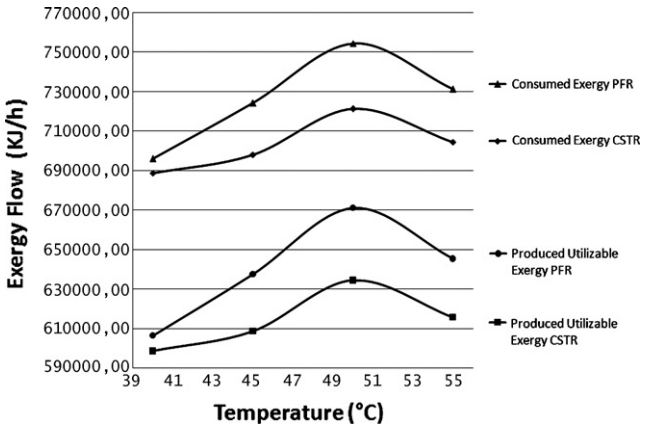

Fig. 4. Exergy analysis results for Continuous Stirred-Tank Reactor (CSTR) and Plug-Flow Reactor (PFR).

within its boundaries. The rest of the exergy that leaves the system with the utilizable exergy stream is a part of the exergy input which has simply traversed the system without undergoing any transformation. Therefore only part of the exergy input is consumed by the system in order to produce new forms of utilizable exergy. Thus, a certain amount of exergy is irreversibly destroyed within the system. This exergy, generally referred to as the internal exergy loss, is directly linked to the thermodynamic irreversibilities in the system. Both bioreactors (PFR and CSRT) had exergy losses, which are associated with: the irreversibility of the system, un-reacted products during the enzyme attack, or other inhibitory effects in the reaction.

The inhibition effect of xylose concentration in exergy efficiency of CSTR and PFR is shown in Fig. 6. An increased 0 and 40 g/kg xylose concentration generated a decrease of exergy efficiency of 35.87% and 30.98% for CSTR and PFR, respectively, suggesting significant xylose inhibition effect.

In this study, competitive inhibition was considered; these inhibitions occur when the substrate and inhibitor have similar molecules that compete for the identical site on the enzyme. The inhibitor substantially reduces the enzyme velocity at low substrate concentrations; hence, the exergy efficiency was reduced for both bioreactors. Furthermore, the rates of biochemical reactions were highly dependent on temperature and had a considerable effect on the output exergy flow from the reactors. The stirring mechanism in CSTR generated higher energy consumption; this is one of the reasons that make PFR more efficient than CSTR for enzymatic hydrolysis.

On the other hand, in the preliminary selection of a reactor, the cost–benefit ratio is one of the most important issues. When using a CSTR for consecutive reactions in the process (for

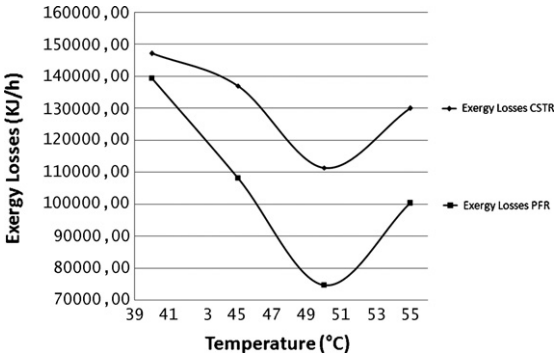

Fig. 5. The influence of temperature of reactor on exergy losses in Continuous Stirred-Tank Reactor (CSTR) and Plug-Flow Reactor (PFR).

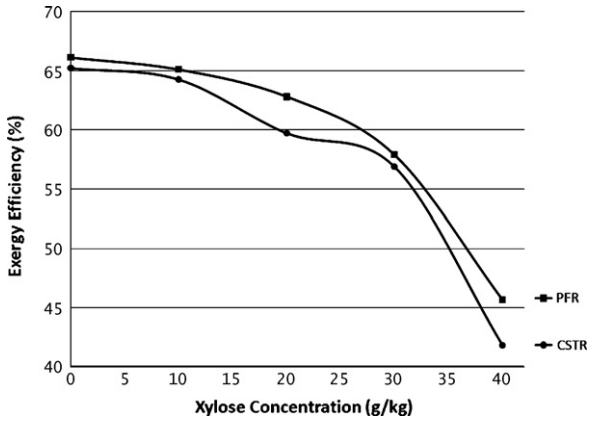

Fig. 6. The influence of xylose concentration on the exergy efficiency in Continuous Stirred-Tank Reactor (CSTR) and Plug-Flow Reactor (PFR).

example, cellulose–cellobiose–glucose) various elements experience differing residence times inside the reactor, causing a non ideal behavior which negatively affects the yield. In contrast, in the PFR, with a minimal mix, the residence time can be adjusted to one which is very close to optimal. In addition PFR allows for a higher glucose yield to be obtained when parallel reactions occur (cellulose–cellobiose, cellulose–glucose), due to the gradual change in cellulose concentration.

5. Conclusions

In this work, the exergy analysis concept was applied to evaluate two types of enzymatic hydrolysis reactors of lignocellulosic biomass for the production process of second generation bioethanol fuels from renewable resources. The results show that the bioreactors have exergetic efficiencies between 64.27 and 68.12% for the CSTR and between 65.21 and 72.06% for the PFR. There was an increase in exergetic efficiencies for both types of reactors when the operation temperature was raised between 40 and 50 °C, which is the operative range of cellulase enzymes. However, temperatures higher than 50 °C represent a decrease of exergy efficiency because the optimum temperature for the enzyme is near 50 °C, and the enzyme gradually inactivates at higher temperatures. Obtained results allow us to recommend the PFR with enzyme packing as the more energy efficient bioreactor for the enzymatic hydrolysis process.

The exergy analysis offers a unified and effective method for the evaluation of the process efficiency for enzymatic hydrolysis reactors for transformation of lignocellulosic biomass to bioethanol. Detailed application of exergy analysis to all stages of second generation bioethanol production will provide a tool to respond to the "energy consumption versus energy content in ethanol produced" debate and to verify the sustainable development of the biofuels industry using lignocellulosic biomass.

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