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Preliminary Conceptual Design of Biobutanol Production Process from Glycerin and Lignocellulosic Biomass

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Biobutanol can be a promising second generation biofuel when the feedstocks employed are lignocellulosic materials or even from by-products of biodiesel production. In particular and related to ethanol, butanol has higher energy content, less vapor pressure, easier to transport, and can be used in gasoline blends up to 100%. As butanol may be obtained by fermentation, the agro-industrial residues can be employed to release the fermentable sugars needed for production of this alcohol. In addition, some bacteria can assimilate the glycerin for producing butanol under specific conditions. The objective of this work is to accomplish the preliminary conceptual design of two processes for biobutanol production. The first process contemplates the utilization of glycerin generated during the biodiesel production from vegetable oils, and the second process uses lignocellulosic materials as feedstock. For this, different fermentation technologies were evaluated. Then, a thermodynamic phase equilibrium analysis was carried out for assessing the behavior of the aqueous mixture obtained after cultivation process. With the obtained data, preliminary separation schemes were defined. In addition, the pretreatment of lignocellulosic materials was evaluated as well as the cellulose hydrolysis step. Process integration possibilities were also assessed. In this way, simultaneous saccharification and fermentation of cellulose to produce biobutanol was studied employing commercial process simulators. The results obtained allowed verify the viability of the biotechnological production of butanol as a fuel alcohol with a high potential for transport sector. Glycerine is a suitable feedstock considering its availability and costs taking into account the big amounts of this chemical generated in current biodiesel production facilities. On the other hand, lignocellulosic residues are the most promising raw materials in the framework of second generation biofuels.

1. Introduction

The increasing energy requirements of the humanity will augment the pressure over research and development centres for finding new renewable sources of energy and for optimizing their production and utilization. The employ of bioethanol as an energy source requires that the technology for its production be fully developed at mid-term, especially from lignocellulosic biomass due to its low cost and big availability (Cardona and Sánchez, 2007). Biobutanol can be a promising second generation biofuel when the

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feedstocks employed are lignocellulosic materials or even from by-products of biodiesel production. In particular and related to ethanol, butanol has higher energy content and less vapor pressure, it is easier to transport, and can be used in gasoline blends up to 100%. As butanol may be obtained by fermentation, the agro-industrial residues can be employed to release the fermentable sugars needed for production of this alcohol. In addition, some bacteria can assimilate the glycerol for producing butanol.
The biodiesel is a mixture of methyl or ethyl esters of fatty acids that can be utilized as a fuel for diesel engines. For producing biodiesel, the transesterification of vegetable oils with low molecular weight alcohols like methanol or ethanol is necessary (Gutiérrez et al., 2009). The mixture of products and unreacted reagents is sent to a decanter where two liquid phases are separated: biodiesel-enriched and glycerol-enriched phases. Then, the biodiesel phase undergoes washing with hot water to remove salts and the non-separated glycerol. Finally, the glycerol is dried by distillation or vacuum flashing. If economically viable, the glycerol is refined to obtain a valuable co-product that can be used as feedstock for other processes. The objective of this work is to accomplish the preliminary conceptual design of two processes for biobutanol production. The first process contemplates the utilization of glycerin generated during the biodiesel production from vegetable oils, and the second process uses lignocellulosic materials as feedstock.

2. Pretreatment and Biological Transformation for Butanol Production

Butanol can be obtained by fermentation using bacteria of the genus *Clostridium*, which have a fermentative type of metabolism, i.e. under absence of oxygen or any other added electron acceptor. Along with butanol, acetobutylic bacteria form acetone and ethanol. These products can be produced by clostridia from starch, molasses, sucrose, wood hydrolyzates, and pentoses. The relative proportion of these metabolites at the end of cultivation depends on the bacterial strain and fermentation conditions. *Clostridium acetobutylicum* is the main microorganism used for butanol production. At concentration less than 0.5%, butanol has no influence on the cells while, at higher concentration, it causes damage on the cell membrane. At concentration above 1.3%, butanol production ends (Vorob'eva, 1989; Zverlov et al., 2006). The industrial process implemented in the past century comprised the batch anaerobic fermentation of a liquid medium based on carbohydrates (molasses, starch hydrolyzates) for 36 h. The pH decreases from 6.5 to 4.3 during the first 18 h, and increases up to 5.8 at the end of fermentation (Vorob'eva, 1989). As the fuel ethanol, butanol can be produced from lignocellulosic biomass. This process is more complex than its production from carbohydrates, but the utilization of lignocellulosic biomass represents a perspective alternative for the global large-scale production of biobutanol as a gasoline oxygenate all around the world. Process systems engineering offers valuable tools for the analysis of the biotechnological process for butanol production from biomass. In particular, process simulation can provide important insight on the process performance. In this work, the simulation of the pretreatment of lignocellulosic biomass, cellulose hydrolysis and fermentation was carried out. For this, it is necessary the analysis of the process.

For butanol production from biomass is necessary the pretreatment of the raw material by processes like steam explosion, pretreatment using dilute acid or alkalis (Sánchez and Cardona, 2008). During the pretreatment, the lignocellulosic matrix is broken down in such a way that cellulose chains reduce their crystallinity degree and increase the portion of amorphous cellulose, which is the most suitable form for enzymatic attack. In addition, main part of hemicellulose is hydrolyzed and lignin is released or even degraded. The hemicellulose hydrolyzate contains significant amounts of soluble pentoses (mainly xylose) that can be used as substrate for fermentation. Glucose is also present in this fraction as a result of hemicellulose degradation. In the hydrolysis step, the hemicellulose hydrolyzate undergoes enzymatic treatment with microbial cellulases in order to produce glucose from cellulose for fermentation. Moreover, cellulases are inhibited by high glucose concentrations provoking the reduction of their efficiency.

For the fermentation step, the bacterium *Clostridium acetobutylicum* was selected as the process microorganism used for conversion of sugars (both hexoses and pentoses) into butanol. Before fermentation, detoxification of the obtained hydrolyzate is required in order to remove the inhibitors formed during the pretreatment of lignocellulosic biomass that can negatively influence on the microorganisms performance in the course of the fermentation (Zverlov et al., 2006). The simulation procedure for the pretreatment and biological transformation (cellulose hydrolysis and fermentation) steps was accomplished by using the commercial process simulator Aspen Plus v. 11.1 (Aspen Technologies, Inc., USA). For this, the sugarcane bagasse was selected as the model lignocellulosic biomass employed in this work. The overall composition of the bagasse considered is as follows (in mass %): moisture 50%, cellulose 25%, hemicellulose 12%, lignin 12%, others 1%. The pretreatment with dilute acid was chosen and simulated by the RStoic module of the simulator, which represents a stoichiometric reactor analyzed through known fractional conversion. Similar approach was applied for description of cellulose hydrolysis and fermentation following the same simulation guidelines applied in previous works (Cardona and Sánchez, 2006; Gutiérrez et al., 2009). Thus, the enzymatic hydrolysis and co-fermentation processes were simulated based on a stoichiometric approach that considered the conversion of cellulose into glucose as well as the transformation of glucose and pentoses (considered as xylose) into cells, butanol and other fermentation by-products as acetone, ethanol, hydrogen and carbon dioxide.

For generation of promising alternatives of the process flowsheets, those configurations including the integrations of two or more reaction processes were preferred. With this aim, the simultaneous saccharification and co-fermentation process (SSCF) was simulated, where a combined fermentation of pentoses and hexoses is carried out by the bacterial cells along with the enzymatic hydrolysis of cellulose.

The stream resulting from the pretreatment of the sugarcane bagasse, cellulose hydrolysis and detoxification are presented in Table 1 for the process where the cellulose hydrolysis and the acetobutylic fermentation are carried out in different units (separate hydrolysis and fermentation, SHF). The composition of the stream resulting from the pretreatment of the sugarcane bagasse and detoxification is also presented in Table 1. This stream is sent to the bioreactor for simultaneous saccharification and co-fermentation process. Due to the previous cellulose hydrolysis, the stream for the SHF contains increased glucose content whereas the hemicellulose hydrolyzate corresponding to the SSCF process contains significant amounts of cellulose. The

distribution of fermentation products is different considering the higher effectiveness of the integrated SSCF process. Thus, the amount of butanol is increased by 33.3 % reaching a concentration of about 20 g/L.

Table 1 Composition (in mass %) of some streams in biomass-to-butanol processes

Process	SHF	SHF	SSCF	SSCF
Stream	Hydrolz.	Broth	Hem. Hydz.	Broth
Water	76.84	84.14	77.05	83.95
Cellulose	1.68	1.65	8.96	1.22
Xylan	1.07	1.05	1.07	1.06
Lignin	8.84	8.72	2.86	8.75
Cellobiose	0.16	0.15	0.00	0.15
Glucose	8.15	0.71	0.69	0.69
Xylose	2.85	0.55	2.86	0.53
Acetic acid	0.31	0.29	0.39	0.21
Sulfuric acid	0.11	0.10	0.11	0.10
Butanol		1.50		2.00
Acetone		0.85		1.00
Ethanol		0.25		0.30
Cells		0.04		0.04

Remarks: Hydrolz.: hydrolyzate obtained after biomass pretreatment, cellulose hydrolysis and detoxification; Hem. Hydz.: hemicellulose hydrolyzate after pretreatment and detoxification

Other promising option for butanol production is the use of glycerol as the main carbon source during fermentation. For this, the bacterium Clostridium pasterianum is able to directly utilize glycerol for converting it into butanol, 1,3-propanediol, ethanol, butyrate and acetate. However, the main fermentation product is butanol. Biebl (2001) reports that 11.12 g/L butanol can be obtained from a medium containing about 50 g/L glycerol during 24 h cultivation. The concentration of 1,3-propanediol was only of 1.98 g/L. The amounts of the other fermentation products were even lower. This author indicates that a maximum butanol concentration of 17 g/L can be obtained from 60 g/L glycerol. Clearly, the fermentation with C. acetobutylicum from lignocellulosic biomass reaches higher concentrations than in the case of C. pasterianum from glycerol, but the increasing availability of glycerol from biodiesel production and the fact that the costly pretreatment of biomass, makes this process attractive for fuel butanol production.

3. Butanol Recovery

The recovery of butanol from fermentation broth is an energy-consuming process due to the low concentration of metabolites obtained after cultivation of bacterial cells. To make this process cost-effective, streams with relatively high concentrations of butanol should be obtained. This can be done by removing the volatile fermentation products (including the butanol) from the culture broth. In addition, the butanol removal from the broth during fermentation decreases the end-product inhibition effect on the growth rate of clostridia. In this way, the fermentation performance can be significantly improved and the downstream operations can be favored.

There exist some procedures for removal of butanol, acetone and ethanol from culture broth as gas stripping (with fermentation gases or steam), vacuum fermentation, extractive fermentation or pervaporation (Cardona and Sánchez, 2007). In this work, stripping of butanol from broth using steam was analyzed. For this, the principles of the topological thermodynamics, in particular, the analysis of the statics (Pisarenko et al., 2001) were employed to synthesize the favorable separation flowsheets in energy terms. Different separation schemes for butanol recovery from aqueous solutions were synthesized by applying the analysis of the statics. The different options synthesized were assessed by simulation to determine the flowsheet with the lowest energy consumption. The approach and principles employed for simulation were mostly taken from a previous work (Cardona and Sánchez, 2006). For most process units, NRTL thermodynamic model was utilized to calculate the activity coefficients of the liquid phases and the Hayden-O´Conell equation of state for describing the vapor phase. In the case of the liquid-liquid separator (decanter), UNIFAC model was employed for the simulation of the properties of the two liquid phases. Using the results of the analysis of the statics, the rigorous calculation of the distillation columns was performed using the RadFrac module of Aspen Plus. Sensitivity analyses were carried out in order to study the effect of the main operation variables (reflux ratio, feed temperature, number of stages, etc.) on the composition of products and corresponding energy costs.

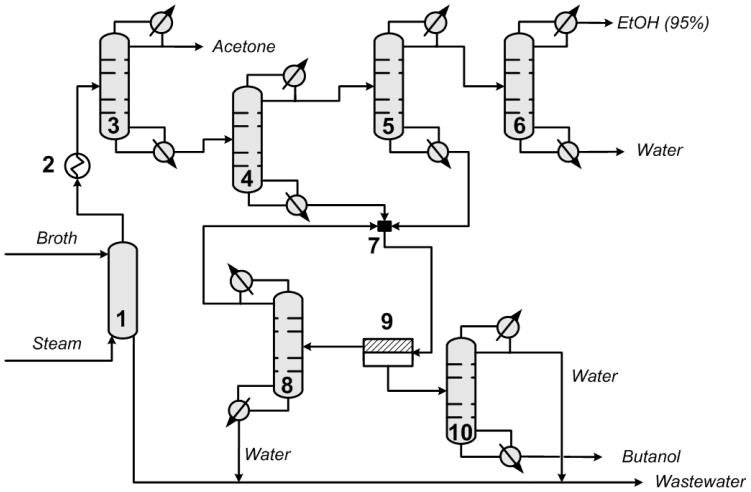

Figure 1: Flowsheet for butanol recovery step (see explanation on the text)

The flowsheet for butanol recovery with the best indicators obtained from the simulation comprised the following unit operations (see Figure 1): stripping of the broth with low-pressure steam (column 1), condensation of the vapor stream (condenser 2), distillation (column 3) of such stream for recovering acetone as a distillate product, subsequent distillation (column 4) of the bottoms from the column 3 to recover an ethanol-water-butanol solution from the top and a butanol-water mixture from the bottoms, distillation (column 5) of the distillate stream from column 4 to obtain an ethanol-water mixture from the top and a butanol-water mixture from the bottoms, concentration (column 6) of the ethanol-water mixture from the column 5 to obtain 95%

ethanol stream from the top and water from the bottoms, mixing (mixer 7) of the streams from the bottoms of columns 4 and 5, phase splitting (decanter 9) of such mixed stream, distillation of the butanol-enriched phase from decanter 9 to obtain pure butanol from the bottoms; the distillate of this column corresponds to wastewater. The second liquid phase from the decanter 9 undergoes distillation to obtain wastewater from the bottoms and a water-butanol mixture from the top that is recycled back to the mixer 7.

4. Conclusions

The analysis performed allowed finding the most appropriate technology for biobutanol production at the conceptual process design level. The thermodynamic analysis demonstrated to be a powerful tool for assessing different separation options. Process simulation showed its usefulness during the evaluation of diverse process flowsheets. The results obtained allowed verify the viability of the biotechnological production of butanol as a fuel alcohol with a high potential for transport sector. Glycerine is a suitable feedstock considering its availability and costs taking into account the big amounts of this chemical generated in current biodiesel production facilities. On the other hand, lignocellulosic residues are the most promising raw materials in the framework of second generation biofuels.

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