

Joint Production of First and Second Generation Bioethanol: Colombian CASE

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Colombia's policy of adding oxygenates to gasoline has led to the development, analysis and improvement of its bioethanol industry. Three bioethanol production pathways from sugarcane were simulated using Aspen Plus and compared using exergy analysis. These correspond to first generation bioethanol (route 1), second generation bioethanol (route 2) and bioethanol joint production (route 3). The objective was to determine whether there is an exergetic improvement in the bioethanol joint production compared to the individual processes. The bioethanol production was 491, 1616 and 2,049 kg/h, and irreversibilities amounted to 17.89; 19.31 y 19.85 MJ/kg ethanol, respectively. As a result, it was concluded that the joint production does not present an exergetic improvement compared to individual processes.

1. Introduction

The bioethanol industry has been developed rapidly in recent years to address the depletion of fossil fuels and the atmospheric pollution from their combustion. First generation bioethanol production started to develop in the early 70s in Brazil. At the beginning of the 80s, United States began to research in this area. The birth of the bioethanol industry in Colombia came later in 2001 with the Law 693 which established the use of an ethanol-gasoline blend starting on September 2005 (Fedebiocombustibles 2012).

The raw materials used to produce ethanol can be fermentable sugars (sugar cane, sugar beet) or starch (corn, wheat) and depending on these, there are more or less stages in the process. The raw material used for the production of bioethanol in Colombia (and Brazil) is sugarcane. First generation bioethanol production consists of multiple stages responsible for transforming sugar cane into anhydrous ethanol, however they can be classified mainly into three stages: Milling, Fermentation and Distillation. In Colombia, bioethanol production is carried out along with the sugar production process. The purpose of the milling step is to extract the juice from the sugarcane in order to ferment it further in the process. It comprises three small steps, namely, sugarcane washing, crushing and grinding. Continuously, the juice goes into the fermentation stage. The microorganisms most commonly used are *Saccharomyces cerevisiae*, *Pichia stipitis* and *Zymomonas mobilis* and their selection depends on the type of sugar that is going to be fermented. Finally, a distillation process is performed to purify the stream exiting the fermentation stage. Two distillation columns are used. In the first column the stream is concentrated up to a range between 37.4 wt% and 63 wt% (Wooley et al 1999). Subsequently, it enters the second column and comes out with a concentration close to the azeotropic point. This stream is dehydrated by molecular sieves which adsorb vapor and allow achieving higher purity ethanol to 99.9 wt% (Quintero et al 2008)..

Using this configuration, Colombia produced in 2012 about 360 million liters of bioethanol, which is roughly equivalent to a production of 1,250,000 liters of ethanol per day (Fedebiocombustibles 2013). However, *Fedebiocombustibles* (a governmental organization in charge of biofuels in the country) expects the production to increase as a part of a plan to reduce energy imports (Sapp 2012). As a result, the country

began to assess the possibility of using sugarcane bagasse, a residue from the milling stage, to produce bioethanol, called second generation bioethanol. One of the great benefits behind this raw material is the fact that it does not compete with the food industry (Ojeda, et al 2011). However, a disadvantage of second generation bioethanol is higher production costs compared to bioethanol from corn or sugarcane (Balat 2011).

The second generation bioethanol production process is currently under development. However, there is a general scheme that has been established. It consists of four main steps: Pretreatment, Hydrolysis, Fermentation and Distillation, and it can be seen in Figure 1 (Hamelinck, et al 2011)

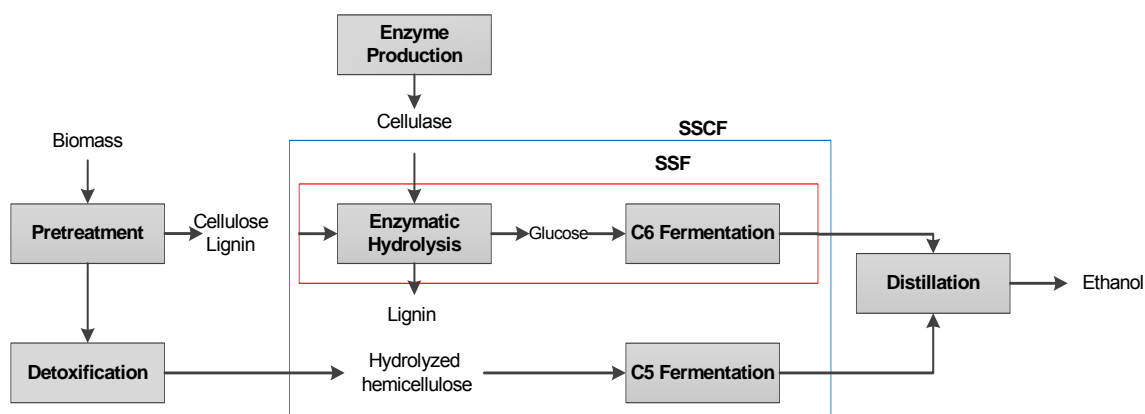


Figure 1. Second generation bioethanol production process and its integration stages (SSF and SSCF).

The first one is carried out in order to modify the structure and the macroscopic and microscopic sizes of the biomass along with its composition and submicroscopic chemical structure (Yang, et al 2008). Thus, carbohydrates, such as cellulose and hemicellulose are more accessible and hemicellulose is usually converted into xylose, mainly. In the second step, cellulose is converted into sugar monomers occurs, mainly glucose. This can be done by chemical or enzymatic hydrolysis. In the first one, the lignocellulosic material is exposed to chemicals, usually acids; while in the last one the transformation into fermentable sugars is carried out by enzymes (Balat, 2011).

The fermentation and distillation stages occur in the same way described in the first generation process. Additionally, it is important to highlight that different technologies related to hydrolysis-fermentation of lignocellulosic materials have been developed. The main two are Simultaneous Saccharification and Fermentation (SSF) and Simultaneous Saccharification and Co-Fermentation (SSCF), seen in Figure 1.

The concept of first and second generation bioethanol joint production lies in the benefits that would represent the merge of common stages to the first and second generation processes, such as the stage of fermentation and distillation. Initially, a reduction in the energy consumption of the process would be expected. However, if the bioethanol joint production is combined with the concept of process integration, significant reductions in the amount of raw material, such as water, and the waste leaving the process would be expected as well, along with an increase in the production of bioethanol. This has been evidenced previously by other authors (Dias et al 2009) and (Giarola, et al 2012). Whereas these emerging technologies, appraisal of these is a vital phase prior to implementing them. Based on this, the realization of exergy analysis identifies opportunities to improve technologically, through individual analysis, the units of the process, which makes it a very useful tool in evaluating emerging processes (Talens et al 2007)

2. Exergy

The concept of exergy provides a measure of the theoretical minimum amount of resources that may require a process (mass and energy) (Ojeda, et al 2009). Exergy is a thermodynamic property that measures the usefulness, quality or potential of a form of energy or a substance to cause changes when it is not in equilibrium with its surroundings. In other words, the greater the deviation of the system, the greater the exergy and the greater the ability to do useful work while it reaches equilibrium (Wall, 1977). For real processes, the exergy entering the system always exceeds the exergy leaving it. This imbalance occurs due

to internal irreversibilities of the system. In this sense, an exergy balance by definition exists only for reversible processes, therefore, for real processes, irreversibilities always exist in the system (Wall, 1994). The exergy of a stream can be calculated as the sum of its kinetic (Ex_{kin}), potential (Ex_{pot}), chemical (Ex_{ch}), and physical exergy (Ex_{ph}), (Tan et al 2010)

Since the variation of kinetic and potential exergy is considered very small, the chemical and physical exergy are considered in chemical systems. To calculate the latter two can be used exergies equations 2 and 3, respectively

$$Ex_{ch} = n \sum_i x_i \varepsilon_i^{ch} + RT_0 x_i \ln(x_i) \quad (1)$$

$$Ex_{ph} = m((h - h_0) - T_0(s - s_0)) \quad (2)$$

Where m is the mass flow, s and h are the specific entropy and enthalpy at the conditions of the system, the subindex 0 represents the reference state, n is the molar flux, x is the mole fraction of the species in the stream, ε_i^{ch} is the chemical exergy of the compound, T is temperature and R is the universal gas constant.

3. Description of the Routes

Three routes were studied and compared. The first route (Figure 2) corresponds to the first generation process, which comprises the milling, clarification, crystallization, fermentation and distillation stages. Some of these steps are performed to prepare the raw material for sugar production. The simulation was based on information obtained from industry related to the distribution of the streams and the stages conditions.

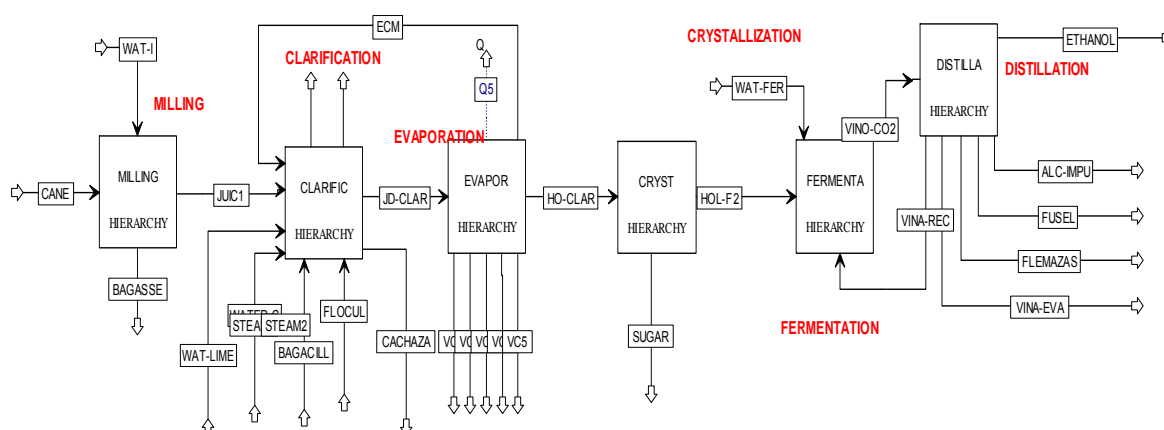


Figure 2. General scheme of the first generation bioethanol production process using sugarcane as raw material (Route 1).

In the milling stage sucrose is extracted from the sugarcane and the bagasse becomes the main residue. Continuously, the clarification stage is carried out to remove residues from the juice that may affect the subsequent sugar and bioethanol production processes. In the evaporation and crystallization stages, juice moisture is adjusted and sugar is produced, respectively. The stream leaving the crystallization stage is directed to the fermentation stage, in which bioethanol is produced using *Saccharomyces cerevisiae*. Finally, the stream is sent to the distillation stage in which a concentration of 99.8 wt% of ethanol is achieved.

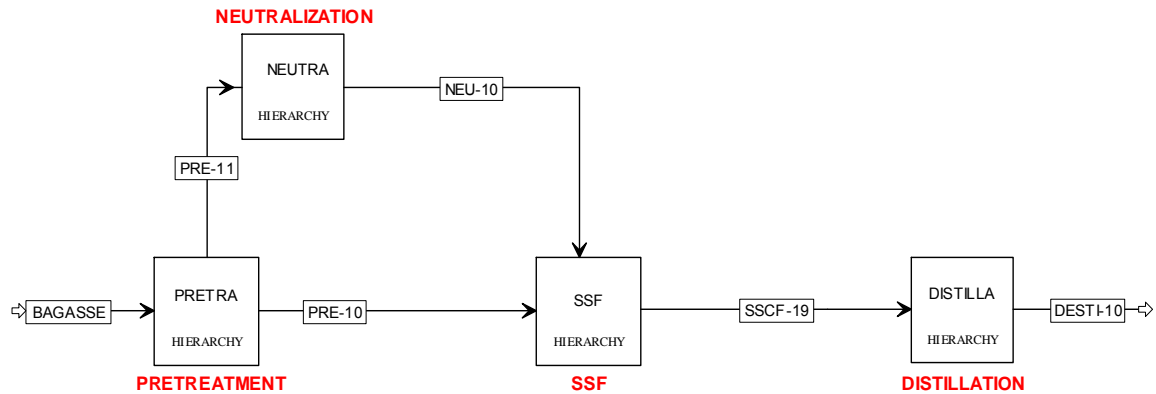


Figure 3. General scheme of the second generation bioethanol production process using sugarcane bagasse as raw material (Route 2)

The second route (Figure 3) corresponds to the second generation process. Bagasse and sulfuric acid are fed to the pretreatment reactor. Subsequently, the reactor is filled with saturated steam, then, biomass undergoes sudden decompression. As a result, hemicellulose is hydrolyzed to xylose with conversion 80.91% and a fraction of cellulose was hidrolizada with a conversion of 5%. The operation condition in this step are 190 °C and P_{sat} (12.36 atm); the exiting stream is separated into a liquid and a solid fraction. The liquid fraction is further neutralized using $Ca(OH)_2$ to avoid inhibition of the microorganisms used in the fermentation stage. The solid fraction and the neutralized liquid fraction are directed into the SSF reactor, in which cellulose is converted into glucose and glucose is converted into ethanol with conversion 80% cellulose-glucose and 92.5% glucose-ethanol. Previously, xylose contained in the liquid fraction is fermented using *Zymomonas mobilis*. The distillation stage occurs in the same way described before.

The third route (Figure 4) corresponds to the joint production of first and second generation bioethanol. The two individual processes are merged in order to take advantage of different exiting streams from either the first or second generation process by recycling them. This allows the use of shared equipment, which in theory renders the process more feasible.

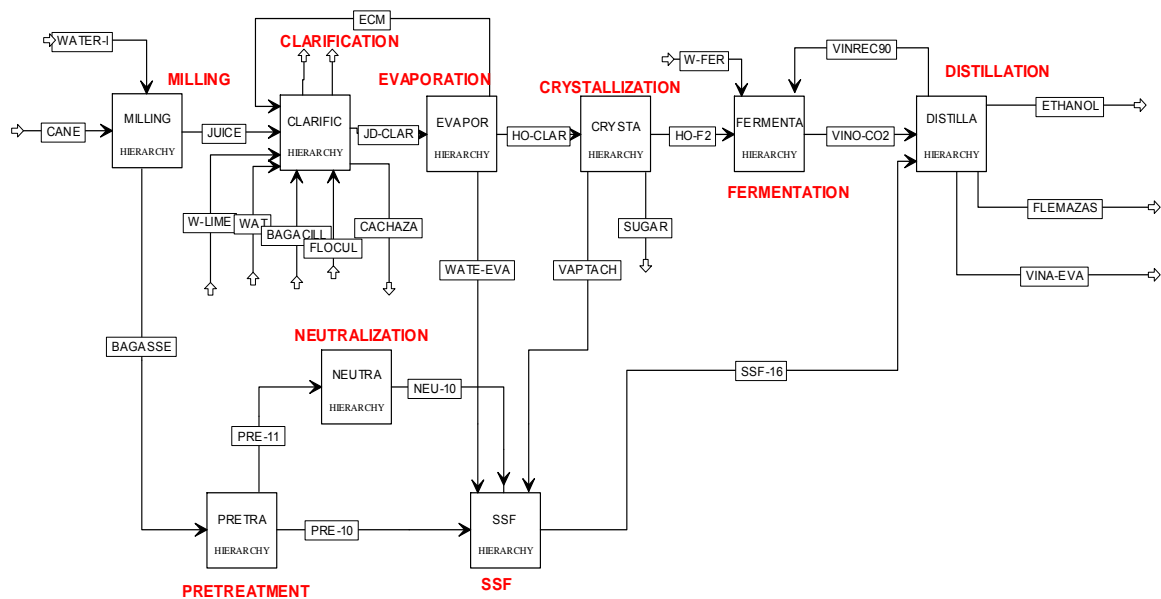


Figure 4. General scheme of the joint production of first and second generation bioethanol using sugarcane as raw material (Route 3)

4. Results and Discussions

The amount of sugarcane used as raw material was 38,000 kg/h. The amount of ethanol produced for all three routes was 491 kg/h, 1,616 kg/h, 2,049 kg/h, respectively. The exergy of the streams was calculated using the equations presented previously. The reference state was assumed as temperature and pressure of 298 K and 101,325 Pa, respectively. Irreversibilities for each of the routes were 17.89, 19.31 and 19.85 MJ/kg ethanol, respectively, which shows that the joint production is not enhanced exergetically while using an SSF technology, compared to separate first and second generation processes. Figure 5 shows a comparison between the irreversibilities of the individual processes (Routes 1 and 2) and bioethanol joint production (Route 3). The values of dark columns belong to each route, i.e., the values of milling, clarification, crystallization and fermentation stages, correspond to Route 1 and the values of pretreatment, neutralization and SSF stages correspond to Route 2. There is an exception in the value of the distillation step, which is the sum of the irreversibilities of Routes 1 and 2. Moreover, Figure 5 evidences that irreversibilities for Milling, Clarification, Evaporation, Crystallization and SSF stages have very small variations between the first and second generation and joint production, which makes sense considering that there is no substantial difference in these stages between individual processes and the joint production process.

There are notable differences in the Fermentation, Pretreatment and Neutralization stages. The difference in the Fermentation stage can be explained by the amount of sugars that is converted in the reactor; irreversibilities are proportional to the flow. The flow in the first generation is lower compared to the joint production, which is explained by the fact that the stillage recycled in the joint production to the fermentation stage is higher than in the first generation. The difference in the irreversibilities of Pretreatment, and therefore Neutralization, are attributed to the difference in the composition between the second generation and joint production streams entering each stage. The second generation, seen as an individual process, uses only lignocellulosic material unlike the joint production which contains the lignocellulosic material and residual sucrose from the milling stage. This creates a difference in the individual contributions of each compound to the total destruction of exergy in the equipment and, therefore, the stages. Distillation in the joint production generates higher irreversibilities compared to the individual processes. The two main reasons are higher heating services in the exchanger that receives the stream from the Fermentation stage and the need to cool down a higher amount of vinasse that is recycled to the fermentation stage. The SSF technology requires a large amount of water due to low solids loading, therefore, the stream that needs to be purified is larger, which leads to higher irreversibilities.

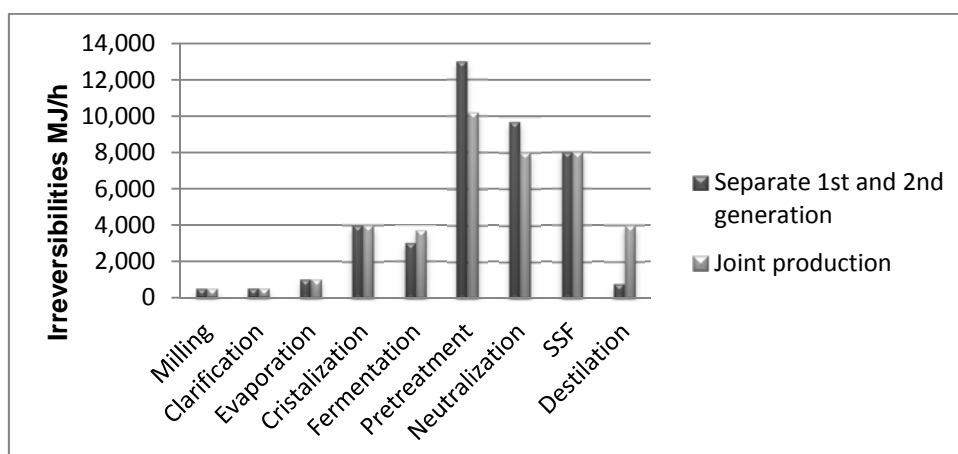


Figure 5. Irreversibilities per stage for first and second generation and bioethanol joint production.

5. Conclusions

The bioethanol joint production (Route 3) exhibits an increase in the irreversibilities compared to the individual processes. This increase occurs in the distillation stage due to higher energy requirements in the joint production. Additionally, the joint production using an SSF technology does not exhibit an exergetic improvement over the individual processes. Finally, considering that the joint production has the advantage of reducing the equipment, it is important to design a configuration that will lead to a decrease in the irreversibilities, in order to be considered viable in the future.

Acknowledgements

The authors appreciate and acknowledge the support provided by the Administrative Department of Science, Technology and Innovation (Colciencias).

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