SIMULATION OF INTEGRATED 1G BIO-ETHANOL PRODUCTION AND 2G MULTI-PRODUCT BIOREFINERY

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ABSTRACT
First-generation technology for the production of ethanol is well established in the world market, while second generation biorefineries in their struggle to overmatch their progenitor are also orientated towards ethanol production. Efficient technologies for production of lignocellulosic ethanol are still under development while challenges concerning its technical, economic and environmental feasibility remain unsolved. Instead of competing with each other, the integration of first and second generation processes may be more economically attractive, efficient and present lower environmental impacts than stand-alone processes. Therefore, integrated first and second generation technologies can improve the feasibility of lignocellulosic biorefinery and foster its industrial implementation. In this work the introduction of process improvements of the integrated first generation ethanol production process and second generation multiproduct biorefinery are assessed through simulation using Aspen Plus. The second generation biorefinery selected is based on CIMV Process™. Sugarcane bagasse is used as a fuel in conventional bioethanol production, providing heat and power for the plant. Thus, the amount of surplus bagasse available for use as raw material for second generation biorefinery is related to the energy consumption of the first generation bioethanol production process, making imperative the need for energy integration.

INTRODUCTION
The gradual depletion of oil along with uncertainties in energy supplies and a commanding requirement to reduce greenhouse gas (GHG) emissions have turned worldwide interest to renewable forms of energy. By far, biomass is the most abundant, the fastest growing and the only carbon-based source of renewable energy. In general, biomass can be divided into first- and second-generation. First generation biomass may include crops such as sugars from sugarcane or sugar beets and starch from corn, rice, wheat. Second-generation energy sources (lignocellulosic biomass) include forest residues like wood; agricultural residues such as sugarcane bagasse, corn cob, corn stover, wheat, and rice straws; industrial residues like pulp and paper processing waste; municipal solid wastes; and energy crops like switch grass [1]. Among the potential bioenergy resources, lignocellulosic biomass has been identified as a cheap and effective feedstock for producing biofuels including bioethanol, biobutanol, and biogas. First-generation (1G) ethanol is well established in the world market and already produced in large scale (Brazil and USA). It can be easily blended with gasoline to operate in spark ignition engines. Sugarcane is known to be the most efficient crop for 1G ethanol production, with an energy balance of 9.3 produced/consumed tonne of oil equivalent (toe) [2]. Additionally, sugarcane bagasse can be used to produce 2G ethanol. Therefore emphasis is also given for the production of second generation bioethanol. The production of 2G ethanol involves in general four different steps: pretreatment, hydrolysis, fermentation, and bioethanol recovery. A lot of research is focused in the recovery step, as the most energy intensive one, and in the step of pretreatment. There is a variety of technologies which fractionate lignocellulosic feedstock components: enzymatic fractionating, hot water or acid chemical hydrolysis, steam or ammonia fiber explosion, alkaline treatment and organosolv processes [3, 4]. Each approach has its own particular solution to the biomass fractionation and conversion processes. Fractionation processes propose ways to produce valuable building blocks, and pretreatment processes suggest efficient methods by enhancing conversion yields and reducing production costs. The choice of the optimum pretreatment process is highly dependent on the objective of the biomass pretreatment since different products are yielded.
Ortiz et al [5] have compared four different pretreatment processes (steam explosion, liquid hot water, ammonia fiber explosion and acid hydrolysis treatment) for the production of ethanol. They have examined not only the potential yield for each pretreatment process, but also its exergy efficiency associating this parameter with economic assessment and environmental impact. In their simulations the Organosolv pretreatment process presents the lowest exergy efficiency because of its dependence with the lignin and hemicelluloses performance recovery. Dias et al [6] studied the integration of 1G – 2G ethanol production process and compared the

following pretreatment methods: steam explosion, hydrogen peroxide and ethanol organosolv, followed, or not, by an alkaline delignification step. In their initial study they did not integrate the streams of the two processes and their conclusion was that the 2G process must be improved in order to improve competitiveness of the integrated design. In their recent study [7] the biochemical route is taken as an example for the 2G pretreatment method but not as the optimal one. They concluded that the pretreatment operations should focus on four main aspects in order to be incorporated in the integrated first and second generation bioethanol production process from sugarcane: reduced energy consumption, decreased sugar losses, low solvent use, and use of high solids loading. Several authors have evaluated the feasibility of different technological alternatives for bioethanol production through process simulation and mathematical modeling [8, 9, 10, 11]. Nevertheless, all these studies are focused on ethanol production. The other fractions of biomass (hemicelluloses and lignin) are burned in order to cover as much as possible of the energy required in order to minimize the bagasse burned for this purpose and therefore maximize the feed to the 2G process.

Current work studies the integration of 1G ethanol production process and 2G CIMV Process™, having sugar cane as feedstock. The 2G process is an existing pilot having its origins in the Pulp and Paper Industry and, mounted by new technology (CIMV Organosolv Process). It has now reached the technological maturity to move on to the next level of industrial demonstration. The CIMV technology is applicable to a wide range of feedstocks including cereal straws, sugar cane, sweet sorghum bagasse and hardwood. Its major breakthrough advantage is that it allows separation without degradation of the cellulose, hemicelluloses and the lignins, while silica imposes no obstacles and could actually add value to the overall process [12]. In analogy to conventional oil-based refineries producing fuels and chemicals, the existing process holds the potential to produce bio-based chemicals and fuels and stands as a promising candidate for a future biorefinery [13]. Its integration with existing 1G ethanol production process may boost its industrial implementation and precipitate the transaction to 2G bio-fuels, but still, the sustainability depends on economical feasibility, and its environmental and social impact. To cope with such challenges, the biorefinery development relies on the structured application of a multitude of methods in the areas of process synthesis, process integration, optimization and modeling at different scales. Energy integration may reveal suggestions for technological improvement for the second generation processes. Process synthesis may contribute to the selection of the most efficient valorization path for sugars and lignin, byproducts of the second generation process. This paper is an introduction to work on the evolvement of a real-life 1G-2G multi-product biorefinery and its necessary design transitions, further highlighting areas and methods in need for future research.

PROCESS DESCRIPTION

The design of first generation process is based on literature (Figure 1) [6, 14, 15, 16, 17, 18, 19, 20]. At first, sugar cane enters the Reception Sector. The efficiency of dirt removal in sugarcane washing is 90%. Sugarcane cleaning is usually carried out using wash water. The amount of sugar lost during the whole sugarcane washing is estimated at 25% for the mechanically harvested sugarcane washing (3,2kg/TC) and the average amount of water dragged with sugarcane during washing is 7,5t per 100 tonnes of cane (TC). However, usually, no washing is carried out for mechanically harvested (chopped) sugarcane due to the high sugar losses that occur. After cleaning, sugarcane is fed to the Extraction Sector, in which a series of equipment (shredder, hammers, etc.) are used to cut open the sugarcane structure and enhance sugar extraction in the following operation. After preparation, sugarcane passes over a magnet that removes residual metallic particles dragged along prior to entering the mills. Juice extraction is usually done using crushing mills, where sugarcane juice and bagasse are separated. Water at a rate of 28 wt% of the sugarcane flow (imbibitions water) is used to improve sugars recovery. The imbibition water temperature is at 50°C and the efficiency of sugar extraction at the mills is 96%. Sugarcane juice contains water, sucrose, and reducing sugars, along with impurities such as minerals, salts, organic acids, dirt, and fiber particles, which must be removed prior to fermentation. A rotary screen is used to remove solid particles from the juice. Efficiency of dirt and bagasse removal in the screen is around 65%.

Thereafter, at the Juice Treatment Sector the goal is to separate as much as possible of the dissolved and suspended juice impurities without reducing sucrose concentration. It must be done soon after milling in order to prevent yeasts and enzymes action. Thus, following extraction, the juice undergoes chemical treatment to remove other impurities. Phosphoric acid is added to sugarcane juice, to increase juice phosphates content and enhance impurities removal during settlement (H_3PO_4 9,5 mg acid/g dry material – initial content 0,01% and final content 0,03%) and then preheated, followed by the first heating operation in which juice temperature increases from 30° to 70°C. Preheated juice receives lime (CaOH 0,9 kg/TC) and is mixed with a recycle stream containing the filtrate obtained at the cake filter and then being heated up again to 105°C. Hot juice is then flashed to remove air bubbles and a flocculant polymer (150 mg/sec polyamide) is added to the de-aired juice, which is fed to the settler. In the settler impurities are removed from the juice and two streams are obtained: mud, which contains the impurities; and clarified juice. One of the main impurities removed in the mud is calcium phosphate, which is a precipitate formed in a reaction between lime and phosphoric acid; during

settlement it drags many other impurities contained in the juice, thus enhancing clarified juice purity. Besides impurities, the mud obtained in the settler contains sugars, thus a filter is used to enhance sugars recovery (washing water 150%). In this filter water and fine particles of bagasse, called bagacillo (0,1-1% in the mixed stream), are added to increase filtration efficiency. The filtrate is then recycled to the process and mixed with the limed juice prior to the second heating operation, while the filter cake can be used as fertilizer in the fields. A fraction of the clarified juice is concentrated up to 65wt.% sucrose and then mixed with the remaining clarified juice resulting to a stream with 22wt.% sucrose. Prior to being fed to the fermentation reactor, juice is sterilized in order to avoid contamination, which would decrease fermentation yields. During sterilization, juice is heated up to 130°C for about 30 min and then rapidly cooled down to fermentation temperature. The filling time is around 5 hours, while the total fermentation time ranges from 8 to 13 hours. After the completion of fermentation reaction, the wine is sent to the centrifuges, where cells are separated from the ethanol solution. Two centrifuges in series are used: in the first, yeast cell concentration is increased to 35% (v); water is added to the second centrifuge, where a concentrated yeast stream (70% cells, volume basis) is obtained. Centrifuged wine is mixed with the alcoholic solution from the absorber and fed to the distillation unit. Some part of the yeast cream, also known as alcohol distillery yeast extract, may be considered as by-product, used mostly as protein source for animal feed. Around 4% of the glucose is not consumed by the yeast.

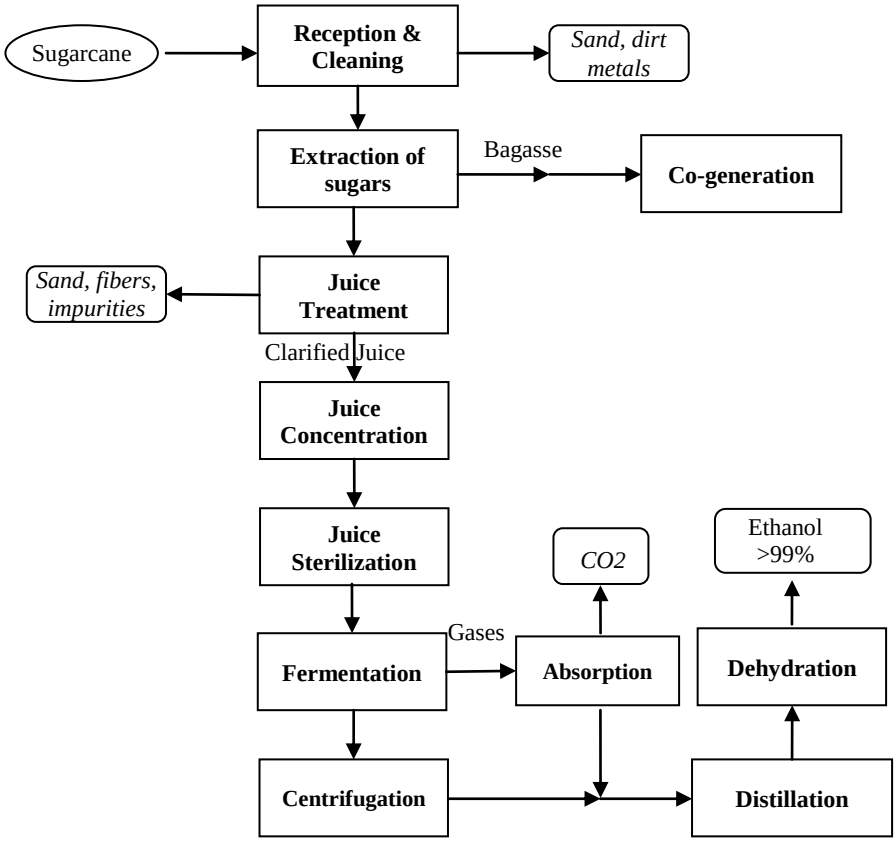

Figure 1. Simplified scheme of 1G ethanol process.

The composition of sugar cane feedstock as well as the composition of bagasse after 1G treatment that enters the 2G process is shown in Table 1 [15, 16].

Table 1. Composition of feedstock for 1G and 2G processes.

	Sugar cane		Sugar cane Bagasse	
	Humid	**Dry**	**Humid**	**Dry**
Sucrose	13,30%	46,78%		
Cellulose	4,77%	16,78%	21,69%	43,38%
Hemicellulose	4,53%	15,93%	12,81%	25,63%
Lignin	2,62%	9,22%	11,62%	23,24%
Reducing sugars	0,62%	2,18%		
Minerals	0,20%	0,70%	1,47%	2,94%
Impurities	1,79%	6,30%	2,41%	4,82%
Dirt	0,60%	2,11%		
Water	71,57%		50,00%	

The existing 2G process (Figure 2) is benefited by a pilot plant (CIMV, Pomacle, France). In operation since 2007, the pilot uses conventional processing equipment holding a capacity to process 50kg of dry biomass per hour and the start date of the demonstation plant (1t/h of biomass) is expected to be in early 2017. Biomass is initially treated by a mixture of organic acids to dissolve lignins and hydrolyse hemicelluloses Raw pulp is delignified with hydrogen peroxide, pressed and dried to remove the solvents that are separated and recycled. The final pulp is hydrolysed into glucose. The remaining syrup from the Extraction -Delignification section is concentrated and treated with water in order to precipitate and separate the lignin. The raw syrup containing C5 sugars, similar to molasses, is fermented to xylose and can be used in numerous industrial applications. The overall yields, based on straw dry matter is 52,20% cellulosic pulp, 25,80% lignin, and 22,00% raw sugar syrup.

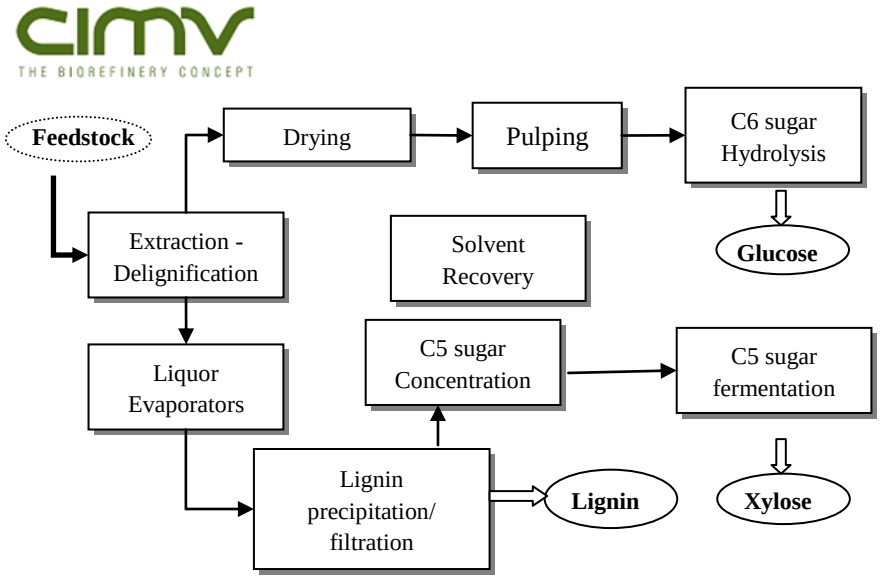

Figure 2. Schematically representation of existing CIMV Process™ (Permission CIMV, 2015).

Trying to avoid prejudged design solutions, the integration of these two processes comes with three basic scenarios depending on the final and/or intermediate products of the 2G process. As a starting point we assume that 50% of the bagasse produced is retrieved in 2G process as feedstock. This quantity will be re-estimated after the minimization of energy required, giving birth to additional studies for the optimization of scales. The first scenario (Figure 3) follows the global trend, targeting maximum ethanol production, but it makes the difference by leaving a degree of freedom for the valorization of lignin.

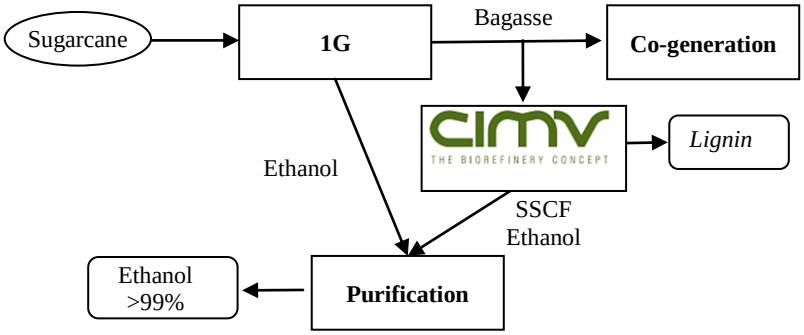

Figure 3. Simplified scheme of 1G 2G integrated process – Scenario with 2 products.

The second scenario (Figure 4) has two degrees of freedom; one for the valorization of lignin and another one for the valorization of xylose. The 2G glucose is mixed with 1G juice and the blend is fermented to ethanol in the same unit. In this case the ethanol produced stays in high levels. Xylose does not have a vital contribution to the quantity of the ethanol produced but its conversion to more valuable products may have a more significant contribution to the profitability of the project.

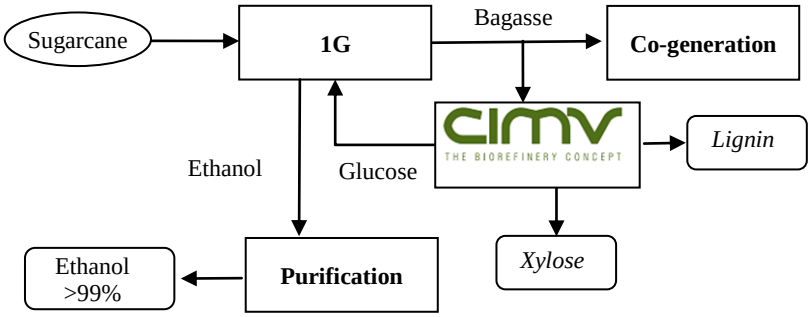

Figure 4. Simplified scheme of 1G 2G integrated process – Scenario with 3 products.

The third scenario (Figure 5) has three degrees of freedom; one for the valorization of lignin, one for the valorization of xylose, and another one for the valorization of glucose. In this case the quantity of ethanol produced is considerably reduced. The motivation behind this scenario is that 1G ethanol may be the economical safety net that allows the fully expansion of the multi-product biorefinery. In that case, when modifying the objective function, the possibility to enter the market with innovative bio-products can be studied.

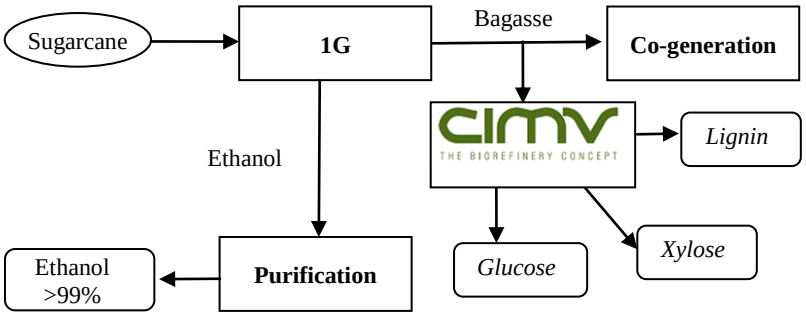

Figure 5. Simplified scheme of 1G 2G integrated process – Scenario with 4 products.

DISCUSSION AND FUTURE WORK

Integrating first and second generation bioethanol processes from sugarcane seems an obvious choice, since feedstock is already available at current bioethanol production facilities. Nevertheless, this project stays theoretical due to the deficiency of viable pretreatment for the lignocellulosic material. CIMV Process™ comes with a propitious wind for the realization of lignocellulosic biorefinery, even in a standalone form. This integration of processes, however, may contribute to a smoother transition from 1G to 2G bioethanol and industrial establishment of lignocellulosic biorefineries. The first generation process needs to be further optimized in order to minimize the energy needs and maximize the surplus of bagasse that enters the second generation process. Minimizing the combined process energy consumption is also of vital importance for the sustainability of the process. The variety of lignin and sugar platform, combined with 1G+2G ethanol production offers opportunities for the integration of new processes and feedstock, in order to increase the ethanol production and/or to obtain valuable products. Alternative feedstocks could also be processed in a 1G+2G plant outside the sugarcane crushing season. Techno-economic studies considering these new possibilities and integration can help in designing profitable processes. Last but not least, minimizing the water use and the treatment of effluents are also of great importance for the reduction of environmental and social impacts. To cope with such challenges, future work addresses the structured application of a multitude of methods in the areas of process synthesis, process integration, optimization and modeling at different scales.

ACKNOWLEDGEMENT

Financial support from the Consortium of FP7 Marie Curie project "RENESENG" is gratefully acknowledged.

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