Combined First and Second Generation Ethanol Production: Analysis of Supercritical Hydrolysis

Juliana Q. Albarelli*[a], Adriano V. Ensinas[b], Maria A. Silva[a]

[a]University of Campinas, School of Chemical Engineering, Cidade Universitária Zeferino Vaz, Avenida Albert Einstein, 500, Campinas, Brazil
[b]Federal University of ABC, Center for Engineering, Modeling and Applied Social Sciences, Av. dos Estados, 5001, CEP 09210-580, Santo André, SP, Brazil
jualbarelli@gmail.com

Supercritical hydrolysis of lignocellulosic materials for ethanol production represents a new trend in the sugarcane sector that needs evaluation. In this work, the commercial software Aspen Plus® was used to simulate ethanol and electricity production at a conventional autonomous distillery processing 500 tonnes of sugarcane per hour and a steam based cogeneration system. The production of lignocellulosic ethanol was simulated using the surplus bagasse produced at the autonomous distillery after thermal integration. The second generation ethanol production was studied with two cases: the enzymatic hydrolysis (Case 1) and supercritical hydrolysis (Case 2) considering in both cases a prior pre-treatment with liquid hot water. For cogeneration system besides bagasse it was considered the use of sugarcane trash as fuel. All data necessary for the simulation was obtained from the literature. Case 1 presented the higher ethanol production, increasing the overall ethanol in almost 13 %. Case 2 required a large amount of energy, to fulfil the thermal requirements of the process and 117 % more bagasse than the available after milling would be necessary. Even accomplishing to supply the energy necessary to the process, Case 2 showed ethanol production much lower than enzymatic hydrolysis.

1. Introduction

Supercritical hydrolysis has been studied for the production of lignocellulosic ethanol on the attempt to overcome the high cost and long reaction time of enzymatic hydrolysis. It was proved that crystalline cellulose was easily hydrolyzed to monomeric sugars by this new technology, and some studies had showed its potential to conversion of biomass (Kim et al., 2010).
Supercritical technology has become an attractive alternative to different process applications due to the use of environmental friendly solvents and small reaction time, overcoming some of the disadvantages of conventional techniques. (Albarelli et al., 2011). Supercrital water hydrolysis has being studied using different lignocelullosic material. Water is a nontoxic and neutral solvent at normal condition, but when in its critical temperature and pressure water does not behave as polar neutral solvent but it acts as a reactive medium such as weak acid and can dissolve most of organic compounds due to change in its dielectric constant, thermal conductivity and ion product (Kim et al., 2010).
Supercritical water presents high capacity for dissolution and catalysis. When in contact with lignocelullosic materials it separates lignin from cellulose and promotes a rapid hydrolysis of cellulose with the catalysis of H+ ionized (Zhao et al., 2012). However, cellulose hydrolysis in supercritical water can produce at the same time a high yield of oligosaccharides and glucose fragmentation products

inhibitors to fermentation. The fragmentation products derived from cellulose decomposition are erythrose, furfural and other unfermentable products. Combined supercritical and subcritical technology has been suggested and proven efficient for hexose production from lignocelluloses. In this combined approach, cellulose in biomass is first dissolved and hydrolyzed in supercritical water to produce oligosaccharides, to which subcritical water is then applied for hydrolysis into fermentable hexoses (Zhao et al., 2011).

Different studies evaluate supercritical and/or combined supercritical and subcritical hydrolysis of lignocellulosic material. This new hydrolysis process represents a new trend in the sugarcane sector that needs evaluation. In this study it was compared two alternatives of hydrolysis: enzymatic and supercritical. It was considered that the second generation production was attached to a first generation ethanol production process using sugarcane in a conventional Brazilian distillery. The second generation process used the surplus bagasse of first generation after thermal integration.

2. Simulation

The simulations were performed using the commercial simulator Aspen Plus®. The thermodynamic model used to represent the process was UNIQUAC model with modified binary parameters proposed by Mathlouthi and Starzak (2006) to adequately represent the elevation of the boiling temperature of the sucrose-water mixture. The components Cellulose, Hemicellulose, Lignin and Enzymes were added to simulator database using the data from Wooley and Putsche (1996).

It was considered the production of ethanol in an autonomous distillery processing 500 t/h sugarcane. The average composition of sugarcane arriving at the process is presented in Table 1. For the simulation it was considered that all the reducing sugars were dextrose, impurities were potassium salt, minerals were K_2O and the soil were SiO_2.

Table 1: Average composition of sugarcane arriving at the process

Component	% (mass/ mass)	Component	% (mass/ mass)
Sucrose	13.3	Reducing sugars	0.62
Cellulose	4.77	Minerals	0.20
Hemicellulose	4.53	Impurities	1.79
Lignin	2.62	Water	71.57
		Soil	0.60

Block diagram in Figure 1 shows the steps comprised in the 1st generation and 2nd generation ethanol production process studied as well as the cogeneration plant.
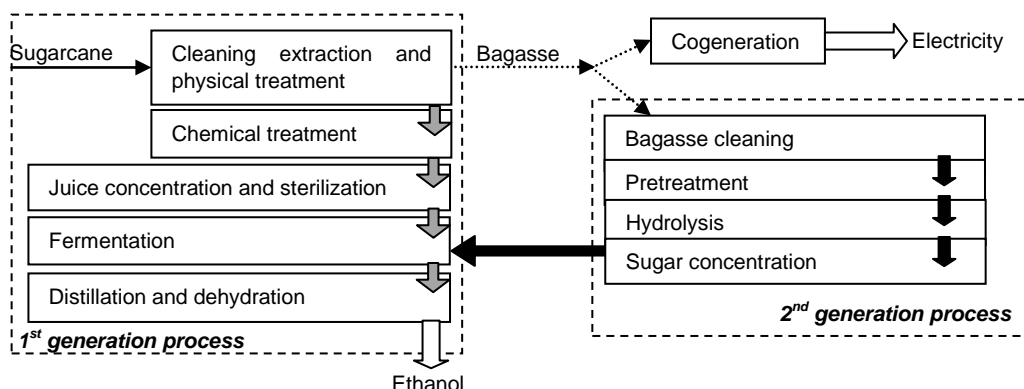

Figure 1. Block diagram of the steps comprised in 1st generation and 2nd generation ethanol production process.

2.1 First generation process

First generation ethanol production from sugarcane consists of the following steps: cleaning of sugarcane and extraction of sugars, juice treatment, concentration and sterilization, fermentation, distillation and dehydration. The data required for simulation of these steps were obtained in Rein (2007) and Ensinas (2008). Main process parameters of 1st generation ethanol production are shown in Table 2.

Table 2: Main parameters of 1st generation ethanol production process

Parameter	Value	Unit
Amount of sugar cane processed	500	t/h
Efficiency of dirt removal on sugarcane cleaning	60	%
Efficiency of sugars extraction on the mills	97	%
Sugarcane bagasse moisture content	50	wt%
Recovery of sugars on juice treatment	99.4	%
Fermentation yield	89	%
Pressure of steam produced in the boilers	65	bar

Cleaning of sugarcane and extraction of sugars: Initially, sugarcane goes through a cleaning step to remove the contaminants brought during harvest. It was considered a dry cleaning system for this stage of the process. Sugarcane is prepared for extraction through shredders and juice is extracted by mills.

Juice treatment: After extraction juice undergoes a physical treatment consisting of cyclones and filters for removing solids and insoluble contaminants. Soluble impurities are removed at the chemical treatment step. Chemical reagents are used to remove soluble solids by flocculation with separation in a decanter and a filter.

Concentration and sterilization: Clarified juice 15º Brix is concentrated until the adequate level for the fermentation. Part of the clarified juice was concentrated until 65º Brix in a five-effect evaporator. This stream is then mixed with the remaining not concentrated clarified juice stream for the required solid content for the fermentation step. This alternative, although not used in most plants, provides lower steam consumption compared to concentration of the entire clarified juice in one or two effects-evaporator until the fermentation Brix. Before fermentation the stream was sterilized.

Fermentation: Fermentation step was simulated based on the fermentation process-Melle Boinot. The concentrated stream together with fermentation yeast is added to the reactor where the sugars are converted to ethanol and other by-products. Recovery of ethanol in the fermentation gas is performed in an absorption column. Yeast is separated, treated and recycled the process after fermentation.

Distillation and dehydration: It was considered traditional distillation process consisting of 5 columns. The first three columns (columns A, A1 and D) work together. At these columns the liquid and vapor phlegm is obtained, they are sent to exhausting / rectifier column (column B, B1) to obtain hydrated ethanol. To obtain anhydrous ethanol it was considered the dehydration process using monoethylene glycol (MEG).

2.2 Second generation process

Liquid hot water (LHW) pre-treatment were adopted for both cases studied due to its simplicity, low generation of inhibiting by-products and projected yields of up to 98 %. (Schacht et al., 2008). It was not considered recovery of the pentoses-rich liquid fraction after the pre-treatment. The solid fraction undergoes a stage of vigorous washing with 30 L water/ kg of dry bagasse.

Second generation ethanol production was studied analyzing two cases: the enzymatic hydrolysis (Case 1) and supercritical hydrolysis (Case 2) considering in both cases a prior pre-treatment with liquid hot water. Supercritical hydrolysis was accomplished in a two step procedure, first cellulose in biomass was dissolved and hydrolyzed in supercritical water producing oligosaccharides, and then it was submitted to subcritical water for oligosaccharides hydrolysis into fermentable hexoses. This process was based in the study of Zhao and co-workers (2011). All data necessary for the simulation

was obtained from the literature. Most important parameters for second generation ethanol production processes studied are detailed in Table 3. The hydrolysis conversion parameters were assumed since the studies on supercritical hydrolysis of lignocellulosic materials are still at the beginning and have not evaluated optimized operational conditions or are still studying batch processes and/or using crystalline cellulose as a base material.

Table 3: Parameters adopted for second generation ethanol production processes studied

	Case 1	Case 2		
Pretreatment	**Value**	**Value**		**Unit**
Reactor solids load	20	20		%
Reactor temperature	180	180		°C
Hemicelulose–xylose conversion	88.0	88.0		%
Cellulose–glucose conversion	3.2	3.2		%
Xylose-furfural conversion	0.1	0.1		%
Hemicelulose–acetic acid conversion	1.0	1.0		%
Hydrolysis	**Value**	**Value**		**Unit**
		1st step	2nd step	
		Supercritical	Subcritical	
Reactor solids load	5	10	10	%
Reactor temperature	50	380	240	ºC
Reactor pressure	1.013	220	90	bar
Reaction residence time	24 h	10s	50	
Enzyme loading (cellulase)	15	-		FPU
Cellulose–glucose conversion	90	95[*]		%
Hemicelulose–xylose conversion	35.7	95[*]		%

[*] Adopted parameters considered for the overall conversion

The hydrolyzate is sent to a concentration system which consists of a four effects evaporator to achieve 20º Brix. The main data of this step are shown in Table 4.

Table 4: Operational conditions of the four effects evaporator for hydrolizate concentration

Evaporator	**Pressure**	
1st Effect	1,69	bar
2nd Effect	1,31	bar
3rd Effect	0,93	bar
4th Effect	0,54	bar

2.3 Cogeneration and thermal integration

For the cogeneration system it was considered a steam cycle operating with live steam at 480º C and 65 bar, using a backpressure turbine to generate mechanical energy and electricity. For the conventional distillery case it was considered only the use of bagasse as fuel to the cogeneration system. For Case 1 and 2 it was considered bagasse and sugarcane trash as fuel to the boiler. The low heating value considered bagasse and sugarcane trash were 7.5 and 15 MJ/kg, respectively. For Case 1 and 2 the flow of sugarcane trash considered was 41,250.00 kg/h, representing 50 % of the trash available. The flow of bagasse was defined by the simulation according to the energy need of each case after thermal integration.

The heat integration of the processes studied was performed using the Pinch Point Method. This method uses enthalpy temperature diagrams to represent the process streams and to find the thermal integration target for them, considering a minimum approach difference of temperature (ΔT_{min}) for the

heat exchange. Thermal integration analysis of the ethanol production process considered the hot and cold streams parameters determined in the simulation of the autonomous distillery.

3. Results and discussion

The flux of bagasse generated after juice extraction was 129.0 t/h with 50 % of moisture. Around 92.3% of this stream is necessary to fulfill the thermal requirement of the conventional 1st generation ethanol production process.

After thermal integration of the conventional distillery using the Pinch Point Method, the hot utility requirement was reduced in 43.4 % resulting in a reduction of 32 % on bagasse consumption necessary for the cogeneration system. The addition of second generation process to the conventional distillery increased the thermal demand and a new thermal integration was performed in order to calculate the new flux of bagasse necessary to the boiler.

The analysis of the Case 1 resulted in an increase of 12 % on the thermal demand comparing to the conventional distillery after thermal integration. In this configuration 43 % of bagasse was designated to ethanol production and the remaining bagasse was used to generate energy at the cogeneration system.

Case 2, with the configuration proposed in this study, showed itself not feasible from the thermal point of view due to the high thermal energy demand to achieve the supercritical phase. This Case showed an increase of 133 % on the thermal demand comparing to the conventional distillery after thermal integration. It would be necessary to have 117 % more bagasse after sugarcane milling to fulfill the thermal requirement of this case using 13.3 tonnes of bagasse/h. Another possibility to increase the thermal energy generated would be the use of residual lignin after hydrolysis as a supplementary fuel to the cogeneration system. In this situation considering PCI of lignin 25 MJ/kg, it would be necessary 6.6 more lignin than the 6.5 t/h of residual lignin generated at the process.

The hot utilities necessary for each case studied are displayed in Table 5. Case 2 show a higher demand of superheated steam 65 bar necessary to provide heat to the supercritical process.

Table 5: Hot utilities necessary for each case studied

	CD*	Case 1	Case 2	
Steam	**Value**	**Value**	**Value**	**Unit**
65 bar 480ºC	--	--	774.1	t/h
11 bar	--	285.5	--	t/h
6 bar	8.2	6.0	--	t/h
2.5 bar	252.7	285.5	49.8	t/h

*convertional distilerry

Table 6 shows the main results for both cases analyzed considering that the thermal requirement of Case 2 was fulfilled. Case 1 has the higher increase in the overall ethanol production. In Case 2 the overall ethanol production increase was of only 2 %. The same or higher increment in the production could be achieved simply with modifications in the first generation process as using extractive fermentation (Dias et al., 2012); in this configuration the surplus bagasse could be used to produce more electricity. This would represent a feasible scenario with better results in energy production and similar results for ethanol production than Case 2. Comparing the second generation ethanol production of both cases, Case 2 presented the lower amount of ethanol per t of bagasse demonstrating that even if Case 2 had no problems with the thermal demand, Case 1 would have higher ethanol productivity per t of bagasse.

The conversion of cellulose in fermentable sugars adopted in this study was an optimistic value since there is no available data in the literature on supercritical hydrolysis using sugarcane bagasse. This shows that to turn supercritical hydrolysis in to an attractive process for second generation ethanol production in conventional Brazilian distilleries it is necessary to reduce significantly the energy

requirement of Supercritical process, and also to find the optimized conditions in order to have the highest possible conversion of fermentable sugars.

Table 6: Main results for the cases studied

	CD	Case 1	Case 2 ¨	
	Value	**Value**	**Value**	**Unit**
Total ethanol production	77.9	87.8	79.5	L/t sugarcane
Increase in the ethanol production	-	12.7	2.1	%
Lignocellulosic ethanol production	-	83.9	60.2	L/t bagasse

¨ only fulfilling the thermal requirement

4. Conclusion

Supercritical hydrolysis of biomass is a new field of study under investigation for different researchers. Using the configuration for supercritical second generation ethanol production available in the literature, the simulation of this second generation process using sugarcane bagasse attached to a conventional distillery showed itself unfeasible. Supercritical hydrolysis requires a large amount of energy, being the thermal demand the most concerning point. To fulfil the thermal requirements of the process would be necessary to have 117 % more bagasse than the available after milling. Even accomplishing to supply the energy necessary to the process, supercritical hydrolysis showed ethanol production much lower than enzymatic hydrolysis. The overall ethanol production increase of process could be achieved without the second generation process with only modifications on the first generation process.

References

Albarelli J.Q., Rabelo R.B., Santos D.T., Beppu M.M., Meireles M.A.A., 2011, Effects of supercritical carbon dioxide on waste banana peels for heavy metal removal. Journal of Supercritical Fluids, 58, 343-351.

Dias M.O.S., Junqueira T.L., Jesus C.D.F., Rossell C.E.V., Maciel Filho R., Bonomi A., 2012, Improving bioethanol production - Comparison between extractive and low temperature fermentation. Applied Energy, DOI: 10.1016/j.apenergy.2012.04.030

Ensinas A.V., 2008. Thermo-chemical and thermal integration and optimization applied to industrial process for producing sugar and ethanol from sugar cane (in Portuguese). 229 f. PhD Thesis – Faculdade de Engenharia Mecânica, Universidade Estadual de Campinas, Campinas, SP, 2008.

Kim K.-H., Eom I.-Y., Lee S.-M., Cho S.-T., Choi I.-G., Choi J.W., 2010, Applicability of sub- and supercritical water hydrolysis of woody biomass to produce monomeric sugars for cellulosic bioethanol fermentation. Journal of Industrial and Engineering Chemistry, 16, 918-922.

Rein P., 2007. Cane sugar engineering. Verlag Dr. Albert Bartens KG, Berlin, Germany, 768 p.

Schacht C., Zetzl C., Brunner G., 2008, From plant materials to ethanol by means of supercritical fluid technology. Journal of Supercritical Fluids, 46, 299-321.

Starzak M., Mathlouthi M., 2006, Temperature dependence of water activity in aqueous solutions of sucrose, Food Chemistry, 96, 346-370.

Wooley R.J.; Putsche V., 1996, Development of an Aspen Plus physical property database for biofuels components. < www.p2pays.org/ref/22/21210.pdf>, Accessed 18/05/2012.

Zhao Y., Wang H.-T., Lu W.-J., Wang H., 2011, Combined supercritical and subcritical conversion of cellulose for fermentable hexose production in a flow reaction system. Chemical Engineering Journal, 166, 868-872.

Zhao Y., Lu W.-J., Wu H.-Y., Liu J.-W., Wang H.-T., 2012, Optimization of supercritical phase and combined supercritical/subcritical conversion of lignocellulose for hexose production by using a flow reaction system. Bioresource Technology, DOI: 10.1016/j.biortech.2012.03.001.