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Integration of Supercritical Water Gasification in Combined 1G/2G Ethanol Production

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The present study investigates the potential conversion of sugarcane into ethanol and synthetic natural gas. The considered conversion path consists in combining ethanol first and second generation ethanol production plant with a catalytic supercritical water gasification system. The main steps of the ethanol conversion consider fermentation of sugars (1G) and enzymatic hydrolysis of bagasse (2G). Enzymatic hydrolysis is selected since it represents a promising alternative for 2nd generation biofuels due to its high conversion efficiency. Among streams that are leaving the ethanol production plant are some high watered streams, whose carbon/energy content is not negligible. These streams should be valorised in an efficient way in order to improve the energy conversion efficiency. In this context supercritical gasification process allows to valorise these flows leaving the ethanol plant. Using supercritical water gasification it is in fact possible to avoid the drying the ethanol production leftovers, thus performing a direct gasification. The conversion of ligno-cellulosic residues into synthetic natural gas is modelled considering a catalytic supercritical gasification plant. Since the goal is to achieve high energy and exergy conversion efficiencies, the potential use of an additional set of utilities, such as burners, steam injected gas turbines or steam networks, is added to the sizing problem.
The mathematical nature of the optimal utility selection problem deals with mixed integer linear programming (MILP) model, in which the type and size of utilities represent the independent variables, having fixed the process size. The results of the integration are showed in terms of Composite and Grand Composite Curves, economic indicators and local CO_2 balance.
Finally, having identified the ratio of sugarcane that goes to second generation ethanol plant as key dependent variables, the results of a sensitivity analysis are presented. The sensitivity analysis results are shown accounting economics for the Brazilian market, energy conversion performance indicators and considering local carbon dioxide balance.

1. Introduction

The conversion of lingo cellulosic biomass into ethanol represent a sustainable way of converting fuel, whose chemical characteristics are suitable for large scale transportation and whose production deals with carbon neutral processes (Cardona-Alzate and Sanchez-Toro, 2006).
First generation ethanol (1G) is converted from sugar cane by biomass pre-treatment, fermentation of sugars and distillation of ethanol. The carbon converted into fuel for this process is quite low, being quite high the energy content of the vinasse output stream, and not efficient from an exergy point of view the burning of the correspondent amount of sugarcane bagasse leaving the pre-treatment step.
Second generation ethanol (2G) is converted through enzymatic hydrolysis of the sugarcane bagasse, followed by fermentation of sugars and ethanol distillation. An economic bottleneck for this technology is related to the use of expensive enzymes in the hydrolysis step (Albarelli et al., 2013).
The advantages in coupling 1^{st} and 2^{nd} generation ethanol conversion process have been highlighted in a thermo-economic model, reaching exergy efficiencies of about 40 %, depending on design specifications (Ensinas et al., 2013). These values are partially constrained by the energy outputs related to waste

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streams, such as vinasse. In addition, the valorisation of the lignin cake separated after the hydrolysis step into electricity through combustion is also representing a low valorisation of lignin carbon.
Catalytic hydrothermal gasification of high watered waste biomass has demonstrated to be a sustainable and high efficient way to convert synthetic natural gas (Luterbacher et al., 2008).
The present paper aims evaluating the energy conversion potential of the combined 1st and 2nd generation ethanol plant studied by Ensinas et al. (2013) when considering the co-production of synthetic natural gas from vinasse and lignin-rich residues through catalytic hydrothermal gasification.

2. Methodology

2.1 Mathematical programming for process/utility integration

The present paper deals with the energy integration of two different processes, for which the primary energy requirement has to be satisfied in terms of hot and cold utilities. The applied methodology consists in using flow-sheeting models to perform mass and energy balance of the process and a set of previously defined utilities, in order to solve mass and energy balance. The second step of the calculus aims to identify the optimal set of utilities in terms of type and unit size and follows the approach presented by Papoulias and Grossmann (1983), further developed by Maréchal and Kalitventzeff (1998). This problem is solved considering Mixed Integer Linear Programming (MILP) model, where the heat cascade acts as constraint and the objective function deals with the minimization of linearized total yearly costs of the plant.

2.2 Performance indicators

In order to compare different plant configuration and the performance of the combined ethanol/sng plant with respect to alternative technologies a set of energy, economic and environmental performance indicators are here considered.
The exergy efficiency and equivalent primary energy efficiency, as defined respectively in Eq(1)and Eq(2), are the main energy performance indicators here considered.

$$\eta = \frac{\Delta k^0_{SNG} \cdot \dot{m}^-_{SNG} + \Delta k^0_{Ethanol} \cdot \dot{m}^-_{Ethanol} + \dot{E}^-}{\Delta k^0_{SC} \cdot \dot{m}_{SC} + \Delta k^0_{leaves} \cdot \dot{m}_{leaves} + \dot{E}^+} \quad (1)$$

$$\varepsilon_{equivalent} = \frac{\mathrm{LHV_{SNG}} \cdot \dot{m}^-_{SNG} + LHV_{Ethanol} \cdot \dot{m}^-_{Ethanol} + \frac{\dot{E}^-}{\eta_{CC}}}{\Delta k^0_{SC} \cdot \dot{m}_{SC} + \Delta k^0_{leaves} \cdot \dot{m}_{leaves} + \frac{\dot{E}^+}{\eta_{CC}}} \quad (2)$$

An additional way to highlight the efficiency of the process is related to the carbon conversion efficiency, which is defined as in Eq (3), and considers the molar flow rates of carbon in biomass input and output material stream products.

$$C_{eff} = \frac{\widetilde{m}_{Carbon\ in\ SNG} + \widetilde{m}_{Carbon\ in\ ethanol}}{\widetilde{m}_{Carbon\ in\ sugar\ cane} + \widetilde{m}_{Carbon\ in\ leaves}} \quad (3)$$

The yearly total costs are calculated for the combined 1st and 2nd generation plant and for the hydrothermal gasification plant. The cost of utilities is also accounted, having solved the optimal utility integration problem. It is assumed an interest rate of 10 %, a life time of the plant of 25 y, with an operating factor that is, depending on biomass cultivation cycle, limited to 60 %.
In order to show the advantages related to environmental impact without performing a complete LCIA analysis, a local CO_2 balance is performed and the negative contributions related to fossil derived fuels substitution are reported. The amount of SNG produced acts as fossil natural gas alternative, the ethanol is considered as gasoline equivalent fuel, while for electricity the equivalent emission related to the Brazilian electricity mix is considered. The Ecoinvent database is used as source for the GWP of the considered flows.

$$Avoided\ Emissions = (eqCO_2)_{El\ mix} + (eqCO_2)_{Gasoline\ substitution} + (eqCO_2)_{Fossil\ NG\ substitution} \quad (4)$$

3. Process description

3.1 First and second generation ethanol plant: flow-sheeting model

The Aspen Plus flow sheeting model developed by Albarelli et al. (2013), and also presented by Ensinas et al. (2013), software is here considered to perform mass and energy balance of the combined 1st and 2nd generation ethanol; a simplified representation of the process is presented in Figure 1. For energy integration purposes it is important to highlight how this model considers the use of multi-effect evaporators for the concentration steps in both 1st and 2nd generation parts. This is frequently reported in literature as a good strategy to increase energy efficiency of ethanol plants (Dias et al., 2011). The fermentation and distillation/dehydration processes for 1st and 2nd generation are considered in unique reactors. The amount of sugarcane bagasse that is sent to 2nd generation, thus the amount of bagasse which is burnt in the cogeneration utility represents an important independent variable, since it affects the size of the 2nd generation plants and consequently the size of the bottoming hydrothermal gasification plant. Among independent variables, the more important one are presented in Table 1.

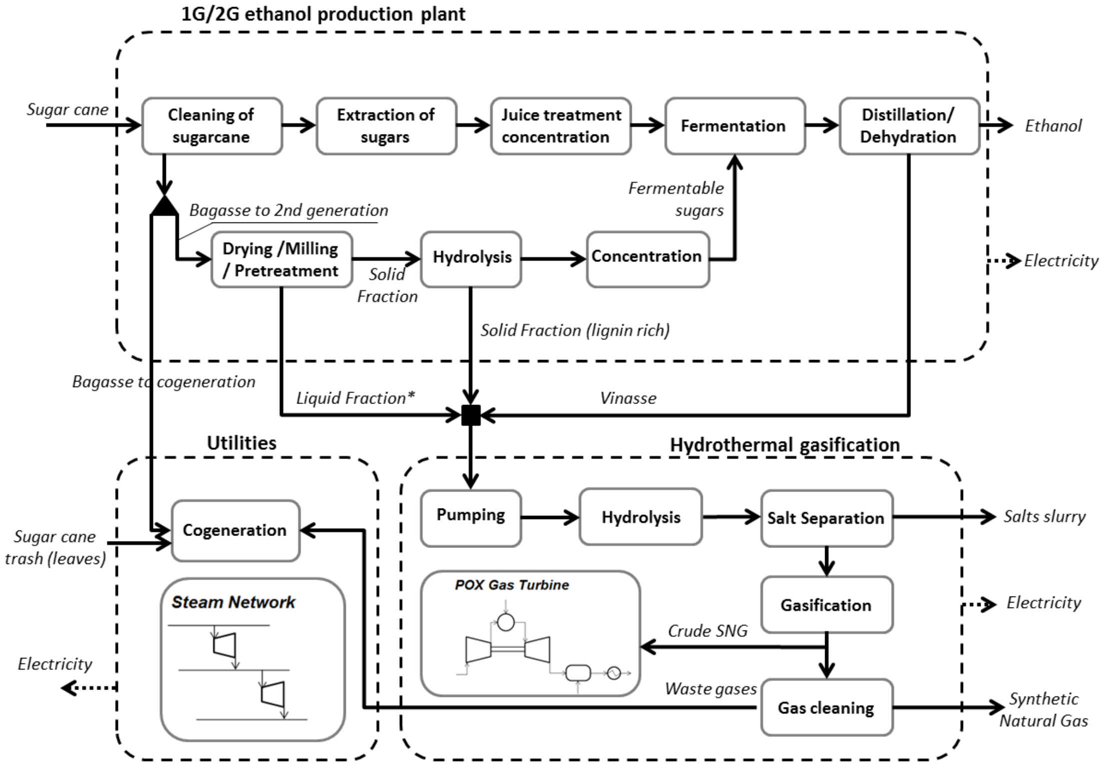

Figure 1: Flow sheet of the considered process, including the possible utilities (Steam Network, Burners, POX STIG GT)

Table 1: Key independent variables of the 1st and 2nd generation plant

Variable	Value	Unit
Input biomass	500	[tons of cane /h]
Sugarcane trash (leaves)	0.066	[tons leaves/tons cane]
Amount of bagasse to 2G	50	[%]
1G concentrated juice	65	[°Brix]
2G concentrated glucose liquor	20	[%]

3.2 Catalytic hydrothermal gasification: Flow sheeting model

A flow sheet developed in Belsim Vali is used to evaluate thermal and electrical energy requirements of the Catalytic Hydrothermal Gasification (HTG) process. A detailed description of the considered model has been published by Gassner (2011). The key independent variables of the process are related to operating pressure, which is set for this study at 300 bar, and the maximum temperature to be achieved in the salt separation step, which is highly affecting the utilities integration problem. Finally, Figure 1 shows the complete process flow-sheet, together with the options related to utility utilization.

4. Results

4.1 Energy Integration

The main results concerning the integration of 1st and 2nd ethanol production with the hydrothermal gasification plant and the utilities that were activated by the MILP model are presented in terms of exergy grand composite curves in Figure 2. Figure 2.a shows the integration which is achieved when sending 50 % of the bagasse to the cogeneration unit, while Figure 2.b depicts the energy integration results when only 20 % of bagasse is burned in the cogeneration plant. Being the size of the 2G ethanol plant and the HTG plant affected by this it is clear how the economic trade off needs to be more investigated, taking into account the economic aspect.

4.2 Sensitivity analysis

A sensitivity analysis is done considering different values of the amount of bagasse to second generation, together with different fuel prices. The considered MILP model is iteratively solved in order to depict energy and material flows, together with the variations of annual benefit. At this stage the investment cost of the overall plant is calculated using cost functions from literature (Ulrich, 2004). The results of the sensitivity analysis in terms of main energy and material flows are presented in Table 2. It is important to highlight that the water balance for the considered process is always positive, and is decreasing with the

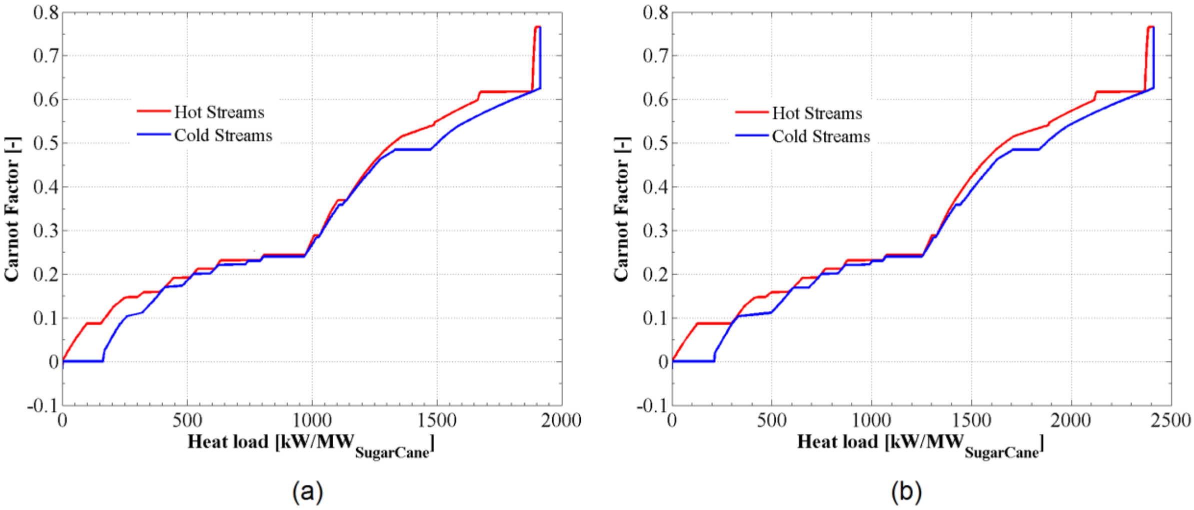

Figure 2: Exergy Composite Curves for the considered plant: 50 % (a) vs 80 % bagasse to 2G plant

Table 2: Main performance indicators after sensitivity analysis

Name	Values							Unit
Bagasse sent to 2G	50 %	55 %	60 %	65 %	70 %	75 %	80 %	
Equivalent energy efficiency: ε	0.57	0.57	0.58	0.59	0.61	0.62	0.64	[-]
Second Law efficiency: η	0.43	0.43	0.44	0.46	0.47	0.48	0.49	[-]
Carbon conversion: ethanol	0.244	0.247	0.249	0.252	0.254	0.257	0.259	[-]
Carbon conversion: (HTG)	0.453	0.457	0.461	0.464	0.467	0.470	0.472	[-]
Carbon efficiency global plant	0.344	0.356	0.367	0.379	0.391	0.402	0.414	[-]
Sugar cane input power	790.97	790.97	790.97	790.97	790.97	790.97	790.97	[MW]
Generated Synthetic NG	116.52	127.09	137.66	148.23	158.80	169.37	179.94	[MW]
Generated Ethanol	287.30	290.27	293.24	296.20	299.16	302.13	305.10	[MW]
Total electricity generated	28.36	22.28	20.79	21.37	21.95	22.52	23.10	[MW]
Water input ethanol	256.09	275.77	295.45	315.13	334.81	354.50	374.18	[kg/s]
Water recycled in HTG without accounting water in salt slurry	145.15	152.68	160.22	167.76	175.30	182.83	190.37	[kg/s]
Water recovered in salt slurry	13.08	13.77	14.47	15.16	15.86	16.56	17.25	[kg/s]
Water recovery from 1G and 2G evaporators	146.83	155.76	164.69	173.62	182.55	191.48	200.41	[kg/s]
Total recycled water	1.19	1.17	1.15	1.13	1.12	1.10	1.09	[-]

increase of the amount of bagasse sent to 2G. This is due to the increase of water demand of 2nd generation ethanol plant with respect of the 1st generation plant. The other important aspect related to the use of HTG is related to the advantage of separating salts and nutrients at high concentrations. Being the salt concentration close to 30 % the related transportation expenses can be quite reduced with respect to the actual nutrients transportation options.

In order to investigate the economics, thus the plant feasibility, the breakeven costs of electricity and synthetic natural gas that will make this technology profitable are calculated considering different prices of ethanol, as depicted in Figure 3. It is here shown how the exportation of ethanol towards markets where the ethanol price can be higher could make the technology feasible and profitable, even with big 2G ethanol and HTG plant size.

The avoided emission contributions of the energy flows leaving the system are depicted in Figure 4, where the main contributions are represented by the substitution of fossil natural gas and the gasoline substitution related to ethanol production. Being the electricity produced one order of magnitude lower with respect to SNG and ethanol, and being the Brazilian electricity rich in hydro power plants, the contribution related to electricity substitution are much smaller.

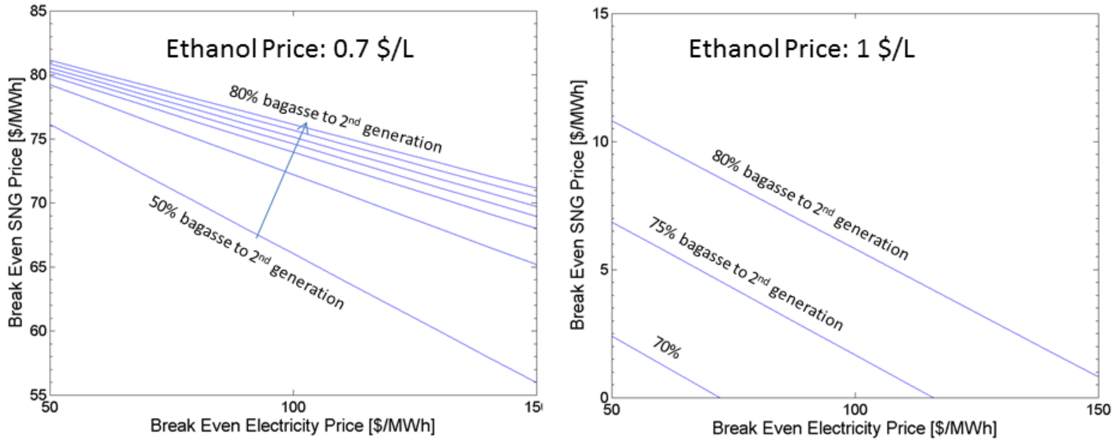

Figure 3: Break even prices of produced electricity and SNG for a given ethanol price and for different plant configurations varying the amount of bagasse which is sent to 2nd generation ethanol plant

5. Conclusions

The present study has shown the conversion potential of a combined 1st and 2nd generation ethanol plant with a catalytic hydrothermal gasification plant. The integration of the two processes, together with the optimal utilities integration, has been calculated by using a mixed integer linear programming model, where energy integration principles act as constraints. The integration results have been analysed with respect to energy, economic and environmental performance indicators, and for different plant configurations, related to the amount of bagasse that is valorised by increasing the biofuel conversion. The advantages of integrating hydrothermal gasification for waste streams treatment have been identified in terms of salt and nutrients concentration and increase of biofuel conversion. The recycling of water has also been taken into account, showing how the total balance is always positive in terms of water utilization. A sensitivity analysis has been considered in order to investigate the impact of the plant configuration, in terms of amount of bagasse valorised through 2nd generation ethanol plant and hydrothermal gasification plant, on energy, economic and environmental performance indicators. It has been shown that the higher the amount of bagasse sent to second generation, the higher the biomass to biofuel conversion potential, as well as the water and nutrients recycling. In opposition to these aspects, capital expenses are increasing with the amount of bagasse sent to 2nd generation ethanol, and as a consequence breakeven prices of the products. With respect to the size of the hydrothermal gasification plant, it has to be noted that additional investigations related to pre-treatment and concentration of solids in at the gasification plant input need to be performed. The trade-off between an expensive pre-treatment unit, where electricity has to be spent to increase the solid content of the feedstock, and the related reduction of gasification plant size could lead to configuration with reduced total costs, and thus higher profitability of the technology.

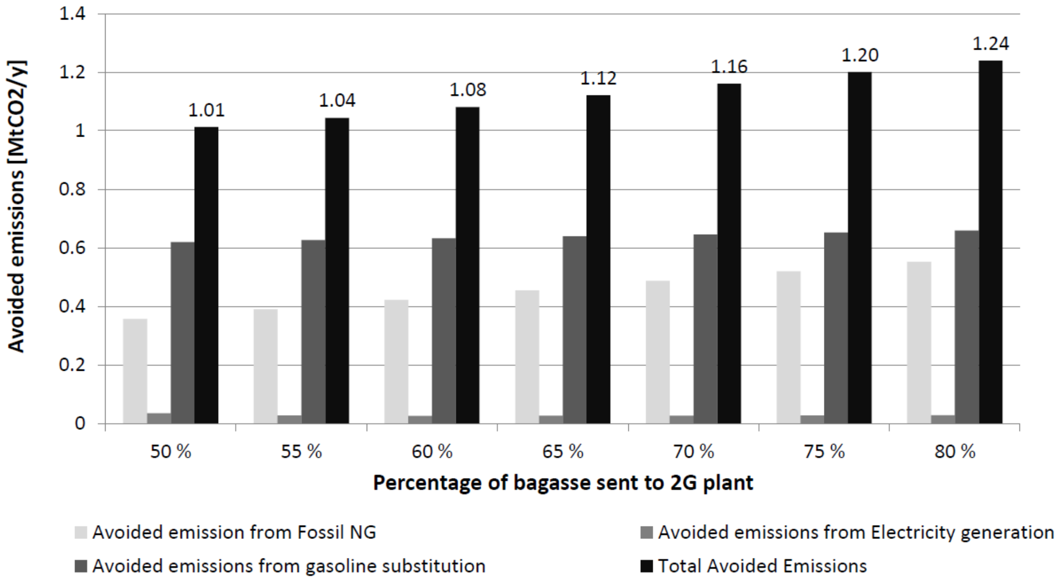

Figure 4: Avoided emissions contributions for different amounts of bagasse sent to 2^{nd} generation

In the economic context it also has been shown how exportation of ethanol at higher price in external markets can play an important role when considering plant economic feasibility. Finally, the advantages of the integration have been reported in terms of avoided carbon dioxide emissions, which are growing with the growing size of 2^{nd} generation ethanol plant and the bottoming hydrothermal gasification plant as well.

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