# Energy assessment of biofuels production from fast pyrolysis of sugarcane straw, and upgrading of the bio-oil produced through hydrotreatment

# Bruna Stella De Freitas Santos<sup>ª</sup>, Milagros Cecilia Palacios-Bereche<sup>c</sup>, Antonio Garrido Gallego<sup>d</sup>, Silvia Azucena Nebra<sup>e</sup> and Reynaldo Palacios-Bereche<sup>f</sup>

 <sup>a</sup> Federal University of ABC, Santo Andre, Brazil, bruna.stella@ufabc.edu.br
 <sup>c</sup> Energy Engineering Modeling and Simulation Laboratory, Federal University of ABC, Santo Andre, Brazil, milagros.palacios@ufabc.edu.br
 <sup>d</sup> Federal University of ABC, Santo Andre, Brazil, a.gallego@ufabc.edu.br
 <sup>e</sup> Federal University of ABC, Santo Andre, Brazil, silvia.nebra@ufabc.edu.br
 <sup>f</sup> Federal University of ABC, Santo Andre, Brazil, reynaldo.palacios@ufabc.edu.br

#### Abstract:

Second-generation biofuels are produced from non-food biomass such as the lignocellulosic residues of sugarcane processing, namely, bagasse and straw. Sugarcane processing is one of the most important economic activities in Brazil, producing ethanol and sugar for domestic and international markets. The use of these lignocellulosic residues would increase the second-generation biofuel production without increasing the sugarcane planted area. Among the second-generation technologies available nowadays, the fast pyrolysis is a thermochemical process that produces mainly bio-oil, which is a liquid that has several advantages in transportation, pumping, storage and handling, in comparison to solid biomass. Moreover, the bio-oil can be upgraded in order to obtain biofuels of higher added-value. Among feasible upgrading technologies for bio-oil, the hydrotreatment is one of the most promising for eliminating the reactive functionalities of the bio-oil by removing oxygen or cracking large molecules in the presence of hydrogen; however, the hydrogen consumption is significant. In this way, the aim of this study is to evaluate the biofuel production by means of fast pyrolysis of sugarcane straw, followed by a hydrotreatment to upgrade the produced bio-oil. The evaluation is performed through an energy assessment. The energy and mass balances of the processes were performed using the software Aspen Plus. Furthermore, the possibilities of the integration of the bio-oil production and upgrading into the conventional ethanol and sugar production process will also be evaluated. The final products of bio-oil upgrading plant showed a yield of 0.086 kg/kg of dry straw and 0.080 kg/kg of dry straw for renewable gasoline and diesel respectively. The heat integration of pyrolysis process, hydrotreating and hydrogen production process presented a significant potential for steam production. This could be integrated into the conventional sugar and ethanol production process, which could save 28.6% of steam and increase the surplus electricity in 6%.

### Keywords:

Sugarcane; fast pyrolysis; bio-oil; hydrotreatment; energy analysis.

# 1. Introduction

The production of biofuels from lignocellulosic residues of sugarcane (bagasse and straw) is presented as a desirable alternative since it would increase the biofuel production without the need to increase the area planted with sugarcane. Thus, these biofuels diversify the Brazilian energy matrix and contribute to the reduction of greenhouse gases (GHG) emissions. In this context, the introduction of the fast pyrolysis of lignocellulosic residues into the conventional sugarcane process plant for bio-oil production, aiming at its further processing, can improve the productivity and sustainability indexes of the integrated process. Pyrolysis is the physico-chemical process of thermal degradation of a material in a non-oxidizing atmosphere, resulting in the formation of a solid residue rich in carbon (charcoal or char) and a volatile fraction composed of condensable organic gases and vapours. The proportions of these products depend on the pyrolysis conditions and the characteristics of the feedstock. Fast pyrolysis is characterised by low residence times in the reactor, high heating rate at moderate temperatures (400 to 600°C). The formation of

bio-oil is prioritised, as it can be used as fuel for boilers or serve as raw material for the production of vehicles fuels. In the literature, some studies have already regarded the fast pyrolysis of lignocellulosic biomass, such as the study of Mesa-Perez et al.[1], where the oxidative fast pyrolysis of sugarcane straw in a fluidised bed reactor was analysed. In addition, Ferreira et al. [2] carried out a study to evaluate the influence of some parameters on the oxidative pyrolysis of sugarcane straw, while Alves et al. [3] experimentally evaluated and compared the fast pyrolysis of sugarcane straw and eucalyptus bark in a fluidised bed reactor at 500°C. Still, raw bio-oil is not suitable as fuel for the transport sector because of some undesirable characteristics such as low energy content, corrosiveness, high viscosity, incomplete volatility and chemical instability. These unfavourable properties are consequences of the high water content and oxygenated compounds [4]. Thus, the bio-oil requires upgrading and fine-tuning in order to achieve product specifications commensurate with existing transportation infrastructures. The upgrading methods aim at stabilising the crude bio-oil by removing its oxygen content and reducing its viscosity, ageing potential, and solid content [5]. Among the different available methods, the hydrodeoxygenation (HDO), also known as hydrogenation or simply hydrotreatment, is the main technology for upgrading pyrolysis oils due to its effectiveness. It was originally inspired by the hydrodesulphurisation (HDS) and hydrodenitrogenation (HDN) used in petroleum refineries. A catalytic reaction of crude bio-oil with hydrogen can significantly reduce the oxygenated compounds through the formation of water. The involved reactions in this process include hydrogenation, hydrodeoxygenation, decarboxylation, hydrogenolysis, hydrocracking, and dehydration. The optimal combination of these reactions requires significantly higher pressures (> 20 MPa) and moderate temperatures (around 400°C) [5]. HDO yields high quality hydrocarbon products for gasoline and diesel substitution, but requires important amounts of hydrogen at high pressure, which affects costs and energy balances. Process conditions and catalyst type have to be carefully adjusted in order to minimise hydrogen consumption and to achieve the desired product [6]. According to Sharifzadeh et al. [5], it is recommended to first stabilise the bio-oil through hydrogenation at a lower temperature, followed by more intense HDO at higher temperatures. Some studies regarding bio-oil upgrading can be found in the literature, for instance, Jones et al. [7] presented a report about process design and economic assessment for fast pyrolysis of woody biomass and bio-oil hydrotreating; in Zacher et al. [8], a study regarding technology advancements in hydroprocessing of bio-oils was accomplished, while Peters [6] evaluated the fast pyrolysis, including the bio-oil upgrading, for the production of second-generation biofuels from thermodynamic, environmental, and economic approaches.

Thus, the present study aims at evaluating the biofuel production by means of fast pyrolysis of sugarcane straw, followed by its upgrading through hydrotreatment. The evaluation being performed through an energy assessment. The energy and mass balances of the processes were performed using the software Aspen Plus v12 [9]. Furthermore, the possibilities of integrating the bio-oil production and upgrading into the conventional ethanol and sugar production process will also be evaluated through the Pinch Analysis.

# 2. Biofuels production from fast pyrolysis of sugarcane straw

### 2.1. Fast pyrolysis of sugarcane straw

This section presents the main characteristics of the fast pyrolysis plant assumed in this study, whose flowchart is shown in Figure 1. This plant, receiving sugarcane straw as raw material, is comprised of the following components: reactor (1), cyclone (2), quench (3), condensers (4), heat exchanger (5), compressors (6), coal and synthesis gas combustor (7), heat recovery steam generator (HRSG) (8), fluidising gas preheater (9), and biomass dryer (10). In this configuration, the pyrolysis process is characterised as autothermal [10], burning the char and syngas to supply energy to the pyrolysis reactor. Furthermore, it is possible to produce steam in the HRSG (8), which is used in a Rankine cycle to produce electricity for the process. The bio-oil produced in this plant is then sent to the upgrading plant.



Figure. 1. Fast pyrolysis process diagram [10]

#### 2.2. Bio-oil upgrading through hydrotreatment

The bio-oil upgrading plant was divided into three subsystems: hydrotreatment, distillation and hydrocracking, and hydrogen production. Figure 2 presents the flowsheet of the hydrotreatment section.

### 2.1. Hydrotreating section

The bio-oil supplied by the pyrolysis plant is pressurised in pump B1 and preheated in the heat exchanger HE1; after that, it is mixed with pressurised hydrogen in M1. The mixture is preheated in the heat exchanger HE2 before entering the first hydrotreating reactor HT-R1, whose operating conditions were assumed at 170 bar and  $250^{\circ}$ C, according to Peters [6]. This reactor aims at stabilising the bio-oil sufficiently to be suited for a more severe treatment in the second reactor. The product of HT-R1 is heated till 370°C and decompressed to 140 bar before entering the second hydrotreating reactor HT-R2. The operating conditions in HT-R2 were assumed at 370°C and 140 bar [6]. The aim of this second reactor is to deeply deoxygenate and stabilise the bio-oil up to an oxygen content of <2% [11],[12]. Both reactors HT-R1 and HT-R2 were assumed to operate with a standard Co-Mo catalyst, according to [6].

The product of HT-R2 is cooled to 137.4°C, in the heat exchanger COOL-1, before entering the flash tank, which operates at 35 bar, where the organic vapours (HTORGANI) are separated from the aqueous liquid phase (HTAQUEOU). The organic vapours are sent to the following subsystem (Distillation and Hydrocracking), while the aqueous stream enters the hydrogen production subsystem.



Figure. 2. Flowsheet of bio-oil hydrotreatment in Aspen Plus

# 2.2. Distillation and hydrocracking

Figure 3 presents the flowsheet of the Distillation and Hydrocracking subsystem. It can be observed that the products of the hydrotreatment step (stream HTORGANI) and the hydrocracking reactor (HC-CRD2) are mixed before being sent to a flash tank (FLASH-2) operating at 20 bar. The liquid phase is preheated in the heat exchanger HE4 and fed to the first distillation column (C-DIST1), while the gaseous phase, containing a significant amount of unreacted hydrogen, is sent to a PSA (Pressure Swing Adsorption) system for hydrogen recovery and recycling. This configuration was assumed according to Zacher et al. [8] and Jones et al. [7]. In this study, it was assumed that a part of the tail gas from the PSA system (OF-GS) is used as fuel in the utility system while the remaining is integrated into the hydrogen production system. In the first distillation column (C-DIST1), renewable gasoline is obtained at the top, while the bottom product is sent to the second distillation column (C-DIST-2). Moreover, in the top of C-DIST1, distillation gases (DISTGAS) are also obtained, which are used as fuel in the utility system.

In the second distillation column (C-DIST2), renewable diesel (stream DIESL-1) is obtained at the top, while the heavier product at the bottom is mixed with preheated hydrogen and sent to the hydrocracking reactor (HC-REACT). In the hydrocracking (HC) reactor, under severe conditions (677°C, 170 bar) and a hydrogen atmosphere, the heavy tar fraction is catalytically split up into smaller chain components, producing hydrocarbons in the range of C1-C18 [6].



Figure. 3. Flowsheet of the distillation and hydrocracking processes in Aspen Plus

### 2.3. Hydrogen production

Figure 4 presents the flowsheet of the hydrogen production section. This study considered the steam reforming of desulphurised biogas (DS-BIOG1), produced from the anaerobic digestion of vinasse, in combination with external natural gas acquired from the grid (SRCH4EXT). The components removed together with some hydrogen lost in the PSA system are obtained as tail gas. Part of this tail gas (stream FLSHGAS2) is used as fuel to meet the energy requirements of the hydrotreatment and distillation sections, while the remaining (FLSHGAS3) is sent to hydrogen production. One part of the FLSHGAS3 stream is compressed till 50 bar and sent to the reform reactor, while the other part is used as fuel in a combustor (COMB), whose exhaust gases are used as hot utility to meet the heat requirements of the reformer. Furthermore, the aqueous liquid stream (HTAQUEOU) obtained in the hydrotreatment section is also sent to the hydrogen production system; where it is mixed with part of the condensate recovered (SRH2O-IN stream) in FLASH-3. Afterwards, the liquid mixture is pumped and heated in HE7 and sent to the reforming reactor (SR-REACT). Biogas and natural gas are sent to the reforming reactor as well. The feed of the reforming reactor is preheated in the heat exchanger HE8 till 500°C, the product of which is then cooled to 310°C and sent to the WGS (Water-Gas-Shift) reactor, which operates at 350°C and 48 bar. The product of the WGS reactor is then cooled to 77°C before entering the FLASH-3, which operates at 46 bar. The gaseous product of FLASH-3 is sent to the second PSA system (PSA-II) in order to separate the hydrogen from the other gases. The tail-gas from the PSA-II system (OFFGS stream), the gaseous product of the distillation column (DISTGAS stream), and part of the tail gas from the PSA-I system (remaining part of FLSHGAS3) are preheated with combustion air in HE11 before entering to the combustor COMB to be burnt.



Figure. 4. Flowsheet of the hydrogen production process

# 3. Methods

#### 3.1. Fast pyrolysis plant

The simulation of the fast pyrolysis plant using sugarcane straw as feedstock was performed in the Aspen Plus software, according to [10]. The Peng-Robinson equation of state with Boston-Mathias modification (PR-BM) was selected as the preferred method for properties calculation in the reactor and combustor system, while the NRTL method was selected in the separation system. A straw availability of 160 kg of dry matter per tonne of cane stalks [13] in the field was considered, the pyrolysis plant processing 50% of this total potential. The kinetic model developed by [14] was applied in this study. Table 1 presents the main parameters assumed in the simulation.

Table 1. Main parameters of sugarcane straw pyrolysis

Parameter	Value
Sugarcane straw, as received (15% moisture content), t/h	47.1
Sugarcane straw, dried (5% moisture content), t/h	42.1
Pyrolysis reactor temperature, °C	475
Pyrolysis reactor pressure, bar	1.5
Residence time, s	20
Fluidising gas and biomass ratio, (mass/mass)	0.5
Outlet temperature in first condenser, °C	75
Outlet temperature in second condenser, °C	25

# 3.2. Bio-oil upgrading plant

The bio-oil upgrading plant was simulated in the Aspen Plus software, according to the procedure presented in [6]. The composition of the bio-oil obtained in the fast pyrolysis simulation was adjusted in order to take into account the same components considered by Peters [6]; in addition, the Pen-Robinson with Boston-Mathias modification (PR-BM) method was selected [15], [16].

#### 3.2.1. Hydrotreating section

In the hydrotreating section, the crude bio-oil from the pyrolysis process is upgraded in a two-stage catalytic hydrotreatment to almost oxygen-free hydrocarbon. Seeing as hydrotreating reactors were modelled as RYield blocks in the Aspen Plus software, the composition of reactor products were a necessary input. Since

there is not detailed information regarding the composition of hydrotreating reactors products from sugarcane straw, the composition presented by [6], who evaluated hybrid poplar wood chips, was taken as a reference. These values are based on a typical bio-oil hydrotreatment with Co-Mo catalyst, based on the literature [11]. In this way, taking into account these data and the specific bio-oil composition obtained in the pyrolysis simulation, a mass balance procedure was performed in MS Excel for each element present in the bio-oil, using proportionality factors, aiming at following a similar product distribution.

Table 2 presents the main parameters assumed in the modelling of the Hydrotreating section.

Parameter	Value			
Outlet pressure – pump B1, bar	170			
Outlet pressure – compressor COMP-1, bar	170			
Number of stages – compressor COMP-1	2			
Outlet temperature – HE1, °C	100			
Outlet temperature – HE2, °C	250			
Operating pressure – hydrotreating reactor HT-R1, bar	170			
Operating temperature – hydrotreating reactor HT-R1, °C	250			
Outlet temperature – HE3, °C	370			
Operating pressure – hydrotreating reactor HT-R2, bar	140			
Operating temperature – hydrotreating reactor HT-R2, °C	370			
Outlet temperature – COOL-1, °C	35			
Operating pressure – FLASH-1, bar	35			
Heat duty – FLASH-1, kW	0			
Hydrogen consumption in hydrotreating section, kg H <sub>2</sub> /kg bio-oil	0.09			

Table 2.	Main parameters	in the	Hydrotreating	section
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#### 3.2.2. Distillation and Hydrocracking section

Distillation columns were modelled as RadFrac blocks in the Aspen Plus software, while a stoichiometric block represented the hydrocracking reactor, and the reactions assumed thereof were adopted from [6]. In Table 3, the main parameters assumed in this stage for the modelling in the Aspen Plus software are presented.

Parameter	Value
Operating pressure in FLASH-2, bar	20
Outlet temperature in HE4, °C	212
Number of stages in C-DIST1	8
Reflux ratio (mass basis) in C-DIST1	1.2
Distillate to feed ratio (mass basis) in C-DIST1	0.48
Operating pressure in C-DIST1 (stage 1), bar	2.5
Condenser temperature <sup>(a)</sup> , C-DIST1, °C	32
Number of stages in C-DIST2	7
Reflux ratio (mass basis) in C-DIST2	1.2
Distillate to feed ratio (mass basis) in C-DIST2	0.85
Operating pressure in C-DIST2 (stage 1), bar	0.01
Outlet pressure in pump B2, bar	90
Operating temperature in the hydrocracking reactor, °C	430
Operating pressure in the hydrocracking reactor, bar	90
Outlet pressure in valve V3, bar	36
Outlet temperature in HE6, °C	32
Hydrogen consumption in the hydrocracking section, kg $H_2$ /kg bio-oil	0.0032
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Table 3. Main parameters for distillation and hydrocracking

<sup>(a)</sup>C-DIST1 was assumed with a partial condenser, while in C-DIST2 there is a total condenser

# 3.3. Hydrogen production plant

The PSA systems (PSA I and II) were modelled as separators. Regarding the steam reforming assumed in this simulation, the reforming reactor considered a conventional nickel catalyst, as it is widely used in this type of reactors, and was modelled as a RGibbs reactor type in the Aspen Plus software, while a REquil type reactor was used in the modelling of the WGS reactor. The reactions within the WGS reactor were limited to the WGS reaction  $(H_2O+CO<-->CO_2+H_2)$ , according to [6]. The temperature approach in the WGS reactor was adjusted in order to achieve a CO conversion in the range of 75%. The combustor COMB was modelled as a RGibbs reactor type as well. The mass flow of combustion air (AIR stream) was adjusted to achieve a temperature of 1500°C at the outlet of COMB, while the split fraction of stream SR2O-IN in the bifurcation BIF2, which determines the amount of liquid condensate recycled to the reforming reactor, was adjusted to achieve a Steam to Carbon ratio (S/C) of 4.5 (mol basis). The split fraction of the FLSHGAS stream specified in the bifurcation 1 (BIF1), which determines the mass flow of FLSHGAS destined for the reforming reactor, was determined from the energy balance. Thus, it was adjusted aiming at calculating the heat duty in HE12 to meet the required heat duty in SR-REACT, maintaining a  $\Delta T_{min}$  of 30°C. Table 4 presents the main parameters assumed in the simulation of the hydrogen production plant. The composition of the desulphurised biogas was assumed as 35.4% CO<sub>2</sub> and 64.4% CH<sub>4</sub> (molar basis) [17], while the composition of the external natural gas was assumed as 3.5% CO2 and 96.5% CH4 (molar basis).

Parameter	Value
Outlet pressure, valve V4, bar	2.3
Outlet pressure, compressor COMP-3, bar	50
Outlet pressure, pump B8, bar	50
Outlet temperature, HE7, °C	259.9
Outlet temperature, HE8, °C	500
Operating pressure, SR-REACT, bar	49
Operating temperature, SR-REACT, °C	950
Outlet temperature, HE9, °C	310
Operating temperature, WGS reactor, °C	350
Operating pressure, WGS reactor, bar	48
Outlet temperature, HE10, °C	77
Operating pressure FLASH-3, bar	46
H <sub>2</sub> recovery in PSA system, %	90
Outlet pressure, compressors COMP-4 and COMP-5, bar	2.2
Outlet temperature, HE11, °C	300
Operating pressure, COMB, bar	1.01325
Heat duty, COMB, kW	0

Table 4	Main	parameters	for	the h	vdrogen	production	plant
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#### 3.4. Integration into the conventional ethanol and sugar production process

The heat integration was accomplished according to the Pinch method [18], performing the following steps: data extraction from the evaluated processes, composite curves construction, evaluation of steam generation, and integration of the cogeneration system, which meets the heat and power demands of the processes.

# 4. Results

#### 4.1. Bio-oil composition

Figure 5 shows the main components of bio-oil produced in the fast pyrolysis of sugarcane straw. The amount of sugar derived, which includes levoglucosan, hydroxyimethylfurfural, xilan and intermediate compounds derived from cellulose and hemicellulose represents almost 50% of the amount of bio-oil. This can be explained because the assumed kinetic model for fast pyrolysis only assumed primary reactions. In second place, the water content reaches 17.8%, followed by the aldehydes with 15.5%, which include

acetaldehyde, glyceraldehyde, formaldehyde, glyoxal, furfural, and acrolein. This composition presents a slightly divergence from the experimental data presented by [6] for bio-oil obtained from fast pyrolysis of pine wood, which contains sugar derived 33%, water 24%, and aldehydes and ketones 21%. Nevertheless, further research is needed in order to try taking into account secondary reactions.



Figure. 5. Main compounds in bio-oil produced from fast pyrolysis

# 4.2 Bio-oil upgrading plant

This section presents the results of the bio-oil upgrading plant simulation. Table 5 presents the main results of this analysis.

Parameter	Value
Hydrotreatment	
Bio-oil production in fast pyrolysis plant <sup>a</sup> , t/h	21.1
Hydrogen consumption in hydrotreatment, t/h	1.8
Water content at the outlet of HT1 reactor (mass basis), %	36.3
Water content at the outlet of HT2 reactor (mass basis), %	49.4
Organic phase stream (HTORGANIC) at the vapour outlet of FALSH-1, t/h	11.49
Water content in HTORGANIC stream (mass basis), %	0.1
Aqueous phase stream (HTAQUEOUS) at the liquid outlet of FLASH-1, t/h	11.43
Water content in HTAQUEOUS (mass basis), %	99.05
Power consumption in hydrotreatment section, kW	3,310.9
Distillation and hydrocracking	
Vapour product of FLASH-2 (FLSHGAS stream), t/h	5.11
Hydrogen content in FLSHGAS stream (mass basis), %	22.37
Hydrogen recovery in H2-RECY stream⁵, t/h	0.97
Hydrogen consumption in Hydrocracking, t/h	0.28
Renewable gasoline (GSLN-1 stream) <sup>d</sup> , t/h	3.45
Renewable diesel (DISEL-1 stream) <sup>e</sup> , t/h	3.2
Power consumption in distillation and hydrocracking section, kW	125.4

Table 5. Main results of the hydrotreatment, and distillation and hydrocracking sections

<sup>®</sup>17.8% of moisture content; <sup>▷</sup>85% of H₂ recovery in PSA system; <sup>°</sup>LHV at 15°C 34.4 MJ/kg; <sup>®</sup>LHV at 15°C 44.3MJ/kg; <sup>®</sup>LHV at 15°C 33.5MJ/kg

It can be observed, in Table 5, that the power consumption in the Hydrotreatment section resulted significantly higher in comparison to the Distillation and Hydrocracking section, because of the high power consumption in the hydrogen compressor COMP-1 (3.18 MW). The final products of the bio-oil upgrading plant showed a yield of 0.086 and 0.080 kg/kg of dry straw for renewable gasoline and diesel, respectively. The reboiler temperatures of columns C-DIST1 and C-DIST2 resulted 283.3°C and 254.6°C, respectively, these operating conditions being important for evaluating the heat requirements and heat integration opportunities. Regarding the hydrogen production, section Table 6 presents the main results.

Parameter	Value
External consumption of natural gas, (or biomethane) <sup>a,b</sup> , kg/h	1232.7
Desulphurised biogas consumption <sup>c.d,e</sup> , kg/h	2325.1
Water consumption in reforming process, t/h	18.1
Recirculation rate of SRH2OIN stream <sup>†</sup> , %	55.9
Condensate sent to waste water treatment system (SRLIQOUT stream), t/h	5.4
Fraction of FLSHGAS3 stream sent to reforming reactor <sup>g</sup> , %	28.6
Hydrogen production in PSA-II system, t/h	1.1
Fuels used in combustor COMB	
Dff-gas from PSA-I system <sup>h,i</sup> , t/h	2.8
Dff-gas from PSA-II system <sup>i</sup> , t/h	9.6
Gas from distillation (DISTGAS stream) <sup>k</sup> , t/h	0.024
Power consumption in hydrogen production process, kW	2,884.7

Table 6.	Main	results	of the	hydrogen	production	process
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<sup>a</sup>96.5% of CH<sub>4</sub> (mol basis); <sup>b</sup>equivalent to 72.4 kmol/h; <sup>c</sup>produced from anaerobic digestion of vinasse; <sup>d</sup>64.4% of CH<sub>4</sub> (mol basis); <sup>e</sup>equivalent to 89.46 kmol/h; <sup>f</sup>split fraction of condensate recycled to reforming process specified in bifurcation BIF2; <sup>g</sup>split fraction of FLSHGAS specified in bifurcation BIF1; <sup>h</sup>Fraction of FLSHGAS3 stream; <sup>i</sup>LHV at 15°C of 34.4MJ/kg; <sup>j</sup>LHV at 15°C, 3.84 MJ/kg; <sup>k</sup>LHV at 15°C, 32.9MJ/kg

#### 4.3 Heat integration results

Stream data adopted for heat integration is presented in Tables A1 and A2 of Appendix A, for the Hydrotreatment coupled with Distillation and Hydrocracking processes, and the hydrogen production process. Simulation results showed that the hydrotreating and the hydrocracking reactors are exothermic. In order to make use of this thermal energy, it was assumed that heat released from exothermic reactors is used to heat thermal oil that can be used as hot utility. Thus, these streams of thermal oil were taking into account for Composite Curves (CCs) and Grand Composite Curves (GCCs) construction. Because of the large amount of gaseous streams in the processes, the contribution to the  $\Delta T_{min}$  was assumed to be 15°C for almost all streams. Process streams with phase change were divided into ranges in order to properly consider the available heat at different temperature levels. Figure 6a presents the GCC for the Hydrotreatment coupled with Distillation and Hydrocracking processes, while the GCC for the hydrogen production process is presented in Figure 6b.

According to Fig. 6a, the target of minimum hot utility consumption above the Pinch resulted in 1328.34 kW, thus, combustion gases with an adiabatic flame temperature of 1500°C were assumed as hot utility to meet this energy requirement using part of FLASHGAS as fuel. Considering that combustion gases are cooled till the Pinch temperature of 320°C, the fuel consumption resulted in 0.0486 kg/s (0.18 t/h) (mass flow of FLSHGAS2 stream in Fig.4).

On the other hand, both GCCs present available heat below the Pinch temperature that can be used to produce steam for the ethanol and sugar production process. The red lines in Figures 6a and 6b show these potentials. Since in Fig. 6a there is heat available at lower temperatures (below to 300°C), in comparison to Fig. 6b, the production of saturated steam at 2.5 bar (127.4°C) from available heat of hydrotreating and hydrocracking sections was assumed. On the other hand, the production of superheated steam at 500°C and 65 bar was assumed in Fig. 6b (represented by the red line). The steam mass flow resulted in 17.1 t/h and 20.9 t/h in Figures 6a and 6b, respectively. Moreover, from the superheated steam obtained in Fig. 6b, there is a power production potential of 3655 kW, using a back-pressure steam turbine. Thus, the exhaust steam from the turbine can be used to meet heat demands in the sugar and ethanol production process.



**Figure. 6.** Grand Composite Curves (GCC) for (a) the Hydrotreatment with Distillation and Hydrocracking processes, and (b) the hydrogen production process

Finally, Table 7 presents the impacts on the cogeneration system; detailed impacts regarding pyrolysis plant integration can be found in [19].

Description	Base Case	Integrated process
Steam consumption in cogeneration system, t/h	214.8	153.4
Steam produced in pyrolysis process, t/h	0	23.4
Steam produced in upgrading plant, t/h	0	38.0
Power consumption in pyrolysis process, kW	0	3,448.3
Power consumption in upgrading plant, kW	0	6,321.0
Power production in pyrolysis process, kW	0	2279
Power production in H <sub>2</sub> production process, kW	0	3655
Surplus electricity, kW	40,600.0	43,060.7

Table 7. Impacts on the cogeneration system

# 5. Conclusions

The modelling and simulation of a bio-oil upgrading plant was performed in this study; moreover, the integration of an upgrading plant into the sugar and ethanol production process was evaluated including the impacts on the cogeneration system. Bio-oil upgrading through hydrotreatment requires high amounts of hydrogen (4.16 kg of  $H_2/t$  cane for 50% of straw recovery from the field), and in this initial assessment, the steam reforming was assumed for  $H_2$  production, taking the biogas produced from the anaerobic digestion of vinasse as feedstock. Nevertheless, from the hypotheses assumed (availability of vinasse in a plant that uses 50% of recoverable sugars in ethanol production), an additional methane source was necessary to complete the required  $H_2$  production (2.47 kg/t cane of biomethane 96.5% mol). Regarding the energy assessment, the pyrolysis process, as well as the hydrotreating and hydrogen production process, presented a significant potential for steam production (28.6% of total steam consumption in the conventional mill), that can be integrated into the conventional sugar and ethanol production process. This could allow the reduction of process steam extraction in the cogeneration system of the conventional plant that operates with sugarcane bagasse as fuel. Thus, the electric energy production in the cycle that operates with condensing-extraction steam turbines would increase. After the power balance, it is possible to achieve a 6% increase in surplus electricity.

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# Appendix A

 Table A1. Stream data for heat integration of the Hydrotreatment and Distillation and Hydrocracking processes

Stream Name	Supply Temp. (°C)	Target Temp. (°C)	dT Min Contrib (°C)	Heat Duty (kW)
Bio-oil preheating – (HE1)	18.8	100		1202.9
Feed stream reactor HT-R1 – (HE2)	93.9	250	15	5094.9
Thermal oil – Reactor HT-R1	210	170	30	4324.2
Feed stream reactor HT-R2 – (HE3)	250	370	15	3709.1
Thermal oil – Reactor HT-R2	350	210	30	7873.8
Product of reactor HT-R2 (1) – (COOL-1)	370	250	15	2332.1
Product of reactor HT-R2 (2) – (COOL-1)	250	35	15	10494.0
Feed stream of column C-DIST1 – (HE4)	81.9	212	15	614.0
Feed stream reactor HC-REACT – (HE5)	132.7	420	15	451.1
Product of reactor HC-REACT – (HE-6)	430.5	32	15	573.8
Hydrocracking reactor – HC-REACT	350	210	15	406.4
Reboiler of column C-DIST1	283.3	283.3	15	1002.5
Condenser of column C-DIST1	32	31.9	15	1213.6
Reboiler of column C-DIST2	254.6	254.58	15	667.4
Condenser of column C-DIST2	80.5	80.48	15	1122.9

Table A2. Stream data for heat integration of the hydrogen production process

Stream Name	Supply Temp. (°C)	Target Temp. (°C)	dT Min Contrib (°C)	Heat Duty (kW)
Water preheating (HE7)	44.6	259.9	15	5353.0
Feed stream SR-REACTOR (1) – (HE8)	204.3	227.7	15	2308.6
Feed stream SR-REACTOR (2) – (HE8)	227.7	270.3	15	6925.8
Feed stream SR-REACTOR (2) – (HE8)	270.3	500	15	3462.9
Steam reforming reactor SR-REACT	949.99	950	15	16841.3
Product of SR-REACT – (HE9)	950	310	15	10457.3
Water-Gas-Shift reactor (WGS)	350	349.9	15	-250.3
Product of WGS (1) – (HE10)	350	210.6	15	2186.7
Product of WGS (2) – (HE10)	211	77	15	9839.9
Feed stream of combustor – (HE11)	115.4	300	15	4947.0
Exhaust gases – (HE12)	1500	980	15	16841.3
Exhaust gases – (HE14)	980	150	15	24002.8

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