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Technical, Economic and Environmental Assessment of Ethanol Production using a Biochemical-Thermochemical Hybrid Route

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The present work proposes, in the context of a Biorefinery, to assess the biochemical-thermochemical hybrid route through the recovery of the residual cellulignin from pre-treatment and hydrolysis of sugarcane bagasse and straw in an integrated first- and second-generation ethanol plant (1G2G plant), by means of residual cellulignin gasification in a thermochemical ethanol plant. In this assessment, a decentralized plant concept is considered, in which four first- and second-generation ethanol biochemical plants (1G2G biochemical plants) processing 4 million tonnes of sugarcane per year (4 MTC/y) each and producing first- and second-generation ethanol supply residual cellulignin for a central standalone feedstock flexible thermochemical plant, configuring an 1G2G biochemical-thermochemical ethanol hybrid scenario. As base scenario, four 1G2G autonomous plants with residual cellulignin burned in the boilers is selected. For the routes comparison, main technical, economic and environmental aspects of each scenario are assessed. Results showed an increase in total anhydrous ethanol production for 1G2G biochemical-thermochemical ethanol hybrid scenario, besides higher alcohols that are also produced in this scenario. An increase of capital investment is observed for the 1G2G biochemical-thermochemical ethanol hybrid scenario justifying the Internal Rate of Return (IRR) lower than the base scenario, yet with a positive net present value (NPV). Environmental results showed similar impacts for both scenarios.

1. Introduction

Through fermentation of fermentable sugars obtained from lignocellulosic feedstock, such as bagasse and straw, second-generation biochemical ethanol can be produced. Besides the biochemical route, ethanol can also be obtained by thermochemical route through gasification of lignocellulosic feedstock to syngas followed by conversion to second-generation thermochemical ethanol.

Second generation biochemical route comprises, among others, the steps of pretreatment (producing a liquor rich in xylose) and hydrolysis of the lignocellulosic feedstock. The material resulting from hydrolysis is separated in two fractions namely, the hydrolyzed liquor, rich in glucose and the unreacted solids (residual cellulignin). In general, residual cellulignin (CLG) is used as fuel in the cogeneration system (Bonomi et al., 2016).

Pinatti et al. (2010) have proposed to use cellulignin from pretreatment of lignocellulosic biomass for syngas production by autothermal reforming, since cellulignin is a treated biomass. The produced syngas is cleaned and compressed at 25 MPa for injection into a two-stroke low speed engine system. The total recovered energy was 98%.

The present work proposes to assess the thermochemical ethanol route via synthesis gas from gasification of resultant residual cellulignin of the hydrolysis of four 1G2G ethanol biochemical plants (1G2G biochemical-

thermochemical ethanol hybrid plant). As base scenario, a 1G2G autonomous plant with residual cellulignin burned in the boilers was selected.
The thermochemical route considered in this work comprises unit operations, such as biomass handling and feeding systems, thermochemical conversion processes (gasification), gas cleaning and conditioning and syngas conversion reactions. Syngas can be considered as a building block since it can be converted to liquid biofuels, bio-based chemicals, and heat and power. Ethanol from syngas can be obtained via catalytic or fermentative route. In the present work, catalytic syngas conversion is the adopted route to obtain ethanol. Through the catalytic route, syngas can be converted to ethanol directly using Rh-based catalysts or can be converted to mixed alcohols (C_1–C_5 alcohols) using methanol homologation with CuZnO based to improve ethanol yield from syngas (Bonomi et al., 2016; Subramani and Gangwal, 2008). In this work, based on Dutta et al. (2011), the used syngas catalytic conversion route to ethanol is the higher alcohols synthesis route using methanol recycling to the synthesis reactor to improve the overall ethanol yield.
The main technical, economic and environmental aspects of a 1G2G biochemical-thermochemical hybrid plant compared with a base scenario are assessed using the Virtual Sugarcane Biorefinery (VSB), a framework integrating agricultural, industrial and use models in the sugarcane production chain.

2. Scenarios Definition

This work proposes to employ a decentralized plant concept in which four decentralized, optimized 1G2G autonomous distilleries provide residual cellulignin to a central standalone feedstock flexible thermochemical plant configuring an optimized 1G2G ethanol autonomous biochemical-thermochemical hybrid plant. The following scenarios are assessed:

Base scenario (1G2G Bio)

- Four optimized 1G2G autonomous distilleries with residual cellulignin burned in boilers.
- Processing of 4 MTC/y during sugarcane harvest season (200 days) by each plant, with sugarcane bagasse and straw storage for the 2G process and CHP unit operation throughout the year (330 days).
- Main products: anhydrous ethanol and surplus electricity (sold to the grid).

Scenario 2 (1G2G Hybrid)

- Four optimized 1G2G autonomous distilleries processing 4 MTC/y during sugarcane harvest season (200 days) each, with sugarcane bagasse and straw storage for the 2G process and CHP unit operation throughout the year (330 days). The residual CLG is supplied to a central standalone thermochemical plant.
- Central standalone thermochemical plant with year-round operation of the residual cellulignin (from the four optimized 1G2G autonomous distilleries) gasification and alcohols synthesys. This plant is self-sufficient in energy (thermal and electrical).
- Main products: anhydrous ethanol, higher alcohols and surplus electricity (sold to the grid).

Figure 1 illustrates the selected scenarios for this assessment.

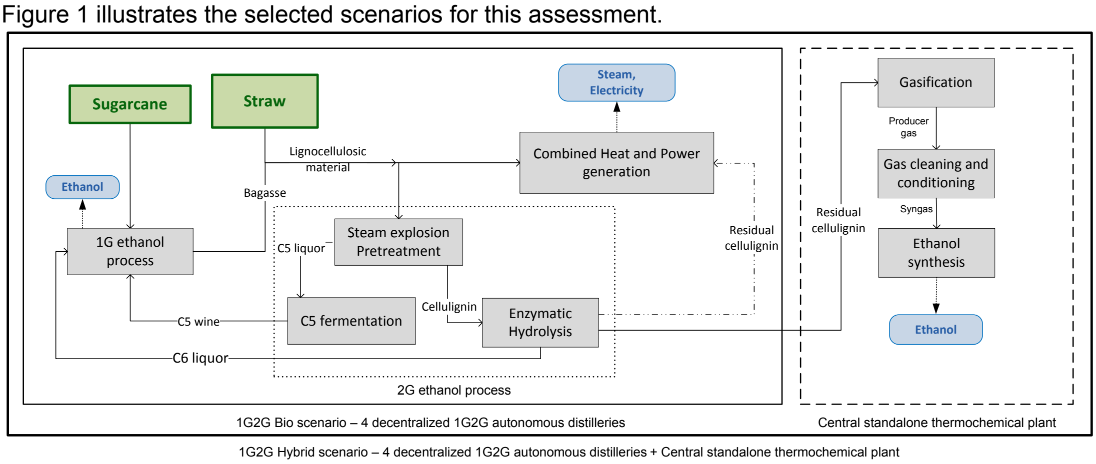

Figure 1: Selected scenarios for this assessment.

3. Process description

3.1 1G2G decentralized plants

The main parameters of an optimized 1G autonomous distillery are presented in Table 1.

Table 1: Main parameters of an optimized 1G autonomous distillery

Parameter	Value
Sugarcane processing capacity	4 million tonnes/year
1G process operation	Season (200 days)
Main products	Anhydrous ethanol (99.3% w/w), surplus electricity
Energetic integration	20% reduction in 2.5 bar steam demand
Straw usage	50% recovery from the field
CHP system	65 bar boilers; 485 °C steam
CHP operation	Year-round (330 days)

The 1G2G biochemical plant integrates 2G ethanol production from lignocellulosic material (sugarcane bagasse and straw) of the optimized 1G ethanol autonomous distillery. The main parameters of the 2G ethanol plant are shown in Table 2, based on the advanced 2G biochemical technology presented by Milanez et al. (2015).

Table 2: Main parameters of an advanced 2G biochemical ethanol technology (Milanez et al., 2015).

Parameter	Value
2G process operation	Year-round (330 days)
Feedstock	Sugarcane bagasse and straw
Pretreatment	Steam explosion, 210°C, 5 min
Enzymatic Hydrolysis	65°C, 36h, 25% solids
C5 sugars fermentation	33°C, 24h
C6/C12 sugars fermentation	Along with sugarcane juice fermentation (1G)

The composition of residual cellulignin from 1G2G biochemical plant is presented in Table 3.

Table 3: Residual cellulignin composition (VSB database).

Component	Fraction (wt%, wet basis)
Water	50.0
Lignin	34.4
Cellulose	12.7
Soil[a]	1.46
Xylan	0.79
Glucose	0.57
Acetyl group	0.08
Xylose	0.043
Others	0.006
Salts[b]	0.001
Minerals[c]	0.0001

[a,b,c] components of ash
[a] Soil is represented by SiO_2.
[b] Salts are represented by KCl (Bonomi et al., 2016), since potassium salts are those present in greater proportion (approximately 60% of the total salts in the ash).
[c] Minerals are represented by K_2O (Bonomi et al., 2016).

3.2 Central Standalone Thermochemical plant

In this assessment, the route comprising unit operations, such as biomass handling and feeding systems, thermochemical conversion processes (gasification), gas cleaning and conditioning and syngas conversion is

considered. The simulation input data used in this work was obtained from Dutta et al. (2011) with some modifications to adapt it to the Brazilian reality.
In order to adequate the biomass moisture content to the required moisture in the gasifier inlet (10% moisture), biomass dryers using residual heat from combustion gases are employed. Biomass gasification occurs in an indirect steam gasifier, in which gasification and char combustion occur in separate equipment. It is worthwhile to mention that the gas from lignocellulosic biomass gasification carries impurities such as hydrogen sulfide, ammonia, hydrogen chloride, and methane. Such contaminants need to be removed depending on the syngas use. According to Table 3, as the residual cellulignin has suffered a pretreatment and hydrolysis steps in the 1G2G biochemical plants, this material does not contain contaminants such as hydrogen sulfide and ammonia, representing an advantage in thermochemical downstream processes since some gas cleaning steps can be eliminated. In this work, after the gasification section, ash removal is performed in a cyclone. A reforming sector is required to increase the H_2:CO ratio through conversion of tar and other compounds. Similarly to the gasification section, the reformer operates with separate equipment for reforming and combustion. Contaminants such as chloride and residual tar are removed through gas scrubbing with water. In order to feed the higher alcohol synthesis, syngas is compressed to 207.8 bar through a six-stage centrifugal compressor. Pressurized syngas is mixed with other recycle streams from the reaction section and sent to the higher alcohol synthesis reactor. In order to increase the ethanol yield, methanol is recycled from the alcohol purification section to the reactor. In the higher alcohol synthesis adopted in this work, contaminants such as CO_2 are removed after the synthesis reactor. More details regarding this approach can be found in Dutta et al. (2011). In order to remove CO_2 from the gas stream, an absorber with dimethyl ether of polyethylene glycol (DEPG) is used. Finally, the higher alcohols from synthesis reactor are sent to the alcohol purification section in order to achieve the anhydrous ethanol specification; higher alcohols are obtained as by-product. More details about the thermochemical plant description can be found in Bonomi et al. (2016).

4. Methodology

Technical Methodology

The scenarios proposed on section 2 are assessed using VSB simulation platform, a framework developed by Brazilian Bioethanol Science and Technology Laboratory - CTBE (Bonomi et al., 2016) that integrates agricultural, industrial and use models in the sugarcane production chain. Through VSB, technical, economic and environmental impacts of the considered scenarios can be assessed.

Economic Methodology

For the economic assessment, capital investment (CAPEX) and operational expenses (OPEX) are estimated for each scenario, based on CTBE database for biochemical scenarios and on 2011 NREL report (Dutta et al., 2011) for thermochemical scenarios with modifications for the Brazilian context. In the methodology employed in this work, a scaling size factor of 0.6 and an installation factor of 2.31 were considered. The values presented in that report were related to 2007 and were updated to December 2015. Product prices follow the average of Brazilian historic series which were also updated to December 2015 (1 US$ = R$ 3.86).
Higher alcohols obtained in the 1G2G Hybrid scenario are considered to be sold to the fuel market, being the price determined by lower heating value (LHV) based on the hydrated ethanol as the reference price.
In order to estimate the 2G ethanol costs in the 1G2G ethanol production, a cost allocation approach was adopted. Details of this approach can be found in Milanez et al. (2015).
In this decentralized approach, it is necessary to take into account the transportation cost of CLG from the biochemical decentralized plants to the central thermochemical plant. Considering the geographic distribution of sugarcane fields for each of the four biochemical plants (4 MTC/year, with average transportation distance of 35 km), and a typical regional location for these plants, a distance of 100 km can be estimated. Based on the CanaSoft, an agricultural model developed by CTBE (Bonomi et al., 2016), transportation costs for CLG was US$ 8.09 per tonne (wet basis), considering trucks with 45 tonnes capacity.

Environmental Methodology

For the environmental assessment, a life cycle impact assessment method, ReCiPe Midpoint, Hierarquist version was employed. SimaPro software and Ecoinvent 2.2 databank, adapted to the Brazilian reality, are also used. Economic allocation is the criteria adopted in the calculations on Life Cycle Assessment (LCA) employed in this work.

5. Results and Discussion

Employing the methodology presented in section 4, a techno-economic and environmental analysis was performed to assess the scenarios described in section 2.

5.1 Technical results

Table 4 presents the technical results reporting the products obtained in each scenario.

Table 4: Main outputs of each considered scenario.

Scenario	1G2G Bio	1G2G Hybrid
Total ethanol production (million L/year)	1992	2000
1G ethanol production (million L/year)	1364	1364
2G biochemical ethanol production (million L/year)	628	463
2G thermochemical ethanol production (million L/year)	-	173
Higher alcohols (million L/year)	-	19
Surplus electricity (GWh/year)	988	845

Technical results show an increase in total anhydrous ethanol production for 1G2G Hybrid scenario. Besides, the 1G2G Hybrid scenario produces 19 million liters/year of higher alcohols that are sold to the fuel market. Both scenarios consider surplus energy to be exported to the grid, being smaller in 1G2G Hybrid scenario, since in this scenario CLG from hydrolysis is not burned in boilers and energy surplus is not considered in the central standalone thermochemical plant.

5.2 Economic results

The financial analysis related to the proposed scenarios is summarized in Table 5.

Table 5: Financial analysis results for each scenario.

Parameter	1G2G Bio	1G2G Hybrid
Total CAPEX (US$ million)	1223	1397
1G	964	910
2G Bio	259	189
2G Thermochemical	-	298
IRR (% per year)	23.6	21.3
NPV (US$ million)	1250	1097
Combined 1G2G Ethanol production cost (US$/L)	0.23	0.24

The results of Table 5 show an increase of total CAPEX for 1G2G Hybrid scenario (around 14.2%) that justifies the lower IRR obtained for this scenario. However, the IRR for 1G2G Hybrid scenario is well above than the minimum acceptable rate of return (MARR) of 12%, with a positive NPV, approximately US$ 1066 million. A slight increase of ethanol production cost was observed for 1G2G Hybrid scenario.

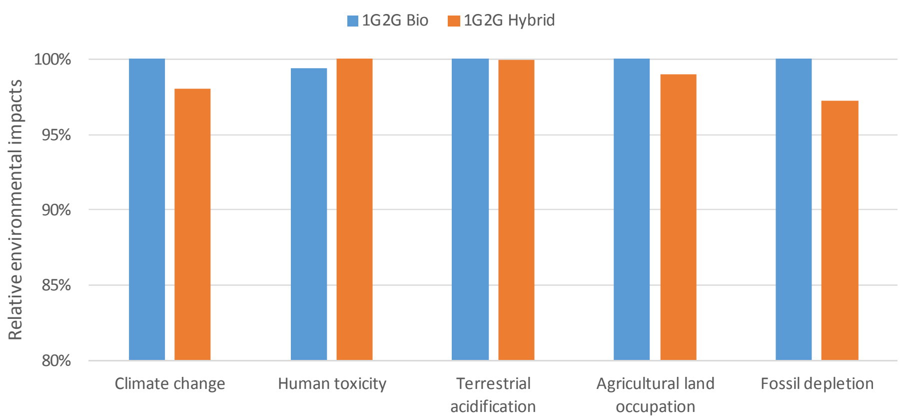

Figure 3: Environmental scores comparison for ethanol production with biochemical and hybrid 1G2G technologies.

5.3 Environmental results

Figure 3 illustrates the environmental scores comparison for ethanol production with biochemical and hybrid scenarios.

The environmental impacts are similar for both scenarios. The liquid biofuels production reduces allocation factor for ethanol in the 1G2G Hybrid scenario.

6. Conclusions

In this study, the technical, economic and environmental assessment of ethanol production using a biochemical-thermochemical hybrid route was carried out. For this assessment, four decentralized plants optimized 1G2G autonomous distilleries supplying residual cellulignin for a central standalone thermochemical plant were considered. This scenario is compared with a base scenario in which four optimized 1G2G autonomous distilleries operate with residual cellulignin burned in boilers. The results showed an increase in total anhydrous ethanol production for 1G2G Hybrid scenario. In this scenario, higher alcohols are also produced and sold to the fuel market. Although the surplus electricity is lower in this scenario, the liquid biofuels output is larger, which is interesting for the transport sector. Even with an increase on total CAPEX for 1G2G Hybrid scenario, the IRR was above the MARR of 12%, with a positive NPV. The ethanol production cost was similar for both scenarios. For both scenarios, the environmental results showed similar impacts. The results presented in this work are related to long term projections. The adopted catalytic route to convert syngas in ethanol is based on the use of methanol recycling to the synthesis reactor. Another interesting assessment would be the conversion of syngas to methanol, which could be used as a precursor of biodiesel.

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Reference

Bonomi A., Cavalett O., Cunha M.P, Lima, M.A.P., 2016, Virtual Biorefinery: An Optimization Strategy for Renewable Carbon Valorization. Springer International Publishing, Switzerland, 2016. DOI: 10.1007/978-3-319-26045-7

Dutta, A., Phillips, S. D., 2009, Thermochemical ethanol via direct gasification and mixed alcohol synthesis of lignocellulosic biomass. National Renewable Energy Laboratory: Golden, CO, US, NREL/TP-510-45913.

Milanez, A. Y. et al., 2015, De promessa a realidade: como o etanol celulósico pode revolucionar a indústria da cana-de-açúcar – uma avaliação do potencial competitivo e sugestões de política pública. BNDES Setorial, 41, 237-294.

Pinatti D.G., Conte R.A., Soares, A.G., Pereira, M.L., Romão, E.L., Ferreira, J.C., Oliveira, I., Marton, L.F.M., 2010, Biomass Refinery as a Renewable Complement to the Petroleum Refinery. International Journal of Chemical Reactor Engineering, 8, A94.

Subramani, V., Gangwal, S. K., 2008, A Review of Recent Literature to Search for an Efficient Catalytic Process for the Conversion of Syngas to Ethanol. Energy & Fuels, 22, 814-839.