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Thermo-Economic Optimisation of Integrated Ethanol and Methanol Production in the Sugarcane Industry

Juliana Q. Albarelli^{*a}, Sandro Onorati^b, Priscilla Caliandro^c, Emanuela Peduzzi^a, François Maréchal^a, Adriano V. Ensinas^a

^a Ecole Polytechnoque Federale de Lausanne (EPFL), EPFL-STI-IGM-IPESE Station 9 , 1015 Lausanne Switzerland ^b Politecnico di Torino, Italy

^c Ecole Polytechnoque Federale de Lausanne (EPFL), EPFL-STI-IGM-FuelMAT Station 9 , 1015 Lausanne Switzerland jualbarelli@gmail.com

The present paper evaluated a sugarcane biorefinery producing ethanol, through the conventional process by sugars fermentation and methanol through bagasse and leaves gasification, hot cleaning and synthesis. The sugarcane biorefinery was modelled using flowsheet modelling software and thermal integration. A thermo-economic model was developed in order to analyze the energy efficiency of the system as well as the total investment. Different configurations are analyzed for the methanol production process. Multi-objective optimization using a genetic algorithm solver is performed, allowing the analysis of several process configurations in terms of conflictive objectives energy efficiency and investment cost. The sugarcane biorefinery is self-sufficient in energy demand after thermal integration with a system energy efficiency increasing when the methanol production is higher, although it also leads to an increase in the total investment. Both Entrained Flow and Circulated Fluidized Bed gasification technologies are modelled and compared for sugarcane residues conversion, showing similar impacts in the system efficiency that can reach more than 55 % (dry biomass input low heating value basis), which is almost two fold higher than the one obtained in the traditional sugarcane ethanol plants currently in use.

1. Introduction

The traditional production of biofuels in the sugarcane industry is a consolidated process where ethanol is produced from sugars and the fibre part of the stalk, the bagasse, is used commonly as fuel for producing heat and power in low efficient steam based cycle systems. Improvements on the process energy integration with investment in heat recovery technology can make a large amount of bagasse available as raw material for novel processes, including second generation liquid biofuels from lignocellulosic material (Albarelli et al., 2013). Biomass gasification technology integrated with methanol synthesis from syngas is an alternative for valorisation of the surplus bagasse available in the ethanol distilleries, which can replace fossil derived methanol used as feedstock in the chemical industry and additives for transportation fuels. This paper presents the analysis of the combined production of ethanol from sugars fermentation, and methanol from bagasse gasification, in the same industrial site using flowsheet modelling software and process integration through MILP optimization. The ethanol production process model is validated with data for current technology used in Brazilian sugarcane mills. Bagasse conversion to methanol is investigated using different alternatives for syngas production and purification. A thermo-economic model is developed in order to analyze the energy efficiency, as well as, the economic impact of the integrated process in the traditional ethanol production process. Multi-objective optimization using a genetic algorithm solver is performed, allowing the analysis of several process configurations for the conflictive objectives energy efficiency and investment cost.

2. Modelling methodology

A sugarcane biorefinery producing ethanol, methanol and electricity was modelled using flowsheet modelling software. Figure 1 shows the diagram of the of the sugarcane biorefinery studied.



SUGARCANE BIOREFINERY

Figure 1. Flowsheet of the sugarcane biorefinery

The model for ethanol production from sugarcane juice was developed in the ASPEN PLUS (Aspentech, 2010) software, while methanol system was performed by Belsim VALI software (Vali Belsim, 2013). A thermo-economic model of the production process was solved in MATLAB based platform OSMOSE, developed at École Polytechnique Fédérale de Lausanne in Switzerland (Bolliger, 2010) using state variables obtained in the detailed simulation of all the equipment and conversion steps of the process. Applying pinch analysis, the optimal process integration was computed and the process heat consumption was satisfied by the cogeneration system.

2.1 Process simulation

Ethanol production: the simulation of the production of first-generation ethanol and electricity was fully described in detail by Ensinas et al. (2013). The biorefinery is dedicated to the production of anhydrous ethanol with 99.3 % (w/w) of purity, which is the specification for blending with automotive gasoline. Ethanol production process was evaluated considering technology available in modern ethanol distilleries in Brazil, including sugarcane dry cleaning, concentration in multi-effect evaporators, sterilization of the juice before entering the fermentation system and ethanol dehydration using Monoethylene Glycol (MEG). After juice extraction part of the bagasse produced is used in the gasification model for methanol production.

Methanol production: the conversion process from lignocellulosic biomass to methanol consists basically of five steps: biomass pre-treatment, gasification, syngas cleaning, methanol synthesis and upgrading. The models developed in this paper are based on previous studies of Gassner and Marechal (2009) dedicated to Synthetic Natural Gas and Tock et al. (2010) treating liquid fueld production, that analysed in details biomass gasification technologies and methanol synthesis respectively. The biomass used as system input was sugarcane bagasse and leaves, being the amount of biomass used is a decision variable in the optimization as it is also necessary to fuel the cogeneration system. The biomass pretreatment is performed by an air dryer (Gassner and Marechal, 2009) in order to decrease the moisture content of the biomass to values suitable for the gasifier operation. Depending on the gasification technology, a torrefaction can be also necessary. Two kind of gasifier have been analyzed: the entrained flow gasifier (EF) and the circulating fluidized bed gasifier (CFB), both require oxygen and steam as gasifying agents. The CFB gasifier has been modelled assuming a pseudo-equilibrium equation for the methane yield and imposing the ethylene yield as a small fraction of the methane one. The water gas shift reaction is supposed to be at equilibrium and the carbon conversion of 95 % is assumed (Hamelinck et al., 2004). The produced syngas contains several contaminants, which can reduce the catalyst activity. The main contaminants are: particulate matter, tar (aromatic Hydrocarbon species), sulphur compounds, HCL, alkali species and nitrogen containing compounds such as ammonia. The tar yield was fixed at 0.83 %(w/w) of the producer gas, assuming also that no benzene is produced during the gasification process. The producer syngas is hence sent to a cleaning unit, where the major contaminants are removed. The particulate matter is removed in a cyclone, and the sulphur species are removed in a zinc titanate bed (Zn₂TiO₄), which operates at high temperature (up to 850 °C) (Aravind and De Jong, 2012). The following tar removal unit consists of two stages: a dolomite tar pre-reformer is used as first stage in order to prevent the poisoning and the deactivation of the downstream metal reforming using Ni as catalyst. In this last step

the water gas shift and the steam methane reforming reactions also occur (Aravind and De Jong, 2012). All these stages operate at the same pressure and temperature of the CFB gasifier (25 bar, 850 °C). The residual pollutants are then removed in a low temperature filter and a scrubber, where also the water is removed. The methanol synthesis is then performed at high pressure as described by Marechal et al, (1997) and to further increase the methanol purity, two steps distillation has been included (Tock et al., 2010). The model of the methanol synthesis considers a multistage reactor containing four beds (Tock et al., 2010). The specification required for the synthesis of methanol is a value of the stoichiometric ratio s, defined in Eq(1), in the range of 2-2.11 (Lurgi, 2012).

$$s = \frac{H_2 - CO_2}{CO + CO_2} \tag{1}$$

In the cases studied, **s** was fixed to 2.05 (Peduzzi et al., 2013). The syngas pressure required for the methanol synthesis is in the range of 50-100 bar (here 85 bar), so a compression step is required between the cleaning and the methanol synthesis units; for the temperature, the range is 250-300 °C (here 260 °C). In order to have optimal activity and selectivity in the methanol reactor, the CO_2 concentration is adjusted at 4-8 % (Wender et al., 1997). A fraction of the off-gases (0.95) is recycled into the synthesis reactors, to increase methanol conversion, while the residual amount is burned. Finally, methanol upgrading is performed. The unreacted gas is first separated in a flash drum and then it is burned. A purity of more than 99 %(w/w) Methanol is reached after two distillation steps at 8bar and 2bar (Tock et al., 2010).

The other gasification unit is represented by an entrained flow gasifier (directly heated), which operates at 30 bar and 1350 °C. Before the gasification, a torrefaction step is required to pulverize the feed (Peduzzi et al., 2013). Because of the high temperature, the product gas is almost tar-free and it does not require a tar removal step, as in the case with the CFB gasifier (Henrich and Weirich, 2004). The produced gas is quenched with steam in order to reach a temperature of 800 °C. After a further cooling to 150° C, the syngas enters the filter and the scrubber for the cold cleaning step (Peduzzi et al., 2013). The water gas shift (WGS) reactor is then used to increase the H₂ to CO ratio to a suitable value for the methanol synthesis. The acid gas removal (AGR) is used to bring the syngas to the specifications required for the synthesis of methanol (Peduzzi et al., 2013), in the same way as previously described. The WGS reactor has to operate with a minimum steam to carbon ratio of 2 (in this case fixed at 2.65), in order to avoid the carbon deposition (Spath and Dayton, 2003). Concerning the heat exchangers, three different ΔT_{min} have been considered and optimized: for gas-phase, liquid and phase changing streams. The main parameters of the process are reported in the Table 1.

Cogeneration system and energy sources: the cogeneration system was modelled as a steam-based cycle with condensing extraction steam turbines supplying heat and power to the process. The system capacity, headers and draw offs pressure levels are set as decision variables in the optimization process. The system is integrated applying the Pinch Method and solving the heat cascade problem is MILP problem. The unreacted gases of methanol synthesis, the off gases from the upgrading, a variable fraction of the available sugarcane-leaves and bagasse and raw syngas, are used to fulfill the energy requirement of the integrated process.

Saving of 5 % of bagasse was considered for use during the cogeneration system startup or sugarcane crushing shutdowns. A flow of 33t/h of leaves available for either gasification or cogeneration was calculated, which represents 50 % of the total amount of leaves produced in the field of a mill with 500 t/h of sugarcane crushing rate.

Technology	Tgasification	Pgasification	T _{quench}	T _{cleaning}	Pcleaning	s	P synthesis
	(°C)	(bar)	(°C)	(°C)	(bar)		(bar)
CFB	850	25	-	850	25	2.05	85
EF	1350	30	800	150	30	2.05	85

Table 1: Main parameters for the methanol production process

3. Performance indicators

The performance indicators evaluated in the present study are energy efficiency (η_e) and total investment cost (*I*).

$$\eta_{e} = \frac{m_{methanol} LHV_{methanol} + m_{ethanol} LHV_{ethanol} + E^{+}}{m_{leaves} LHV_{eaves} + m_{sugarcane} LHV_{sugarcane} + E^{-}}$$

In the Eq (2) E⁺ and E⁻ represent respectively the net electricity surplus and the electricity deficit of the overall system in the scenario considered, respectively. Table 2 shows data for the performance indicators calculation. A multi-objective optimization was accomplished, setting the efficiency as objective function to be maximized and investment as objective functions to be minimized. The decision variables for the optimization are the percentages of bagasse and leaves for methanol production, the ΔT_{min} in the heat exchangers for liquid, phase changing and gas streams and the pressure levels for the steam network and the draws off.

(2)

Table 2: Parameters for the economic and energetic evaluation

Parameter	Value	Unit	Parameter	Value	Unit
M&S Index	1,477.7	-	LHV _{sugarcane} (wet basis)	4,710	kJ/kg
Interest rate	10	%	LHV _{leaves} (wet basis)	14,000	kJ/kg
Working days	210	days	LHV _{ethanol}	30,000	kJ/kg
Life time	25	years	LHV _{methanol}	19,868	kJ/kg

4. Results

Figure 2 and 3 are the composite curves of methanol production configurations with the maximum energy efficiency in the sugarcane conversion (gasification technology entrained flow on the left and circulating fluidized bed on the right). These configurations are reached when the maximum amount of bagasse and leaves are used as raw material for methanol production. The energy efficiency values in the two cases are respectively 57 % for the EF gasifier and 56 % for the CFB gasifier. The slightly lower efficiency for the CFB case with respect to EF case is due to the activation of the pinch point at low temperature that avoid proper steam cycle integration.

Figure 4 represents the Pareto frontier for the two objectives defined in the multi-objective optimization problem. In this graph two slopes can be recognized: the first slope, in which the energy efficiency ranges from 0.35 to 0.45, and the second, where energy efficiency ranging from 0.45 to 0.57. The first slope corresponds to the increase of the efficiency by only changing the pressure levels of the steam network, sending all bagasse and leaves as fuel to the cogeneration system. In the second part of the curve a fraction of bagasse and leaves are sent to methanol production. The methanol production increases the energy efficiency of the system, up to \sim 57 %, but it also has an important impact in total investment. Higher investments are found for the EF gasifier case comparing to the CFB, reaching the double when compared with the biorefinery producing only ethanol and electricity.



Figure 2. Grand composite curve for EF gasifier case with steam cycle integration

Figure 3. Grand composite curve for CFB gasifier case with steam cycle integration

Figure 5 shows the trends of the steam network power produced, the net system power (excess electricity available for sale, calculated after subtracting the electricity demand of the process from the electricity produced by the steam network) and methanol equivalent power with respect to the efficiency for the EF gasifier. This graph highlights that, for obtaining higher efficiency, the cogeneration system has to be limited while the production of methanol has to be preferred. By using the EF gasifier, the methanol conversion efficiency is lower, but the size of the plant can be bigger than in the CFB case, since more heat is available for the ethanol process and, therefore, less bagasse and/or leaves are necessary as fuel to the cogeneration system. This explains why the investment costs are different, even if the efficiency is almost the same.





Figure 5. Different power output contributions with respect to the efficiency of the EF gasifier case

The production cost for the methanol decreases when the overall efficiency increases. In the present study, the minimum methanol production cost calculated was of 1.07 and 0.95 USD/kg, for the EF and CBF technologies respectively. It represents a cost 73 % and 53 % higher than the current price for methanol in the market, 0.62 USD/kg (Methanex, 2014) mainly due to the high investment required.

5. Conclusion

The integrated production of ethanol, methanol and electricity from sugarcane, evaluated in the present study, showed to be thermally feasible, being self-sufficient in energy demand after thermal integration. The system energy efficiency is higher with the increase in methanol production when more biomass (bagasse and leaves) is sent to the process. However, the increase in methanol plant decreased the amount of electricity produced by the cogeneration system making necessary to buy electricity from the grid when the methanol production is higher than 125 MW. The overall investment increases with the energy efficiency, due to the higher investment in a more efficient cogeneration system and also the bigger scale methanol production plant. The size of the methanol production process can be bigger when considering the entrained flow technology, since more heat is available for the ethanol process and, therefore, less bagasse and/or leaves are necessary as fuel to the cogeneration system. This has also a negative impact in the investment that must be 25 % higher for EF case with respect to the CFB case when energy efficiencies as high as 55 % are reached. The combined ethanol and methanol biorefinery shows to be very promising for the energy efficiency point of view, being almost two fold higher than the one obtained in the traditional sugarcane ethanol plants currently in use. Further studies can be conducted for reducing the production cost in commercial scale with residues valorization and improvements in the integration between the two production processes.

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