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# Valorization of sugarcane biorefinery residues using supercritical water gasification: A case study and perspectives



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#### ABSTRACT

The present study evaluates the use of supercritical fluid technology, particularly supercritical water gasification (SCWG), to add value to residues from a sugarcane biorefinery that produces first and second generation ethanol. This case study aims at elucidating how process system engineering tools such as thermal process integration, life cycle analysis, economic evaluation and multi-objective optimization can contribute to minimizing some future challenges of the industrial implementation of supercritical fluid-based technologies, which were discussed in the Workshop on Supercritical Fluids and Energy – SFE'13. In addition, this case study exposes future perspectives in terms of the requirements to further develop this field. The optimized solutions of the evaluated case showed that the SCWG process increases the overall efficiency of the process in terms of energy and carbon fixation. It decreases the CO<sub>2</sub> equivalent emissions and it leads to a thermally self-sufficient process. The economic analysis showed a high investment cost but a feasibility of using the current market prices for the produced fuels and electricity.

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#### 1. Introduction

The sugarcane industry is one of the major activities contributing to the Brazilian economy. This sector has experienced major modernization, and different alternatives are considered to compose the future scenario of sugarcane use in Brazil. One of the most studied technology is the production of ethanol from sugarcane bagasse [1]. This technology can increase the ethanol production per harvested area and decrease the requirement for expanding sugarcane harvesting. Nevertheless, ethanol production from lignocellulosic material and the production of other biofuels from biomass continue striving to find a method to commercialize, and the competition with first generation biofuels and oil-derived products is usually a challenge. Product diversification in a biorefinery concept, which maximizes utilization of biomass, has demonstrated an important role in enhancing the economic feasibility of

http://dx.doi.org/10.1016/j.supflu.2014.09.009 0896-8446/© 2014 Elsevier B.V. All rights reserved. second generation biofuels [2,3]. A biorefinery involves the separation and conversion processing of biomass to produce various products, which is similar to a petroleum refinery. Because biorefining strives to recover the maximum value from each fraction at minimum energy cost, and this aim can be achieved using different production processes, several biorefinery options have been addressed [4–6].

For the second generation ethanol production process, the most studied route is the enzymatic one after the sugarcane bagasse pretreatment to enhance its biodigestibility; some pilot and demonstration plants were constructed worldwide following this approach. From this technological route, three main residues are formed: one solid (a lignin-rich material, which is obtained after the enzymatic hydrolysis) and two liquids (vinasse and pentoses-rich liquors, which are obtained after distillation and the biomass pretreatment, respectively) [2]. Those residues can be used as raw material for production of chemicals and biofuels [6]. Some options to valorize these residues in the form of gasification derived fuels are: for the liquid wastes (vinasse and pentoses liquors), (i) the anaerobic biological digestion, or (ii) the use of the supercritical water gasification (SCWG) process; for the lignin-rich stream, (i) the conventional gasification, or (ii) direct burning [7–11].

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Sometimes referred to as hydrothermal gasification, SCWG benefits from the special properties of near-supercritical and supercritical water as the solvent and the reactant, respectively. This process is performed in an aqueous system at conditions above the critical point of water: 647 K (374 °C) and 22.1 MPa. This technology achieves high conversions and avoids energy-intensive biomassdrying processes, which are required in conventional gasification technologies [12,13]. However, for continuous gasification systems, the feedstock must be a fluid possible to pump [14], which is not the case for all sugarcane biorefinery residues. Although transposing some of the bottlenecks for hydrothermal technical feasibility is required (e.g., a low solid concentration is required for pumping and the salt separation system), it is also important to evaluate the current state of this technology from a process system engineering (PSE) viewpoint. PSE is an interdisciplinary field of engineering that focuses on the design, operation, control and optimization of engineering systems over their life cycles. It uses domain knowledge and mathematical and experimental techniques to build computer models of chemical, physical and/or biological processes using tools as: process modeling and simulation, process and energy integration, process systems design, optimization, supply chain management, advanced process control. This requirement implies analyzing the insertion of a supercritical fluid-based process into the global process using simulation, thermal process integration, life cycle assessment and economic tools [15–17]. This insertion forecasts new bottlenecks for industrial application of the evaluated technology and reassures or dismisses the laboratory scale

Some major barriers for the transfer of supercritical technology applications to the industry and for future development of supercritical technologies were drawn in the Workshop on Supercritical Fluids and Energy – SFE'13, which was held in Campinas, Brazil, December 2013 [18]. Some of the topics discussed were the difficulty of communication with industrial partners and the need for evaluating/reducing the energy demand of the process. In this context, the present study aims at discussing the SCWG process from a PSE viewpoint. In this study, a multi-objective thermoenvironomic (i.e., thermodynamic, economic and environmental) optimization of a new proposal to valorize sugarcane biorefinery residues (vinasse and pentoses-rich liquors and lignin-rich material) was assessed as a case study. In this proposed case, the combination of all residues allows the direct pumping of this stream to the gasification reactor due to the low solid content of the stream. No other work on the thermochemical treatments and valorization of these bioresources as a unique stream has been performed to our knowledge.

#### 2. Process description and methodology

#### 2.1. Process description

In the present study, the production of first and second generation ethanol, synthetic natural gas (SNG) and electricity from sugarcane in a new biorefinery concept was evaluated. A simplified representation of the process is presented in Fig. 1.

## 2.1.1. First and second generation ethanol production process from sugarcane

The ethanol production process was simulated using the commercial flowsheeting software Aspen Plus [19] considering the available technology in modern ethanol distilleries in Brazil, such as sugarcane dry cleaning, concentration in multi-effect evaporators, sterilization of the sugarcane juice before entering the fermentation system, ethanol dehydration using monoethylene glycol and the use of sugarcane bagasse for saccharification through steam explosion pretreatment and enzymatic hydrolysis.

The simulation of the production of first and second generation ethanol and electricity, as well as the property models used, were fully described in details elsewhere [2,7]. In short, the first generation ethanol production considered the steps of sugarcane cleaning, juice extraction, juice treatment and concentration, glucose fermentation, ethanol distillation and dehydration. The second generation ethanol production process considered using the part of the sugarcane bagasse, which is obtained after juice extraction. In the second generation ethanol production process, the bagasse is dried and milled; then, it was cleaned with water and sent to an SO<sub>2</sub>-catalyzed steam explosion pretreatment, and the treated material was washed and sent to enzymatic hydrolysis. The resulting sucrose solution was concentrated and sent to fermentation when it was mixed with the concentrated juice of the first generation process. Table 1 shows the main parameters that were considered for the simulation.

From the ethanol production process, only three main waste flows were considered in the supercritical water gasification (SCWG) process:



Fig. 1. Block diagram of the sugarcane biorefinery that was integrated to the supercritical water gasification process to produce ethanol, synthetic natural gas and electricity.

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