

FAPESP BIOENERGY PROGRAM

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BIOREFINERY IN AGRICULTURAL AND FOOD INDUSTRY: RECYCLING WASTE FOR NEW CHEMICALS AND BIOHYDROGEN

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Figure 1

Figure 2

Figure 1. The operating diagram of the operational unit hydrolysis and gasification sub-supercritical water in detail hydrolysis reactor [from: Perez DL, Berni MD, Forster-Carneiro T, Meireles MAA. Pilot plant for residues of food industry in supercritical gasification process and hydrogen production. In: SLACA - Latin American Symposium of Food Science, 2013, CAMPINAS. Acta of Latin American Symposium of Food Science. Campinas: Galoá - Academic events, 2013. p. 1.]

Figure 2. Overview of the process for the production of 1st and 2nd generation bioethanol and images of scanning electron microscopy (FESEM) for samples of bagasse initial sugar cane and hydrolyzed with an average particle diameter with an increase of x100 micron scale bar [from: Rostagno MA, Prado JM, Mudhoo A, Santos DT, Forster Carneiro T, Meireles, MAA. Subcritical and supercritical technology for the production of second generation bioethanol. Critical Reviews in Biotechnology. 1-11, 2014].

Waste recycling technologies to produce new products with energy recovery are emerging as an efficient and economically viable alternative with a great potential in terms of production and market value. Sub/supercritical hydrolysis and gasification are among these emerging technologies. Recent research indicates that supercritical fluid technology is economically viable when compared with thermal gasification due to high solubility of the components of biomass in supercritical water generating a gas cleaner (no tar and pitch) and the highest concentration of bio-hydrogen. The challenge of this technology is the optimization of operating parameters involved in the process to maximize the effect of temperature and pressure. In this project, a new line of research is proposed to develop new products with high added value chemicals from the waste of food industry in the context of industrial units known as biomass biorefineries. This will be achieved by integrating two emerging technologies, hydrolysis and gasification with subcritical/supercritical water. Extensive tests with different operating parameters will be needed, as well as determination of gas composition and the performance of different wastes (soy, sugarcane, peanuts and tomatoes wastes). This project proposes the production of a clean gas with high bio-hydrogen concentration at lower temperatures (subcritical conditions, 200-374 °C) seeking the reduction of production costs of sub /supercritical gasification at large scale.



SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

Biomass is an important renewable and sustainable source of energy. The rational utilization of biomass wastes is important not only for the prevention of environmental issues, but also for the effective utilization of natural resources. Reducing sugars obtained from sugarcane bagasse, as a waste biomass energy precursor, can be further transformed to fuel alcohol in a fermentation process. Subcritical water is an environmentally friendly solvent and attractive reaction medium. In this work, a subcritical water process was used for the hydrolysis of sugarcane bagasse with the aim of producing fermentable sugars. The present study evaluates the use of subcritical fluid technology, particularly subcritical water hydrolysis, to add value to residues from a sugarcane biorefinery that produces first and second generation ethanol. This paper is the first in a series examining the use of biomass as a fuel source via a two-step process consisting of hydrolysis (reactor 1) using subcritical water followed by gasification (reactor 2) in supercritical water. Hydrolysis in subcritical water performance was studied under semi-batch conditions in a 110 mL reactor (reactor 1). Hydrolysis was conducted for different sample loadings (3 and 5 g), flow-rates (9 and 12.5 mL/min), temperatures (100, 150, 200 and 250 °C) and pressures (2.5, 5, 10, 15 MPa). The experimental results show that the highest reducing sugar yields could be obtained at temperature above 200°C. Under these conditions, the reducing sugar yield reaches 13%. Scanning electron microscopy (FESEM) was used to analyze the sugarcane bagasse undergoing supercritical water hydrolysis and confirmed that high temperature (max 200-250 °C) disrupts the cell walls, enhancing production of monosaccharides. Diffuse reflectance infrared spectroscopy (DRIFTS) was used to characterize the residual solids, with results consistent with the removal of hemicellulose during hydrolysis. In addition, further experiments were performed to study the conversion of other important organic waste (green coffee powder and coming green coffee residue of coffee oil extraction). The operating conditions were sub-critical temperature conditions (200-250 °C) and pressure (22.5 MPa). The study includes evaluating the physicochemical characterization of raw materials for moisture content, extractives, ash, carbohydrates and lignin in the standard method of the National Renewable Energy Laboratory. The liquid fraction or hydrolyzate was analyzed for total sugar content by a colorimetric technique. The experimental results show que the highest reducing sugar yields could be obtained at temperature above 150-175 °C. Finally, the results will compare the best production of hydrogen for each agri-food waste.

MAIN PUBLICATIONS

Lachos-Perez D, Prado JM, Torres-Mayanga P, Forster-Carneiro T, Meireles MAA. 2015. Supercritical water gasification of biomass for hydrogen production: variable of the process. *Food and Public Health.* **5(3)**: 92-101.

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Prado JM, Vardanega R, Rostagno MA, Forster-Carneiro T, Meireles MAA. 2014. The study of model systems subjected to sub- and supercritical water hydrolysis for the production of fermentable sugars. *Green chemistry letters and reviews.* **8**: 16-30.

Prado JM, Forster-Carneiro T, Rostagno MA, Follegatti LA, Maugeri FF, Meireles MAA. 2014. Obtaining sugars from coconut husk, defatted grape seed, and pressed palm fiber by hydrolysis with subcritical water. *The Journal of Supercritical Fluids*. **89**: 89-98.

Forster-Carneiro T, Berni M, Dorileo IL, Rostagno MA. 2013. Biorefinery study of availability of agriculture residues and wastes for integrated biorefineries in Brazil. *Resources, Conservation and Recycling.* **77**:78-88.

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