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学位論文題目	Valorization of Sugarcane Bagasse as Novel Emulsifiers by Hydrothermal Liquefaction Technology (サトウキビバガスの高付加価値化をめざした水熱液化技術による新規乳化剤の開発)		
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Abstract of thesis

As natural resources continue to be depleted and rise in greenhouse emissions, biomass valorizations are significant research interests for most governments and research institutes. Biomass resources are forestry residue, agricultural residues, marine products, and municipal solid, to name a few. As agricultural residue bagasse is the most abundant agro-industrial by-product and is composed of bagasse is 40–45% of cellulose, 20–30% lignin, 30–35% hemicelluloses and minor amounts of extractives and inorganic compounds. Cellulose is a linear homopolymer composed of D-glucopyranose units linked by β -1,4-glycosidic bonds. It is associated with hemicellulose molecule via hydrogen bonds and is linked to lignin through covalent bonds. Hemicelluloses are branched polymers of low molecular weight with a degree of polymerization, with xylans being the most abundant hemicellulosic polymers with enormous potential for industrial applications.

Bagasse is a potential source of hemicellulose and cellulose for conversion in biorefinery concepts, and it has been thoroughly studied. It is a fibrous by-product from raw sugarcane processing and usually weighs up to 280 kg / ton of sugarcane being crushed. With the global production of bagasse around 279 million metric ton, it is abundant and 50% is usually left unutilized after burning in high-pressure boilers to produce electrical energy. It contains polymeric cellulose of 40–50%, hemicellulose at 25–35% and lignin from 7 to 24%. Minerals,

waxes and other compounds exist but to a lesser content. Bagasse represents a highly productive candidate feedstock for valorization because it has a faster growth cycle and has a high yield compared to sorghum or switchgrass. With cell walls composition having high proportions of pentoses in the wall polysaccharides such as arabinoxylan, disintegrating the complex structure is a limitation. From an industrial viewpoint, thermochemical conversions such as combustion, gasification, pyrolysis and hydrothermal liquefaction (HTL) or a combination of each has been gaining interest for their robustness to treat biomasses. In hydrothermal liquefaction, water is an important reactant and catalyst, as a region of operation is between 150 to 370 °C and between 4 to 25 MPa. Water properties such as the high value of the ionic product of water (K_w) in the subcritical range means that high levels of H^+ and OH^- will accelerate biomass hydrolysis. Therefore, biomass not usually soluble at room temperature are potentially soluble in these conditions. Batch reactors are the most common type of reactor set up and eventually developed into a more advanced semi-continuous or continuous reactors. Also, HTL treatment is a much quicker, more efficient technique to solubilize and achieve complexation to compounds that have poor water solubility. As technologies continue to evolve, HTL is breaking into territories instead of being regarded as just a pre-treatment technique such as it uses on emulsion systems. As a thermodynamically unstable system of two immiscible liquids, an emulsion is achieved by an emulsifier and a homogenization step. As much as synthetic additives dominate the food additives application, natural alternatives are more appealing, yet its availability and functionality are debatable. This thesis mainly focuses on the HTL treatment of bagasse and characterization as a natural emulsifier in Oil-water-emulsion.

The author used an HTL reactor to treat 3% (w/w) grounded bagasse (particles sized around 500 μm) at 160 °C, 30 min, and 1 MPa. For the 3% initial solid concentration used in this study, 47.4% of bagasse was solubilized, and 52.6% remained as insoluble solids. The composition of the bagasse extracts mainly composed of carbohydrates at 510.3 mg/g, with approximately 45% of the bagasse extracts existing as the higher molecular weight oligosaccharides other than xylotriose and xylobiose. Together with the presence of organic acids, phenolics compounds contributed to a lower pH of 3.9 detected after HTL. The use of such a treatment technique is an effort to promote more eco-friendly technologies with less dependency on the use of solvents.

The author separated and freeze-dried the liquefied portion, before re-dissolving it in 5 mM Phosphate buffer solution (0.5 - 4 wt%) as a continuous phase. Polytron (10,000 rpm, 5 min) and high-pressure homogenization (100 MPa, 4 passes) achieved O/W emulsions with soybean oil before storage at 25 °C. Three wt%, bagasse extract from HTL was able to stabilize emulsion for 11 days at 25 °C with a d_{av} of 0.79 μm . Likely, the adsorbed layers of the lignin-carbohydrate complex from the bagasse extracts stabilized the O/W emulsion through steric repulsion, and further studies are needed to characterize the potential surface-active macromolecular complexes in bagasse extract.

The author also investigated the stability mechanism of the bagasse extract-stabilized emulsions. Three samples, Raw Bagasse (RB), Pith (P), and Rind (R), all derived from different parts of the bagasse were treated with HTL and applied as emulsion the different bagasse extracts were able to stabilize emulsion using the high-speed polytron and high-pressure homogenizer. In comparison to RB-stabilized emulsion with 3.3 μm , both P and R-stabilized emulsion achieved 4.1 and 7.1 μm droplet sizes, respectively. The phenolic content in the RB-stabilized emulsion at the interface was 0.02 $\mu g/kg$ emulsion, while the content in the continuous phase

was 0.88 mg/kg emulsion with the stability of emulsions attributed to the high concentration of carbohydrate that sterically congregate at the aqueous phase.

Bagasse extracts containing both hemicellulose and lignified compounds can be valorized using eco-friendly HTL treatment. Therefore, an agro-industrial by-product has potential for application in emulsion such as low-fat salad dressings but, more importantly, adding value through treatment and its applications.

Abstract of assessment result

【Review】

Bagasse, a fibrous by-product from raw sugarcane processing, traditionally burned for energy production, has been gaining attention as a potential source of hemicellulose and cellulose for conversion in biorefineries. Such conversion processes conventionally employ a combination of chemicals and biological enzymes to fractionate the structural complexity of bagasse. However, these methods are costly and time-consuming and generate by-products which may be harmful to the environment. In these regards, the applicant investigated the application of Hydrothermal Liquefaction (HTL) technology, using only water at subcritical condition (such as 160 °C, 1 MPa for 30 min) as solvent to hydrolyze biomass, which is not usually soluble at room temperature. Furthermore, the emulsification ability of bagasse extracts meanwhile stabilizing oil-in-water (O/W) emulsions was also investigated, as compared to another commercial emulsifier. The experimental results indicated that emulsions stabilized by bagasse extracts from HTL were considerably stable having average droplet size (d_{av}) 0.79 μm upon storage at 25 °C for 11 days, which was similar to gum arabic (GA)-stabilized emulsions (d_{av} of 2.24 μm). Therefore, this study indicates that the application of hydrothermal liquefaction, a green technology employing no other solvent besides water, to hydrolyze bagasse is a promising strategy, demonstrating the potential application of bagasse extracts as natural emulsifier for oil-in-water emulsions.

【Result】

The final examination committee conducted a meeting as a final examination on June 19, 2020. The applicant provided an overview of dissertation, addressed questions and comments raised during the question-and-answer session. All the committee members reached a final decision that the applicant has passed the final examination.

【Conclusion】

Therefore, the final examination committee approved that the applicant is qualified to be awarded Doctor of Philosophy in Food Innovation.