

# HYDROTHERMAL CARBONIZATION BEHAVIOUR OF SUGARCANE BAGASSE IN HOT COMPRESSED WATER

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## 論文内容の要旨

Recently, crude oil prices have escalated into the high level due to the depletion of worldwide oil reserves. These reserves may be depleted by excessive use in the coming 50 years. Therefore, it is highly desirable to look for practical solutions for reducing the consumption of fossil fuel and stimulating a renewed interest in the search for developing alternative sources of fuel and chemicals.

There are many abundance energy resources around the world that can be stored, converted and amplified for use. Biomass is one of the energy resources that can be derived from all of earth's living matters such as growing plants. Biomass has potential for use as an alternative transportation fuel, a feedstock for chemical products and power generation. It is abundant, renewable and environmentally friendly. Biomass derived from agricultural waste is particularly suitable as it does not compete with food industries.

Among agricultural wastes, sugarcane bagasse has the potential to be transformed into energy and chemicals. Bagasse is the fibrous residue obtained after the extraction of sugarcane juice. Although the hydrothermal carbonization for the conversion of sugarcane bagasse has been extensively studied, most of those studies focused only on the pre-treatment and saccharification processes for monomeric sugar and bio-ethanol production and very few studies have concerned about production of solid biofuel and chemicals resources. Therefore, in order to utilize of this biomass effectively, the behavior and mechanism of hydrothermal carbonization of sugarcane bagasse were studied.

This thesis consists of 5 chapters. Chapter 1 explains the research background such as the importance and the advantage of utilization of sugarcane bagasse as a raw material for producing bio-fuel as renewable energy and chemicals. Objective and outline of thesis are presented as well. Chapter 2 mainly explains the characterization of liquid products obtained from hydrothermal carbonization. The effect of temperature and time on decomposition of the material was discussed based on its chemical composition changes. The chemical composition of the products was evaluated by high-performance liquid chromatography (HPLC) and gas chromatograph-mass spectrophotometer (GC-MS). Based on the characterization results, it was concluded that the decomposition reaction was influenced by temperature and reaction time. Degradation of hemicellulose began at 200°C (3 min) and was completed at 240°C (5 min) to form arabinose and xylose.

Cellulose started to decompose at 240°C (5 min) and was completely degraded at 270°C (30 min) producing glucose. Further, sugars products of cellulose and hemicelluloses were dehydrated to form 5-hydroxymethyl furfural (5-HMF), furfural and organic acids. Lignin decomposed at temperature range 200-300°C, and produced aromatic and phenolic compounds such as 2,6-dimethoxy phenol, phenol, 1-hydroxy-2 propanone and 2-methyl 1,3-benzenediol. However, complete decomposition of lignin was not possible due to re-condensation or polymerization reaction.

In addition, the results showed that acetic acid is predominantly produced under hydrothermal carbonization with the highest yield of 6.5% at temperature range of 270-300°C. The best conditions for furfural and 5-HMF were 200°C (30 min) and 270°C (10 min), with the yield of 5.1 wt% and 3.1 wt%, respectively. All of these chemical products of sugarcane bagasse are valuable and important products for chemical industries and for biofuel feedstock.

Chapter 3 mainly describes the characterization and fuel qualities evaluation of solid products obtained from hydrothermal carbonization. The solid products were evaluated by proximate and ultimate analysis, as well as caloric value, percentage of chemical composition recovery, Fourier transform infrared (FTIR) spectroscopy, and combustibility by thermogravimetric analysis (TGA). The proximate analysis showed that the treated biomass has improved fuel qualities compared to the raw biomass, where it decreased volatile matter and increased the fixed carbon. The solid products resulting from the treatment showed higher carbon content and lower oxygen content leading to increases gross caloric value from 14.4 to 27.0 MJ/kg (dry ash free basis). As the results of these changed, the energy densification of solid products also increased by 1.1-1.9 times (energy content per weight) were higher than the raw material. The hydrothermal carbonization progressively changes the functional groups of raw material. The data from FTIR indicated that -OH group of raw material decreases with the increase in temperature. This result explains that the treatment increases the hydrophobicity of solid product. The product produced at higher temperature (300°C) had higher caloric value and fixed carbon, and comparable compositions with typical solid fuels such as sub-bituminous coal.

In addition, it was found that the combustibility of sugarcane bagasse after the treatment changed significantly due to the chemical compositions. Comparison of TGA curve of raw and treated material showed that the material with higher hemicellulose and cellulose content have lower ignition and combustion temperature than material with higher lignin content. In addition, it can be seen that the maximum weight loss rate of treated material increased with increasing hydrothermal carbonization temperature and time.

Chapter 4 provides calculations for the kinetics of hydrothermal decomposition reactions of sugarcane bagasse. In this chapter, the kinetics calculation for decomposition reactions such as hydrolysis and dehydration reactions are adopted as the heterogeneous reaction model. The model assumes that solid particle is cylindrical shape and this size is shrinking with reaction (cylindrical shrinking core model). Results of calculation indicated that the reaction is controlled with the diffusion through product layer. From these calculation results and the results of chapter 2 and 3, decomposition mechanism can be explained as follows: sugarcane bagasse consists of cellulose, hemicellulose and lignin. With hydrothermal carbonization cellulose and hemicellulose are decomposed preferentially and un-reacted lignin part to be diffusion layer. The calculation results showed that the hydrolysis and dehydration reaction started at 200°C and 240°C respectively and reaction rate increased with increasing temperature.

Chapter 5 summarizes the general conclusions of this study.

## 論文審査の結果の要旨

本研究は、サトウキビバガスの水熱炭化処理によって得られる水溶性生成物および改質固体の収率と組成を系統的に調べ、それら産物に及ぼす処理条件の影響、改質固体の組成と燃焼性との関係および水熱炭化機構を明らかにし、最適な水熱炭化プロセス構築のための重要な指針を与えたものであり、資源工学上重要な知見を得たものとして価値ある業績であると認める。