

# Studies on Catalytic Hydrothermal Reforming of Biomass and Its Derivatives for the Production of Fuels and Chemicals

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## 論 文 内 容 の 要 旨

Biomass is the only renewable and sustainable carbonaceous resource, and production of secondary fuels and chemicals from this resource has been drawing attentions. Thermochemical gasification is a most reasonable way to convert biomass into synthesis gas rich in hydrogen ( $H_2$ ) and carbon monoxide (CO) or methane ( $CH_4$ ). The gasification has so far been performed employing steam and oxygen (or air) as the gasifying agents with recovery of chemical energy at most 60–80%. Catalytic hydrothermal reforming (CHTR) is a type of gasification that employs not steam but highly compressed liquid water under subcritical or supercritical conditions. The chemical energy recovery by the CHTR is theoretically around 100% because of balance between endothermic  $H_2/CO$  formation and exothermic  $CH_4$  formation from the

H<sub>2</sub>/CO. CHTR also has practical advantages over conventional gasification of biomass, which are no need of either use of O<sub>2</sub>, drying of feedstock, or generation of steam, which brings about large energy penalty. The CHTR enables conversion of various types of organic substances in aqueous media at temperature lower than critical one of water, 374 °C. Production of CH<sub>4</sub>-rich fuel gas from biomass-derived compounds such as phenol and glucose is a representative example of successful application of the CHTR. The conversion of the organics is often as high as 99%, which is not enough to allow discharge of the processed water to the environment. It is also known alkaline aqueous media largely inhibits the CHTR of phenols and carboxylic acid. The primary purpose of the author's studies was to develop/demonstrate catalysts that show activities higher than the existing ones for the CHTR of biomass-derived water-soluble compounds and oils in not only acidic/neutral but also alkaline aqueous media. The second purpose was to examine/demonstrate production of gaseous/liquid fuels and also simultaneous production of liquid/gaseous fuel and valuable chemicals by the CHTR of biomass.

This thesis consists of five chapters. Chapter 1 first describes the significance of utilizing renewable energy resources, mainly biomass energy, and then reviews biomass conversion technologies for energy and chemicals productions associated with CHTR in sub- and super-critical water conditions. The purpose and originality of the present study are mentioned at the end.

Chapter 2 deals with CHTR of water-soluble fractions of bio-oil derived from the pyrolysis of biomass, which generally regarded as wastewater. Among the metals examined as catalysts such as Ni, Co, Cu, Fe and Zn, Ni supported on a carbon support (Ni-C) showed the highest catalytic activity, leading to reforming of organics with a conversion on an organic carbon basis of 98.4 % to fuel gas that consisted mainly of methane at temperature and pressure of 350 °C and 20 MPa, respectively. However, the product liquid still contained 160 ppm of organic carbon that was composed of refractory compounds such as acetone. A newly developed Pt/Ni-C showed catalysis high enough to convert acetone and reduce the total organic carbon concentration (TOC) to a level as low as 6 ppm, which corresponded to a conversion of 99.94 %. Such a high activity was maintained during a continuous CHTR with 24 h duration. It was also found that Pt helped Ni maintain its metallic state, which was essential for high activity toward the reforming. The CHTR using the Pt/Ni-C catalyst was thus effective on fuel gas production simultaneously with clean water.

Chapter 3 proposes CHTR as a method to upgrade vegetable oil into gaseous/liquid fuels without consuming any reagents, such as methanol and hydrogen, other than water. *Jatropha* oil, a type of inedible vegetable oil that consisted mostly of triglycerides, was employed as the feedstock. *n*-Alkanes were produced by participation of hydrogen that was generated in situ from a primary product, glycerol, while the direction of catalysis varied depending on the metal of the catalysts. The main products of CHTR over Pt/C were pentadecane and heptadecane, which were formed by a sequence of hydrolysis of the oil to form fatty-acids/glycerol and decarboxylation of the fatty acids, with a total yield of more than 46 % at 350 °C. Ni-C had catalysis toward oxidative carbon-carbon-cleavage of fatty acids, causing selective formation of methane at yield of 73 %-C. Thus, two options with Pt/C and Ni-C have been suggested for the production of liquid fuel and gaseous one. Meanwhile, insufficient recoveries of chemical energy of the feedstock, ranging 48.2–99.6 % on HHV basis, for Pt/C in particular indicated the requirement for suppression of

side reactions producing heavy by-products during the CHTR.

Chapter 4 proposes a novel process for fuel gas production and/or simultaneous production of fuel gas and valuable chemicals from lignin dissolved in alkaline aqueous media. The catalysis of Ni-C was not enough for gasification of the lignin due to its macromolecular nature and stabilization of acidic hydroxylic/carboxylic groups in the alkaline environment. A Ru catalyst supported on activated carbon showed higher catalytic activity and constantly reduced TOC of the lignin solution from 5,000 ppm to 70 ppm during a CHTR period of 10 h. The alkaline aqueous solution after CHTR was nearly free from organics and, therefore, can be reused for the process. Alternatively, with CHTR at milder conditions and use of a Pd/C catalyst, valuable monomeric phenols were successfully produced with a total yield of 11.9 %-C at 225 °C, and this was accompanied by the formation of fuel gas. The organics dissolved in the liquid after liquid-liquid extraction of the phenols are ideally subjected to the CHTR with the Ru catalyst for an additional fuel gas production and regeneration of the alkaline water.

Chapter 5 summarizes the findings described in the preceding chapters and provides a future perspective of catalytic hydrothermal reforming in biomass processing.

#### 論文審査の結果の要旨

本論文は、バイオマス水熱ガス化における課題の解決と液体燃料、化成品製造への応用を提案し、提案法の有効性を実験結果に基づいて示したものである。本論文に示された新知見は、次世代のバイオマス転換技術開発に有用であるばかりでなく、炭素資源利用に関する化学反応工学への学問的寄与が明らかである。よって、本論文は博士（工学）の学位論文に値するものと認める。