

## 論文の要旨

題目 Supercritical water gasification of palm oil mill effluent  
(パーム油工場廃液の超臨界水ガス化)

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Increasing energy demands, fossil fuel depletion, and environmental degradation are some of the issues that motivate the search for renewable energy sources. Biomass is an alternative energy source, which is abundant, carbon neutral, and environmentally friendly. Indonesia is rich with the potential of biomass that can be utilized as bioenergy feedstock. Palm oil is the foremost industry in Indonesia with severe waste byproducts that are harmful to the environment; however, it has excellent potential as biomass resource. Palm oil mill effluent (POME) is the most problematic waste generated from palm oil production process. It is made up of water, oil, solids, suspended solids, and many valuable nutrients such as phosphorus. Supercritical water gasification (SCWG) is a promising method for thermochemical conversion of biowaste into valuable gas. Due to its use of water as the reaction medium, eliminating the drying pretreatments required by conventional technologies. Water above its critical point (374 °C, 22.1 MPa) is a convenient medium for dissolving many organic compounds. Furthermore, under these conditions, water is very reactive, and gasification takes place easily. Additionally, if valuable nutrients can be recovered in parallel with energy production, the recycling of POME becomes even more economically beneficial. There are no comprehensive studies on gas and phosphorus production from POME. Thereby, evaluation of the products, reaction mechanism, and reaction kinetics are essential to optimize the process. Besides the POME conversion, the kinetic study of model compound (glyceraldehyde) will give the key point for the detailed mechanism of lignocellulosic biomass conversion in hydrothermal gasification. This study will also be discussed in this research.

First study discussed new application of supercritical water gasification to palm oil mill effluent. The effect of temperature and residence time on the product of gas composition and reaction kinetics of carbon conversion were studied in detail. Palm oil mill effluent was gasified in a continuous flow reactor under supercritical conditions. The reactor was made of SS316 steel (inner diameter 2.17 mm, outer diameter 3.18 mm, and length 12 m). The reaction temperature was set to 500, 550, and 600 °C and residence time 5, 10, 20, 30, 40, and 50 s, while reaction pressure was controlled at 25 MPa. Results show that carbon balance yield confirmed the reliability of the data. Major gas products found were H<sub>2</sub>, CO<sub>2</sub>, CO, and CH<sub>4</sub>. A methanation reaction occurred, as shown by the increment in CH<sub>4</sub> with temperature and residence time. The reaction model was developed for carbon behavior. The kinetic parameters of POME gasification were determined by employing least square error (LSE). The reaction model expressed the experimental results well.

The new application of supercritical water gasification to palm oil mill effluent also studied the behavior of phosphorus during SCW in parallel with gasification process. The gasification and phosphorus recovery experiment were carried out simultaneously. The effect of temperature and reaction time on phosphorus behavior was then determined. The results indicated that temperature affects the phosphorus conversion. There were three kinds of phosphorus elucidated in this study, namely organic phosphorus (LOP), inorganic phosphorus in liquid phase (LIP), and remaining inorganic phosphorus (rIP). The reaction network developed shows that LOP is converted to LIP first, and then when the

concentration of LIP reaches its saturation point, it is converted to solid precipitates (rIP). The behavior of phosphorus conversion was determined to be first-ordered and obeyed Arrhenius law. The reaction of LOP to LIP is slower than that of the LIP to rIP. The reproducibility of experimental data by calculation results was achieved.

The challenges to enhanced the gasification efficiency and possibility of separation phosphorus as precipitation could be accommodated via various technics. One of them is by modulating the heating rate. In this study, variation of preheater lengths 1,2 and 4 m were employed to modulate the heating rate. The temperature was set at 600 °C and a pressure of 25 MPa. Two variations of flowrates were used 2 and 3 g/min. Results show that shorter preheater has faster heating rate. The heating rate had a greater influence on POME decomposition. These results indicated that the primary reactions of this process were completed within the preheater. The organic phosphorus in the POME was completely transformed into inorganic phosphorus, with a significant amount being precipitated as rIP in the reactor. A higher heating and flow rate resulted in less rIP precipitation, suggesting that IP precipitation is a slow process and is dependent on residence time within the reactor.

At last, in the supercritical water gasification of biomass compounds such as glucose and xylose, the retro aldol condensation reaction was dominant. Furthermore, the retro-aldol reaction was found to occur via a radical reaction in hydrothermal conditions. However, common knowledge stated that retro-aldol reaction is known as ionic reaction. To elucidate the correct mechanism, glyceraldehyde, the simplest sugar to undergo retro-aldol reaction was employed in this study. It was dissolved in deionized water and then heated to 350–450 °C at a fixed pressure of 25 MPa in a continuous reactor. The reaction rate of glyceraldehyde followed Arrhenius's Law, irrespective of subcritical or supercritical temperatures. The Arrhenius plot of the retro-aldol reaction was a straight line for both the sub- and supercritical water regions. Thus, the retro-aldol reaction of glyceraldehyde under hydrothermal conditions is a radical reaction.