

# Hot Compressed Water Treatment of Biomass

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The aim of this work is to compare the effect of reaction conditions on the products obtained by supercritical water treatment of different biomass feedstock such as phyto mass and zoo mass in a batch reactor at 500°C, 30 MPa and 1 h of reaction time. The glucose / K<sub>2</sub>CO<sub>3</sub> system is selected as a model for the phyto mass. Since cellulose is the main unit of most biomass feedstock and the hydrolysis of cellulose to glucose is rather fast, glucose was selected as a model compound. The chemistry of glucose degradation is easier to observe than the degradation of biomass, so the model compound helps to identify the main reactions of biomass degradation during the gasification.

## INTRODUCTION

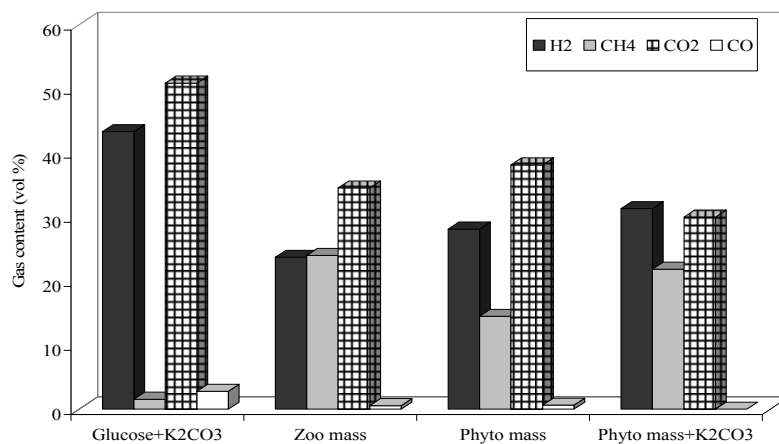
To understand better the nature of biomass hydrolysis, several studies on the real and model biomass conversion in supercritical water were reported [1, 2]. First experiments to convert carbohydrates to liquid products in hot compressed water were performed by Modell in the mid 1970s at MIT [3]. Systematic experimental investigations for the conversion and gasification of biomass, for waste model compounds and for real wastewater under hydrothermal conditions were conducted at the PNL (Pacific Northwest Laboratories) and at the University of Hawaii. In addition, in the Karlsruhe Research Center numerous experiments with model compounds and with real biomasses were performed in supercritical water [4,5]. This study aims to compare the some of the reaction products obtained by different biomass feedstock and Glucose / K<sub>2</sub>CO<sub>3</sub> system selected as a model for the phyto mass. Since glucose is the main unit of the carbohydrates in most biomass feedstock, it was selected and used, as a model compound to monitor biomass behaviour during the gasification. Real biomass consists of many salts, minerals etc. acting catalytically during the

conversion. In order to give a realistic response to the questions arising in the biomass conversion process,  $K_2CO_3$  is also added to Glucose. The  $K_2CO_3$  is used as a substitute for the minerals in real biomass.

## MATERIALS AND METHODS

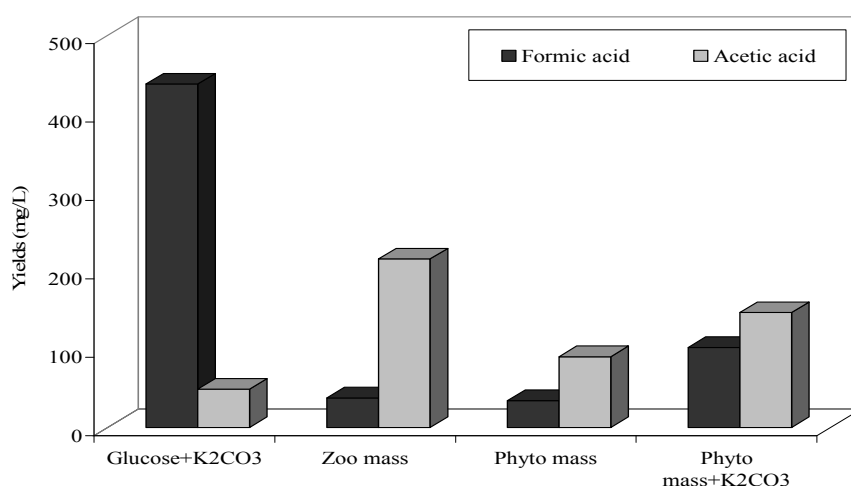
The batch reactor used for the experiments has an internal volume of 1 L and is constructed for a pressure of up to 500 bar and a temperature of up to 500°C. All experiments are conducted at 1 h of reaction time, 30 MPa and 500 °C. Glucose with  $K_2CO_3$  is taken as a reference feedstock, which is compared with two different biomass feedstocks. One is a biomass originating completely from plants (phyto mass) nearly without proteins, the second includes meat (zoo mass). Glucose (5 wt %) and  $K_2CO_3$  (0.5 wt %) are supplied by Merck. The phyto mass used in the experiments was a finely chopped mixture of carrots and potatoes (baby food by Hipp Co.).

## RESULTS



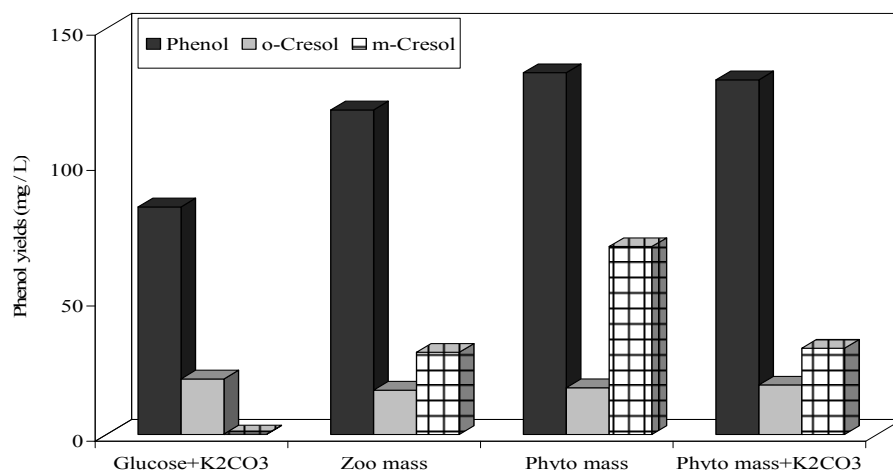
**Figure 1.** Gas products obtained by hydrolysis of various biomasses and the Glucose/ $K_2CO_3$  system at 500°C and 30 MPa

Figure 1 shows the gas composition evolved during the hydrothermal treatment of zoo mass, phyto mass, phyto mass/ $K_2CO_3$  and Glucose/ $K_2CO_3$ . The increased yields of  $H_2$  and  $CO_2$  in the case of phyto mass comparing to zoo mass might be related to the protein content of zoo mass. As explained by Kruse et al. [5], carbohydrate gasification can be influenced by the presence of proteins: Proteins hydrolyze fast to amino acids, which further degrade to amines. These amines may react with carbohydrate degradation products via a Maillard reaction. By this reaction heterocyclic compounds were formed which can easily further react to relative stable free radical ions. These compounds can inhibit free radical chain reactions as so-called free radical scavengers. Most of the gases are formed by free radical reactions, and therefore, amino acids or proteins reduce the gas formation.



**Figure 2.** Acetic acid and formic acid content of aqueous phases for the hydrolysis of various biomasses and Glucose/ $K_2CO_3$  system at  $500^{\circ}C$  and 30 MPa

Acetic and formic acid are important key compounds because they are direct precursors of gaseous products and their concentration in the aqueous phases obtained by hydrothermal conversion of feedstocks are shown in Figure 2. The formic acid yields in the case of phyto mass, zoo mass and phyto mass/ $K_2CO_3$  system are much lower than that obtained by Glucose/ $K_2CO_3$  pointing to an enhanced reaction rate of the water-gas shift reaction in case of the biomasses. Nevertheless, the produced relative  $H_2$  and  $CO_2$  amounts in the case of biomasses are lower than that obtained by Glucose/ $K_2CO_3$ . One possible explanation for this, at the first view, contradictive observation, is that alkali salts are more than a catalyst. It is possible that the formation of  $HCOOK$  not only leads to an increase reaction rate of the water-gas shift reaction but also shifts the equilibrium. Acetic acid is produced with higher yield in the case of biomasses comparing to the Glucose/  $K_2CO_3$ . In regard of the lower gas yield of the biomass compared to Glucose/ $K_2CO_3$  and the very low methane yield in Glucose/ $K_2CO_3$  in the acetic acid formation pathway: The formation of acetic acid and the consecutive production of methane seems to be more favored in the biomass than the model system. It is possible that the presence of salt unequal potassium compounds supports the acetic acid formation in real biomass leading also to higher methane yields.



**Figure 3** The amount of phenol and phenol derivatives found in the aqueous phases collected after the hydrolysis of various biomasses and Glucose/K<sub>2</sub>CO<sub>3</sub> system at 500<sup>0</sup>C and 30 MPa

The phenol yields in the aqueous phase obtained by all feedstocks are given in Figure 3. In the case of phyto mass, more phenols are generated comparing that obtained by the other biomasses and the Glucose/K<sub>2</sub>CO<sub>3</sub> system.

In the case of biomasses, Phenol and m-Cresol yields are increased because of the salts in biomass comparing to the Glucose/K<sub>2</sub>CO<sub>3</sub> system. A possible explanation would be that alkali salts lowers the activation energy of the phenols formation by di- or trimerisation from smaller compounds by complex formation. In this case, also the reverse reaction, the degradation of phenols should be supported by alkali salts.

## CONCLUSION

Free radical reactions and the influence of polar substances like salts should be considered in view of the gas production during biomasses and Glucose/ $K_2CO_3$  system. Acetic acid and formic acid are important key compounds, because their degradation leads to the gas production in the case of all feedstocks. Differences in the concentration monitor changes in the reaction pathways for gas formation. The degradation of phenols to gases occurs via acids and aldehydes and is strongly influenced by potassium salts, e.g. via complex formation.

## ACKNOWLEDGEMENT

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