HYDROTHERMAL BIOMASS GASIFICATION: NEW RESULTS ON THE ROLE OF WATER AS REACTANT

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Energy produced from biomass may contribute in a considerable amount to the growing future energy demand. A large portion of biomass wastes is wet biomass containing up to 95 % water. This wet biomass causes high drying costs if classical gas phase gasification or liquefaction processes are used. This can be avoided by using a gasification or liquefaction in near- or supercritical water.

In order to optimize the gasification process in supercritical water (SCW) an improved knowledge of the chemical process is necessary. Here the role of water is of special interest, because it is a process in water. In spite of the relative high temperature of up to 600 °C, the hydrothermal gasification is a process highly determined by chemical kinetics and the presence of water support the gasification. That is why dry processes need a much higher temperature.

In the hydrothermal gasification water is reactant, e.g. in hydrolysis reactions, and solvent. Both roles influence the reaction strongly. The key reaction of hydrothermal gasification is the water-gas shift reaction ($CO + H_2O \Leftrightarrow CO_2 + H_2$) also a reaction with water, leading to the high hydrogen yield and influencing various reactions, especially if

- Alkali salts catalyses the water-gas shift reaction
- reactors with strong back influences leads to a reaction of active hydrogen with early intermediates

The reaction of hydrogen formed via the water-gas shift reaction can be shown by the reaction of deuterated glucose in water.

INTRODUCTION

The water contained in the biomass acts as both reaction medium and reaction partner during gasification in supercritical water. Under the reaction conditions, the biomass reacts with water, thus forming hydrogen and carbon dioxide. About half of the hydrogen formed originates from the water. The – stoichiometrically possible - maximum hydrogen yield from biomass may be formulated as follows when using glucose as a model substance for the biomass:

$$C_6H_{12}O_6 + 6\ H_2O \rightarrow 6\ CO_2 + 12\ H_2 \tag{1}$$

Mostly, the hydrogen yield is smaller, as varying amounts of methane are formed depending on the reaction conditions and the initial substance used.
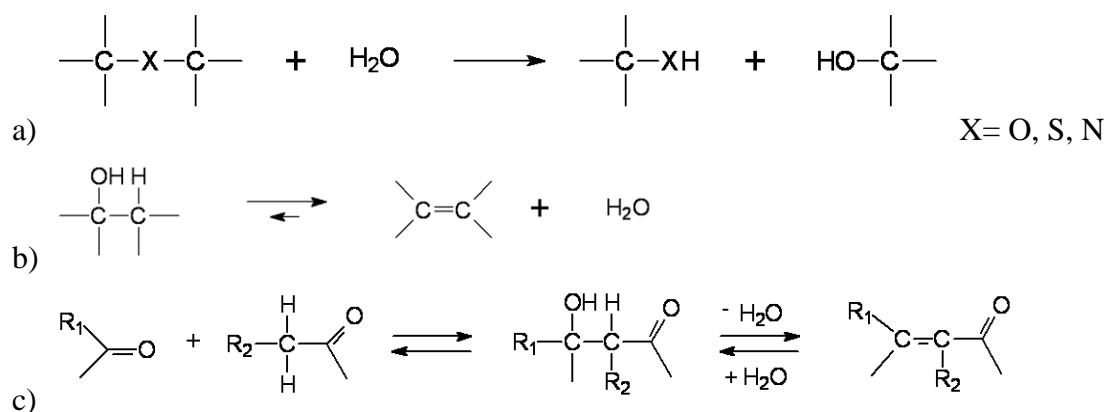
Figure 1: Reactions of biomass, biomass model compounds and their consecutive products accelerated in near-critical water: Hydrolyses (a), water elimination (b), aldol cleavages, and aldol condensations (c).

The properties of near-critical and supercritical water differ from of those of water under normal conditions. In addition, they vary strongly as a function of temperature and density. At increased temperatures and below the critical point, for instance, the ion product of water is higher by about four orders of magnitude than under normal conditions. As a consequence, reactions that normally require the addition of either acids or bases now reach high reaction rates even without the above additions. As far as the conversion of biomass is concerned, this means that e. g. hydrolyses, water cleavages, aldol cleavages, and aldol condensations (see Fig. 1) take place very rapidly in this range and lead to a large number of products. Above the critical point, the relative static dielectricity constant decreases very strongly. Here, water possesses the properties of a non polar solvent. For this reason, gases and most organic substances are dissolved excellently in supercritical water, while salts are less soluble. These special properties result in a number of advantages of gasification in supercritical water as compared to "dry gasification processes":

1. Less tar and coke are formed. As the biomass is decomposed very rapidly by hydrolysis and the cleavage products of the biomass are dissolved in the supercritical water, less polymerization reactions take place than in the solid-gas systems obtained from dry processes. In the latter case, the local concentration of polymerizable substances on/in the solid is very high. Accordingly, they may polymerize very rapidly.
2. At very small CO contents (typically < 1 vol.% of the product gas), a high H_2 yield can be reached. This is a result of the reaction of the biomass with water at a high water excess (see above).
3. H_2 may be obtained under pressure. It is not necessary to compress H_2 e.g. for transportation.
4. CO_2, the second main product apart from H_2, can be separated easily, as the solubility of CO_2 in water under pressure and at room temperature is much better than the solubility of H_2.
5. The high space-time yield results from the use of a high-pressure process with an accordingly increased density and from the high reactivity of the biomass under these conditions.
6. No drying of the "wet biomass" is necessary.

7. Inorganic constituents are not volatile, but remain in the aqueous solution. This prevents corrosion effects along the gas path, which were found to be very problematic when using dry processes with salt-rich biomass [1,2].

It is clear that the water-gas shift reaction is necessary to get high hydrogen yield and low CO yields as usually observed in supercritical water gasification of biomass [3,4]. Another aspect is the consequence of the water-gas shift reaction during the process. It is observed that the reaction order is respect of the initial concentration or biomass dry matter content changes from a tubular reactor to a CSTR [5]. This was explained by the reaction of hydrogen formed via the water-gas shift reaction with intermediates inhibiting polymerisation reaction. The goal of this work is to prove this type of reactions.

EXPERIMENTAL

The experiments were conducted in a 1L tumbling batch reactor, with a liner made of Inconel 625 (for details see [6]). The heating rate was 3 K/min. up to 500 °C. The reaction time at 500°C was 60 min. At these conditions, the pressure was around 30 MPa. Here, normal glucose [0.16 % (g/g)] or deuterated glucose [Fig. 2, D-*Glucose*-1,2,3,4,5,6,6-*D7, 97% atom% D by Sigma-Aldrich, CAS:* 23403-54-5; 0.16 % (g/g) in the feed], as well as in both cases $KHCO_3$ [0.016 % (g/g)] are solved in water and used as feedstock.
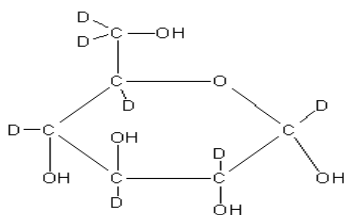
Figure 2: Deuterated Glucose

RESULTS

Figure 3 shows the identified products found by SPE-GC-MS [7] with the most likely position of deuterium. These are highly deuterated 3-methyl-2-butanon (1), hydroxyaceton (2), toluene (3), three different cyclopentanones (4-6) and three different phenols (7-9). In the case of carbon-carbon-double bonds, the carbon is connected to deuterium. In the case in which more than hydrogen is bonded to a carbon, at least one is deuterium and one is light hydrogen.
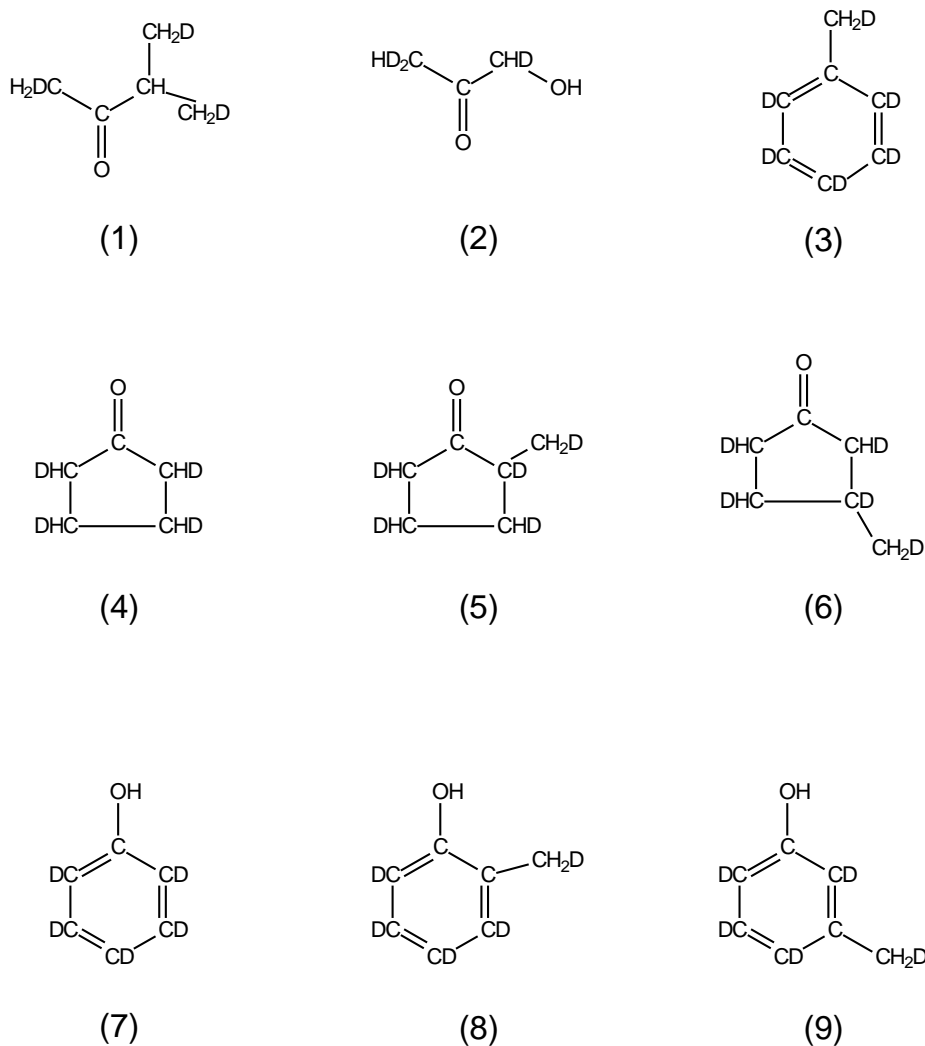
Figure 3: Identified deuterated products with most likely position of deuterium.

DISCUSSION

The products identified after conversion of glucose (Fig. 3) are no primary products. The products show still the C-D-bonds pointing to its origin from deuterated glucose. In product (1), methyl-butanone, one carbon atom is not bonded to a deuterium atom but instead to light hydrogen atom. This hints to hydrogenation step. A possible reaction pathway is shown in Fig. 4: Butanone, a degradation product of glucose (e.g. [4]), and formaldehyde (see e.g. [8]) reacts via aldol condensation. These compounds posses, if they are originating from deuterated glucose at least one deuterium atom bonded to each carbon atom. The double bond formed is than hydrogenated by H_2 formed by the water-gas shift reaction.

In addition, the relative high H-content of the cyclopentanones (4-6, Fig. 3) are a consequence of the hydrogenation of double bonds with H2, formed via the water-gas shift reaction.
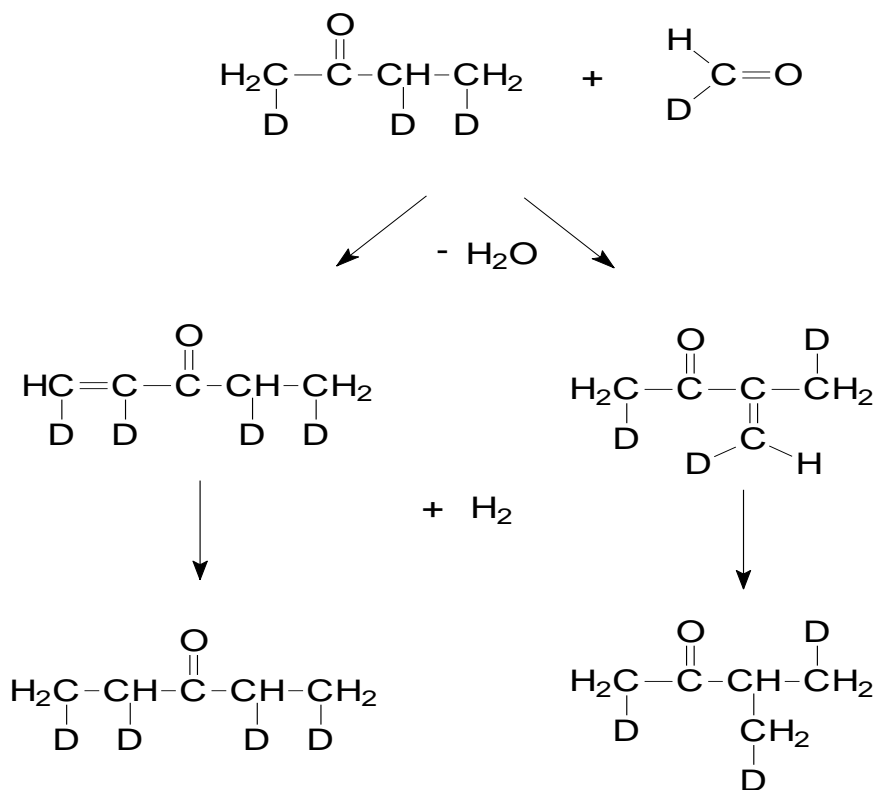
Figure 4: Reaction of butanone with formaldehyde

CONCLUSION

The C-D bond of the glucose is still found in the consecutive products like phenols. In addition, products formed by hydrogenation with H_2 from prior intermediates were detected. H_2 is formed via the water-gas shift reaction. This proves the assumption that hydrogen formed via gasification and reaction with water by the water-gas shift reaction is able to react with intermediates [5].

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