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Water – A magic solvent for biomass conversion

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ABSTRACT

Hydrothermal biomass conversion processes provide the opportunity to use feedstocks with high water content for the formation of energy carriers or platform chemicals. The water plays an active role in the processes as solvent, reactant and catalyst or catalyst precursor. In this paper, the different hydrothermal processes of carbonization, gasification and liquefaction are introduced and the specific role of water is discussed for each of them. The high reactivity of the polar components of biomass in hot compressed water and its changing properties with temperature are the key to obtain high selectivities of the desired products. Despite the obvious advantages of hydrothermal conversion examples for industrial applications are rare. The main reason for not commercial application of water in the high temperature state is that there are no products that can be sold with profit and cannot be produced cheaper, with less capital risk, and with more simple processes.

1. Introduction

Hydrothermal biomass conversion processes are interesting techniques to produce renewable solid, liquid/tarry or gaseous fuels. The most important advantage of hydrothermal processing is that wet biomass, typically with 70 wt.% or more water can be converted without drying. Drying of biomass to optimal water contents below 10 wt.%, as necessary for "dry" biomass conversion processes, costs substantial amounts of energy [1]. Therefore, hydrothermal conversions are attractive to extent the resource base for bioenergy production. The reason why no drying is necessary is that hydrothermal processes are conducted in liquid water. The water inside the biomass is the same component as the solvent. In addition the reaction is supported by water as catalyst or catalyst precursor as well as reactant. Every particular role of water is connected with the special properties of superheated liquid water above 100 °C [2–6]. The reaction temperatures are above 100 °C; therefore, hydrothermal processes require a pressure above the vapor pressure of water at the corresponding temperature to keep water in its liquid phase. This means that hydrothermal processes are chemical reactions in a solvent; in this case a solvent changing its properties depending strongly on temperature. As a consequence the chemical processes are influenced by the different solvent properties depending on reaction conditions. By adjusting the reaction parameters the reactions can be tuned selectively to obtain different products, namely solids (biochar), liquids, or gases (methane and hydrogen).

2. Overview of hydrothermal conversion processes

The hydrothermal processes can be assigned in terms of reaction temperature and, accordingly, pressure (see Fig. 1). At relatively low temperatures pretreatment methods are conducted. The most important one is "steam explosion" [8,9]. Here, the biomass is heated up under pressure typically to 140–240 °C. Then, the pressure is reduced rapidly to ambient pressure e.g. by opening a valve. The water inside the biomass evaporates thereby disrupting its structure like in an explosion. This way the cellulose and the lignin, covering it, are separated. This is important because in non-treated biomass this lignin protects the cellulose fibers against attack of enzymes, solvents or other agents. Therefore, steam explosion is a useful pretreatment method e.g. for bio-ethanol production from lignocelluloses by fermentation. By this pre-treatment, the yield is increased because of the higher reactivity of cellulose [8,9]. This

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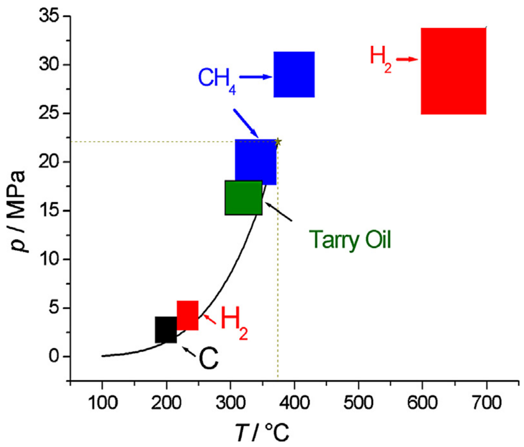

Fig. 1. Overview of different hydrothermal biomass conversion processes and the vapor pressure curve of water (simplified) [7].

points to an important aspect of hydrothermal processes: They can be combined with biological or biochemical processes because they are carried out in the same solvent [10]. Depending on the reaction conditions and especially in the case if acids are added the biomass is not only disrupted, but already partly hydrolyzed during steam explosion [11].

Hydrothermal carbonization (HTC) occurs at around 200 °C. Here, the carbohydrates are completely solved after hydrolysis and polymerize subsequently to a product called “HTC-coal”. The process usually needs 2–4 h reaction time and has been demonstrated with a lot of different types of biomass [12–17]. This “HTC coal” has a heating value similar to lignite, but with a higher content of volatile substances and a higher biodegradability in soil, which is important if it is used for soil improvement [18]. Here, the phytotoxicity of fresh HTC coal is an important issue to be considered, likely a consequence of water soluble products like phenols, which are adsorbed at the HTC coal surface [19]. The production of HTC coal overcomes three major disadvantages of untreated biomass as fuel:

A) The heating value of untreated biomass is low because of the high oxygen and water content. By the elimination of water (and smaller amounts of CO_2 [20]) the HTC coal has a higher heating value and lower oxygen content than biomass [14,16,17,21,22].
B) Mechanical dewatering of HTC products is very effective because of its highly hydrophobic properties. Studies with sewage sludge show, that the easier dewatering alone justifies hydrothermal carbonization as a first drying step. Thermal drying, usually applied as the second step, needs much more energy in the case of biomass, where mechanical dewatering leaves a lot of water in the material. On the other hand the water has to be removed to burn the biomass and to reduce transportation costs [12,23].
C) Biomass has a high potassium content. This leads to low ash melting temperatures, which makes burning more complicate. Special techniques are required to prevent corrosion and to handle the ash melt or the burning temperature is limited to below 600 °C. This is too low for efficient power generation, like in conventional power plants like pulverized coal firing systems with 1300–1500 °C. During hydrothermal carbonization the potassium is solved in the water. The lower potassium content in the ash leads to higher ash melting temperature of e.g. 1200 °C. This is similar to the ash melting temperatures of fossil lignite [13,24].

In regard of the aspects mentioned above, HTC coal is a more suitable energy carrier than untreated biomass. In addition, HTC coal can be modified to be used as adsorbent for organic compounds or as an ion exchanger [25,26]. In the case that not biomass [27,28], but pure compounds like glucose are used in the process, advanced materials like micro- or nano-spheres as well as nano-tubes can be produced [29]. At slightly higher temperature aqueous phase reforming (APR) can be performed by means of catalysts to produce hydrogen or hydrocarbons [27,28]. This process for hydrogen production is only possible at very low concentrations of the feed material because of thermodynamic limitation [30]. At higher concentrations methane is the thermodynamically favored product. For this APR process catalyst like Ni, Pt, Pd and others are used [28]. Since these are solid catalysts, they cannot work with solid biomass. In most cases hydrogen-rich, soluble compounds produced from biomass show the highest hydrogen yields. This process is therefore appears to be useful for aqueous effluents of other hydrothermal processes [31] or other aqueous effluents [32]. Poisoning and long term stability of the catalyst is often a challenge of this process [33]. The hydrogen produced can be used for hydrogenation of the feedstock to produce hydrocarbons [28] or to up-grade bio-oils [34]. For this process, in principle the same type of catalyst can be used as for hydrogen production before, but the selectivity varies [27,28]. After formation of hydrogenated products, other reactions like the formation of aromatic rings can be carried out [35]. Therefore, APR is discussed as process to produce a substitute for terephthalic acid.

In the temperature range between 300 °C and 350 °C hydrothermal liquefaction takes place [36–39]. The process is also known under the original SHELL trademark HTU$^{(r)}$ for “Hydrothermal upgrading” [40]. Here, the biomass is converted to a highly viscous tarry oil of a high heating value [1]. Some significant differences occur compared to the dry conversion technology, the flash pyrolysis. In hydrothermal liquefaction and at optimized conditions no solid product is formed. In flash pyrolysis the solid yield is usually in the range of 20 wt.%. Very short reaction times of a few seconds at 500–600 °C are necessary to reach high yields of pyrolysis oil of around 60 wt.%. This oil is an intermediate and longer reaction time would convert it to gas and solid. As a consequence very fast heating-up (ca. 1000 K/s) and rapid cooling down of the vapors formed during pyrolysis have to be realized. For hydrothermal liquefaction this is not necessary. No further reactions to solid or gaseous products occur at reaction conditions, with much lower temperature. The heating value of the hydrothermal liquefaction product (30–36 MJ/kg) is much higher than that of pyrolysis oil (20–25 MJ/kg). The reason is that pyrolysis oil includes a wide range of polar compounds like acids, alcohols, aldehydes and even sugars. In addition, ca. 15–20 wt.% of water is formed during pyrolysis that is in the pyrolysis oil after cooling down. In hydrothermal liquefaction polar, oxygen-containing compounds are solved in the water and only the compounds of lower oxygen content, namely phenols are found in the oil phase [1].

A special issue of liquefaction is the decomposition of lignin [41]. Here the goal is to get phenols, e.g. for the production of resins. Lignin is less reactive as lignocellulosic biomass and requires therefore a temperature of around 400 °C and maybe the support of a catalyst.

Near the critical point of water there is the range of catalyzed gasification to produce methane. For this reaction noble metal catalysts are necessary [42–44]. The active metals are Ni, Rh, Pd, Pt, suitable for hydrogenation of e.g. CO to methane [43]. There are two approaches applying subcritical or supercritical[1] conditions. The subcritical approach has the advantage that salts are mostly solved and therefore plugging by salt precipitation is less likely [45]. The supercritical reactions have the advantage that organic

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[1] The term “sub- or supercritical” here refers, as usually done, to the critical point of water as the solvent. This does not mean that the mixture is supercritical in the sense that pressure and temperature are above the critical point of the mixture.