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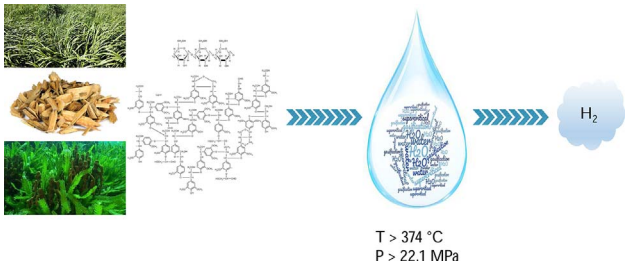
Review

Supercritical water gasification of biomass for hydrogen production – Review☆

Catalina Rodriguez Correa, Andrea Kruse*

University of Hohenheim, Institute of Agricultural Engineering, Department of Conversion Technology and LCA of Renewable Resources, Garbenstrasse 9, 70599 Stuttgart, Germany

GRAPHICAL ABSTRACT



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ABSTRACT

The paper summarizes the recent developments in the field of supercritical water gasification (SCWG) of biomass. Chemical and chemical engineering studies are introduced and sorted into categories, which are the main factors influencing the chemical reaction pathways of SCWG. These are: the components of biomass (carbohydrates, lignin, ash, proteins and lipids), reaction conditions e.g. concentration and the possible addition of heterogeneous catalysts. Most studies focus on model compounds, here the interference of the components in mixtures give a deeper understanding in view of the conversion of real biomass. Also studies with biomass are reported; here in most cases the effect of salts, catalyzing hydrogen formation, is dominating. The progress in knowledge is evaluated in view of the hurdles to overcome for a wide industrial application. Recent paper hints to a future of hydrothermal gasification as part of a bio-refinery and with an internal use of hydrogen produced.

1. Introduction

In the past decade, it has been consistently shown that a hydrogen economy is one of the most promising alternatives to reduce greenhouse emissions to almost zero, especially if the production source is renewable (e.g. biomass or water). However, this concept has lost momentum due to a lack of hydrogen gas availability and the hurdles that need to be overcome concerning production, storage and utilization technologies [1]. On the other hand, hydrogen still plays a crucial role in the current economy in processes such as ammonia production and petroleum refining. Additionally, in the context of bio-economy hydrogen is also indispensable to increase the H/C ratio of biomass in order to convert it into biofuels similar to petroleum [2]. Traditional ways to produce hydrogen are steam reforming, partial oxidation (gasification) or pyrolysis of fossil or renewable sources. Another available technology is water electrolysis, however only a small percentage of the worldwide hydrogen production occurs this way because of its high energy demand. It is well known that global warming and the depletion of fossil sources are problems that need to be urgently addressed. For this reason, the use of biomass or biomass byproducts (e.g., lignin) has

☆ In Memory of Michael J. Antal.

* Corresponding author.
E-mail address: andrea_kruse@uni-hohenheim.de (A. Kruse).

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been proposed as an alternative solution. Due to its renewable nature, biomass has high potential for hydrogen production. Hydrothermal gasification of biomass involves the splitting of organic compounds with supercritical water. This is described in Eq. (1) as the ideal case of complete conversion to hydrogen with glucose as model compound for biomass. Primarily, carbon monoxide is formed, which reacts with water to carbon dioxide and hydrogen (Eq. (2)). The equilibrium of the water gas shift reaction is shifted towards the hydrogen side due to the presence of large water quantities. This means that water is an important reactant, not only in reaction (2) but also for the hydrolysis of biomass to glucose. The water gas shift reaction is kinetically inhibited but this can be overcome with alkali metals, which act as catalysts for this reaction [3–6]. Hydrogen formation is favored at temperatures significantly larger than the critical point of water (T_c = 374 °C and P_c = 22.1 MPa) because of its endothermic nature [7]. Reactions (1) and (2) consume water, therefore – according to the Le Châtelier principle – are favored at high dilution conditions. Consequently, at very low feedstock concentrations (e.g. 1 wt.%), hydrogen formation is also possible at rather low temperatures. This effect is used in *Aqueous Phase Reforming* in the presence of nickel or other noble metal as catalyst. The presence of a solid catalyst limits the use of solid biomass, because biomass hydrolysis at these temperatures is rather slow. Only if dissolved organic compounds like model substances (e.g. glucose, sorbitol or glycol) are used as feedstock, significant amounts of hydrogen are attainable [8,9].

At temperatures near to the critical point of water, methane is the preferred product. Methane and carbon dioxide (Reaction (3)) are thermodynamically favored at lower temperatures and higher concentrations or biomass dry mass content [7]. At temperatures around the critical point, water hydrolysis and CO formation are fast enough to enable the hydrogenation of CO on a solid catalyst (Eq. (4), [10]). This reaction needs typical hydrogenation catalysts like nickel or other noble metals, which also catalyze the reverse reaction depending on the equilibrium conditions. Therefore, the same hydrogenation catalysts (e.g. Ni, Rh, Pt) that are useful for CO hydrogenation to methane, are also useful for the hydrogen formation from hydrogen-rich compounds used in *Aqueous Phase Reforming* (Reaction (4)).

$$C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 12H_2 \quad (1)$$

$$CO + H_2O \rightleftarrows CO_2 + H_2 \quad (2)$$

$$C_6H_{12}O_6 \rightarrow 3CH_4 + 3CO_2 \quad (3)$$

$$CO + 3H_2 \rightleftarrows CH_4 + H_2O \quad (4)$$

Hydrothermal gasification is a biomass conversion process that takes place at significantly higher pressures (approximately 30 MPa) but relatively lower temperatures (around 600 °C) than to reforming and dry gasification (800–1200 °C). Also, it makes use of water as reaction medium; therefore, it is compatible with wet biomass. Depending on the reaction temperatures, hydrothermal gasification processes can be divided into three sub-categories:

- Aqueous phase reforming (T = 215–265 °C) – Main products: H_2 and CO_2. When using biomass derived compounds (glucose, sorbitol, glycerol, methanol, and glycol) under subcritical conditions, it is thermodynamically possible to obtain hydrogen if the feedstock concentration is very low (around 1%), however the hydrolysis of biomass is slow. Noble metal catalysts are necessary for the hydrogen formation. High molecular weight constituents like lignin or cellulose are difficult to gasify in this way [11–13].
- Near critical[1] catalyzed gasification (T = 350–400 °C) – Main product: CH_4. Biomass or biomass compounds are gasified at near critical gasification conditions to obtain high degrees of carbon conversion to methane. Catalysts help to enhance the methane formation from CO hydrogenation [14].
- Supercritical water gasification (SCWG; T > 374 °C) – temperatures higher than 500 °C are usually employed to obtain H_2 and CO_2 as main products. This process show high conversion rates; however, it is highly dependable on factors like operation conditions, feedstock, the nature of the catalyst (if used) or the reactor design. The gaseous products obtained from SCWG are mainly H_2, CO_2 and, in lower but varying amounts, CH_4 [15]. Short-chain hydrocarbons, such as ethane, ethene, propane and propene, as well as CO are found in small amounts, since CO is partially consumed by the water shift (Reaction (2)) and, if a catalyst is present, by methanation (Reaction (4)) reactions.

By considering the main global reactions and equilibria involved in the production of hydrogen and methane, it becomes obvious that the most important criteria that influence biomass gasification are:

1. Temperature: Higher temperatures favor hydrogen and lower methane production.
2. Biomass to water ratio (usually expressed as dry matter content).
3. Catalysts; for promoting Reactions (2) and (4) or to avoid unwanted side reactions.

Biomass consists of many different components; therefore, it is a complex task to understand their influence on biomass gasification. As it was previously stated, hydrogen is crucial for the development of a bio-economy. In this scenario, biomass is not only used to produce hydrogen with a low CO_2 print but also the hydrogen and the biomass is used to produce bio oil. This review covers some of the older key studies as well as several earlier reports [16–26] to contextualize the fundamentals of SCWG of biomass. In addition, the knowledge is updated by incorporating recent literature.

2. Influential factors on the hydrogen production in supercritical water gasification

2.1. Biomass composition and structure

Lignocellulose is the abundant construction material of the cell walls of all terrestrial plants and contributes almost 90% to the available land biomass. Its use in form of agricultural, forestall and industrial residues and wastes is not in direct competition with food and feed production; therefore, it is a versatile feedstock to produce second-generation biofuel. The simplified average composition of lignocellulosic biomass consists of 40–55 wt.% cellulose fibers and 15–35 wt.% hemicellulose embedded in 20–40 wt.% of lignin represented by $C_6H_8O_4$ as approximate sum formula. Most of the cellulose in biomass is crystalline and a small portion is amorphous. Crystalline cellulose is built up by 5000–15000 glucose units β-1,4 glycosidic and hydrogen bonds. Amorphous hemicellulose consists of branched C_5- and C_6-sugars (xylose, manose, arabinose, glucose and galactose) linked by β-1,4 glycosidic bonds with a polymerization degree of 100–1000. The most abundant sugar unit in hemicellulose differs depending on the type of biomass. In the case of softwood glucomannan, a polymer composed of glucose and manose, is more abundant and in hardwoods glucuronoxylan predominates [27]. Lignin is composed from *p*-Hydroxy-propyl-benzene structures, namely *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol, which are connected by ether and C—C bonds to build a three-dimensional network. The proportion of these units vary from species to species: grasses consist of *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol units; softwood lignins are mostly conformed by coniferyl alcohol, and that from hardwoods is rich in coniferyl alcohol and sinapyl alcohol units [28]. In addition, varying amounts of moisture, inorganic ash and other constituents like proteins

[1] The terms „sub-critical“, „near critical” and “supercritical” refers to the critical point of water not of the mixture.

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