Catalysis Today 247 (2015) 33–46

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

The role of water in catalytic biomass-based technologies to produce chemicals and fuels

László T. Mika [a,b], Edit Cséfalvay [a,b], István T. Horváth [b,*]

[a] Department of Chemical and Environmental Process Engineering, Budapest University of Technology and Economics, Budafoki str. 8, H-1111 Budapest, Hungary
[b] Department of Biology and Chemistry, City University of Hong Kong, Tat Chee Avenue 83, Kowloon, Hong Kong

ARTICLE INFO

Article history:
Available online 4 January 2015

Keywords:
Water
Biomass
Hydrolysis
Hydration
Dehydration
Deoxydehydration

ABSTRACT

Water can have many different roles in catalytic biomass-based technologies to produce chemicals and fuels. Since water is one of the two basic chemicals of nature used during photosynthesis, biomass contains different amount of water, which can be advantageously utilized during the conversion schemes. Water could be the solvent of the reactions or just either the eliminated product or the reactant resulting in hydration and hydrolysis. Since some of these roles are intrinsically part of the natural system, their change could be very difficult or not even possible. Therefore, the designer of the chemistry or the process must understand the possible roles of water at both the molecular and the macroscopic levels.

1. Introduction

Water is one of the most abundant molecules on Earth which has its own global cycle [1]. It plays many important roles by providing a very stable and mostly neutral medium for life [2], serving as solvents for many different reactions, and participating in a large number of chemical transformations [3,4]. The water cycle involves a continuous global distillation process resulting in two distinct aqueous environments having higher and lower level of dissolved salts – 96.5% salted water and 2.6% fresh water. While the salted water in the oceans and seas contains dissolved sodium chloride and some other salts that make it useless for human consumption, fresh water in our rivers and lakes generally contains much less salts and other solutes. Consequently, evolution has adjusted the chemistry of the living habitats of the two different aqueous environments [5]. Unfortunately, human activities have increased the levels of dissolved man-made contaminants, including inorganic and organic chemicals and materials, which could have very negative health and environment effects. The societal acceptance of the potential negative impacts of “dirty water” [6] and the recognition of the important role of pollution prevention or “green chemistry” [7], we are discharging less and less contaminated water to the environment because of the increased use of cleaner technologies as well as closed waste water systems combined with state-of-the art waste water treatment technologies.

Although the complete depletion of coal, crude oil, and natural gas will probably take several centuries if not millennia, we should produce more and more carbon-based chemicals from biomass to slow the depletion of the fossil resources and use carbon neutral consumer products [8]. Interestingly, the largest component of biomass is water, which could be as little as few percent in an old tree, but as high as 80% of corn kernel or living cells [9]. If our drive to use biomass-based technologies for the production of all carbon-based consumer products will be successful, the volume of water from converted biomass could be large enough to consider it for the production of drinking water. Because of the aqueous nature of biomass, most of the molecules involved are highly functional and many have oxygen-containing functional groups. This can be simply demonstrated by carbon, hydrogen, oxygen, and nitrogen content of the dry matter of biomass and younger components of fossil resources (Table 1).

Conventional productions of carbon-based chemicals and fuels are based on the separation of saturated and aromatic hydrocarbon constituents of fossil resources followed by the introduction of oxygen, nitrogen, and sulfur containing functional groups. In contrary, most of the components of biomass are multifunctional and their conversion to chemicals and fuels require selective defunctionalization. One of the key strategies of the development of successful biomass-based chemical and fuel industry is how to match the properties of the components of biomass with proper

* Corresponding author. Tel.: +852 3442 7402; fax: +852 3442 0522.
E-mail address: istvan.t.horvath@cityu.edu.hk (I.T. Horváth).

http://dx.doi.org/10.1016/j.cattod.2014.10.043
0920-5861/

Table 1
Elemental composition of materials on dry weight basis.

	Carbon (wt%)	Hydrogen (wt%)	Oxygen (wt%)	Nitrogen (wt%)	Sulfur (wt%)	Ref.
Miscanthus fresh	47.3–47.6	5.77–5.95	42.1–43.5	0.33–0.45	0.05–0.08	[10,11]
Switchgrass	43.5–47.5	5.75–6.18	37.57–44.82	0.36–0.77	0.04–0.19	[12,13]
Sorghum stalk	40.0–46.1	5.20–5.76	40.63–40.70	0.39–1.40	0.20–0.27	[14,15]
Sugar cane bagasse	48.6	5.87	42.85	0.16	0.04	[12]
Wheat straw	42.9–47.6	5.11–5.8	40.39–42.41	0.43–0.73	0.09–0.29	[16,17]
Straw (average)	45–47	5.8–6.0	40–46	0.4–0.6	0.05–0.2	[18]
Corn stover	42.60	5.06	36.52	0.83	0.09	[18]
Bark	48–52	5.7–6.8	24.3–40.2	0.3–0.8	< 0.05	[18]
Forest residues	48–52	6.0–6.2	40–44	0.3–0.5	< 0.05	[18]
Wood without bark	48–52	6.2–6.4	38–42	0.1–0.5	< 0.05	[18]
Peat	52–56	5.0–6.5	30–40	1–3	0.05–0.3	[18]
Black coal	76–87	3.5–5.0	2.8–11.3	0.8–1.5	0.5–3.1	[18]
Lignite (North-Dakota)	31.80	4.51	26.35	0.59	0.84	[18]
Bitumenous coal (Pennsylvania coal)	83–89	4–6	3–8	1.4–1.6	1.4–1.7	[18]
Anthracite (Pennsylvania coal)	91–94	2–4	2–5	0.6–1.2	0.6–1.2	[18]

conversion technologies to produce the products with minimal structural changes and by energy efficient methods. For example, it seems counter intuitive to use vegetable oils for the production of a highly functionalized product and *vice versa* use carbohydrates for the production of alkanes.

2. Discussion

The production of biomass-based chemicals and fuels should consider the relationships of the chemical composition of the feedstocks and the product(s) including the molecular structure of their constituents. Water is an intrinsic part of biomass, which could be as little as few percent in an old tree, but as high as 80% in plants (Table 2) and living cells. Therefore, the overall efficiency of the conversion of biomass is highly dependent on how well can be matched its water content with the conversion technology, as the removal of excess water could be extremely energy demanding. In this chapter, we provide a short summary of the water content of various biomass resources; the pre-treatment processes involving water followed by the review of conversion opportunities using water as a solvent and/or as a reagent.

2.1. *Water contents of various biomass resources*

In general, grains with moisture contents from 12 to 22 wt% (based on wet weight) are mature enough to be harvested and dry enough for storage. While switch grasses and Miscanthus usually have lower, the stalk of sugarcane and sweet sorghum have significantly higher water content than grains. Stalks have 67–72 wt% water, which is frequently squeezed to form a “raw juice” resulting in an easily accessible sugar rich aqueous raw material.

With the exception of direct energy generation, the utilization of biomass often requires physical and/or chemical pre-treatment in order to modify advantageously the physical and/or chemical structures of the components. The most frequently used process is the hydrolysis, which converts polysaccharides to mono- and disaccharides. For the enzymatic conversion of the latter to ethanol [30,31], butanol and acetone [32], and lactic acid [33], higher moisture content could be an advantage since the enzymatic reactions are performed in aqueous environments.

Biomass wastes are generally classified into three main groups: forestry residues, agricultural residues, and food wastes (Table 3). Forestry residues are commonly divided into primary and secondary residues. Primary residues accruing from cultivation and secondary residues are produced by the wood processing industry. Although forest product industries could generate the same residues and they could have been used as raw materials, they are beyond the scope of this review.

While forestry residues are usually combusted in power generation plants, high water content of the biomass could have negative effects on the overall energy output [34]. Pre-drying of forestry residues can decrease the water content to the typical value of 8–10 wt% leading to better combustion properties. Alternatively, forestry residues with high moisture levels can be burned with coal [35].

Considering other types of utilizations such as extraction of cellulose and its conversion to sugar *via* hydrolysis [30], and anaerobic digestion to biogas [57], the water content is a required component in these technologies.

Agricultural residues are produced and collected at land fields. By far, the largest source of crop residues is the straw and stover from grain crops representing a wide range of moisture content. Those having higher moisture content are suitable for forage or fermentation. While dry biomass, such as straws, can be utilized *via* gasification or combustion to produce energy, wet biomass has been used for chemical transformations or fermentation to produce chemicals. Biomass with even high water and nutrient content is usually used for forage.

Animal excrements, manure and slurry can be considered as a significant part of agricultural residues [53]. Among the various livestocks, the largest population include swine, cattle and poultry, which generate an enormous volume of slurry and manure, for example, China’s manure production was 1900 million tons in 2010 [58]. The water content of slurry can be as high as 99.5 wt% so it is used for land applications in crop fields. (Table 4) [59]. Due to its nutrient content, solid manure can be dispersed on crop fields as fertilizer, however, its volume is influenced by physical, chemical and biological properties of the soil as well as local environmental standards [60]. Although surplus manure was treated as waste in the 1990s [60], its valorization has become an issue in the last two decades.

Additional treatment and utilization technologies are based on composition analysis (Table 5) including composting [63], anaerobic digestion, and co-composting with municipal wastes [64]. Since dairy cattle manure contains the highest level of lignocellulose, its hydrolysis to monosaccharides [65] is a possible form of utilization.

Food wastes can be produced before and during the preparation of meals as well as discarded in the manufacturing/production, distribution, wholesale/retail and food service sectors including restaurants, schools and hospitals. Food wastes consist of a broad range of chemicals and materials and moisture content could be as high as 70–80%.

While composting has become less important in the last two decades due to the large area requirements and VOC formation, the anaerobic digestion has gained increased attention as a better processing alternative for food waste aiming to produce biogas