J. of Supercritical Fluids 96 (2015) 46–52

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

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

Review

High pressure water reforming of biomass for energy and chemicals: A short review

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ARTICLE INFO

Article history:
Received 25 April 2014
Received in revised form 4 June 2014
Accepted 4 June 2014
Available online 11 June 2014

Keywords:
Sub- and supercritical water
Hydrothermal reforming processes
Glycerol
Sewage sludge
Biomass and organic wastes
Bio-oil

ABSTRACT

The conversion of different organic substances, including wastes, sludge, biomass to biofuels and biobased chemicals has attracted a lot of attention recently, largely due to the environmental and socio-economic problems associated with the use of fossil fuels.

In recent time many novel technologies have been introduced for conversion of biomass to energy and chemicals. Hydrothermal (HT) processes that use sub- or supercritical water as processing media are considered as promising technologies for the conversion of organic substances into biofuels and biobased chemicals.

A short review of the hydrothermal processes and potentials of their use for the conversion of organics wastes and biomass into fuels and chemicals is given.

Contents

1. Introduction

One possibility to implement green chemistry approach is to use water as solvent. This approach has received a great deal of attention in the last years due to the fact that water is an inexpensive, environmental benign and safe media and can be used in different processes, i.e. chemical synthesis, hazardous waste destruction and biomass processing, which includes biomass extraction to obtain valuable compounds and conversion of biomass into fuels and chemicals.

The literature review on subcritical water extraction of hydrophobic organic compounds from plants, soils and foods, the solubility of organic compounds in subcritical water and modelling the solubility data was published by Carr et al. [1].

Supercritical water (SCW) has received considerable attention especially as a reaction medium for reforming wastes and byproducts, being attractive from an environmental point of view. The method is suitable to convert very wet biomass and liquid streams and to obtain gases or other biobased chemicals. Therefore, residues from different industries can be further used to obtain value added products, thus avoiding the problems related to waste disposal. The

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http://dx.doi.org/10.1016/j.supflu.2014.06.008
0896-8446/

method has been investigated for wastes generated by a wide range of processes, such as domestic and industrial wastewater treatment, wastes from oil and biodiesel industry, wastes from food, biomass processing and chemical industry. Sub- and supercritical water reforming, often named also hydrothermal (HT) reforming, is based on the capacity of sub- and supercritical water to oxidize organic compounds, leading to the formation of bio-oils, smaller liquid compounds and gases. These HT reforming products can be further used as raw materials in chemical reactions or as energy carriers, thus improving the overall economic efficiency of the industrial process.

Processes involving supercritical fluids (SCFs) require less energy and are environmentally friendly compared to traditional processes involving organic solvents. This is due mainly to the advantages of SCFs associated with their physical and chemical properties, which allow processing at lower temperatures, and eliminate the need of energy-consuming stages for solvent separation. Still, it is clear that several SCF industrial applications may be often more costly than the conventional methods, mainly due to the specific equipment requirements and safety measures; however products with customer designed properties could be obtained, while the environmental impact is lower than in the case of traditional technologies. Moreover, SCF technologies can be also applied for energy production. Supercritical water reforming may contribute to the development of biomass as green alternative to the fossil fuels used today. Still it has to be considered that biomass, except for wood from sustainable forestry, is a poor renewable energy source. Its energy return on invested energy (EROI) is the smallest of all energy carriers, and the impact of its exploitation on biological diversity is often disastrous. However, according to new politics regarding the use of renewable resources for energy production, the relatively expensive technologies for biomass processing may be used as additional energy sources for meeting the excess demand during the periodic fluctuation of energy consumption.

The present paper is focused on the conversion of organics, wastes and biomass waste into fuels and chemicals by using high pressure water reforming, as sustainable alternative to traditional processing methods (pyrolysis, combustion, steam reforming, thermochemical conversion, digestion, composting, etc.).

2. Hydrothermal reforming processes

The production of biobased chemicals and energy carriers is considered to be carbon-neutral, since the CO_2 generated during processing can be absorbed by plants during their growth. Promising technologies for the conversion of biomass into biofuels and biobased chemicals are hydrothermal (HT) processes, which use subcritical (SubCW) and supercritical water (SCW) as processing medium.

In general, hydrothermal processes can be divided into four main processes, regarding the type of the product: HT carbonization, aqueous phase reforming, HT liquefaction, and HT gasification. The important advantage over other processing methods is the ability to use wet substrate without prior dewatering. Due to unique properties of water at elevated temperatures versatile chemicals and fuels in gaseous, liquid, or solid state can be produced. In these processes water may act as solvent, reactant or a catalyst.

During the treatment of biomass in sub- or supercritical water numerous reactions can occur parallel in the system, e.g. hydrolysis, dehydration, decarboxylation, aromatization, condensation, depolymerization/polymerization, hydrogenation/dehydrogenation, rearrangements, isomerization reactions, etc. Mechanisms of reactions in sub- and supercritical water have been reviewed by Kus [2], Jin and Enomoto [3], Yu et al. [4] and Brunner [5].

Table 1 summarizes the operating conditions of the main HT processes for biomass conversion and the main products obtained by the processes.

HT carbonization can be performed at high-temperatures (573–1073 K) or at low-temperatures (453–523 K) [6] and in both processes a carbonaceous material named hydrochar is produced. A high-temperature process is based on wet pyrolysis of biomass with or without the use of catalyst and produces various carbon structures (nanotubes, films, microspheres, fibres, etc.) [6], that possess various functional groups on their surface and can have high adsorption capacity. The hydrochar made by high-temperature HT carbonization of barley straw [7] and peanut hull [8] showed high adsorption capacity for the separation of metals from wastewater. By low-temperature HT carbonization, which is more favourable as high-temperature process, hydrochar with controllable morphology and surface functionality is synthesized through similar reactions as at high temperatures and is interesting for different applications such as for catalyst support, energy storage, drug delivery, and enzyme immobilization [6,9].

Aqueous phase reforming is a very promising route for the production of H_2 and alkanes from biomass, at relatively mild reaction conditions. It is a process in which biomass carbohydrates or biomass-derived alcohols (methanol, ethylene glycol, glycerol, and sorbitol) convert over appropriate heterogeneous catalysts at temperatures of 493–523 K and pressures typically of 1.5–5.0 MPa to produce primarily H_2 and CO_2 [10]. Concerns are related to detection of several side reactions that occur at these temperatures that produce alkanes, acids, aldehydes, and other liquid or solid products [11,12]. Identifying and improving the catalysts and catalyst support to increase H_2 yield are major concerns of a great number of research teams throughout the world [11]. The nature of the feedstock has also a strong influence on reaction selectivity. By using sugar alcohols as feedstock and by increasing the acidity of the metal catalyst, the aqueous phase reforming process is more selective for alkane production [11,13,14].

HT liquefaction is performed at medium temperatures and high pressures (523–643 K, 10–25 MPa) at which biomass hydrolyzes and decomposes to unstable small components, which further repolymerize and produce highly viscous water-insoluble bio-oil, water soluble substances, char, and light gasses. The reaction mechanism is influenced by temperature, pressure, reaction time, type of feedstock and catalysts. In general, both acids and bases catalyze liquefaction of biomass. Acids enhance production of water-soluble products such as sugars, carboxylic acids, furfural, and 5-hydroxymethyl furfural, whereas alkali salts enhance bio-oil yield and reduce residue formation at subcritical conditions [15].

Bio-oil (biocrude) is a hydrophobic mixture of over several hundred oxygenated compounds of various molecular weights, originating from the decomposition of three main constituents in biomass: cellulose, hemicelluloses, and lignin [16]. Although the product distribution in bio-oil varies with the composition of the raw material and process conditions, the same groups of compounds are detected in almost all bio-oils [17].

HT gasification is a process in which biomass reacts with water at high temperatures and pressures to form gaseous products, mainly CH_4, H_2, CO, CO_2, and C1–C4 carbon gases. As side products, also some bio-oil, char, and tar are formed, which decrease the yield of gases. HT gasification can be performed at low temperatures (573–773 K) and is named catalytic wet gasification (in sub- and near-critical water) or at high temperatures (773–1073 K) and is named supercritical water gasification (SCWG). In the catalytic wet gasification catalysts must be applied in order to enhance the conversion rate of biomass to gases and to increase the selectivity to CH_4, the dominant gas at lower temperatures. In SCWG, H_2 is the