



Review Paper

Applications of subcritical and supercritical water conditions for extraction, hydrolysis, gasification, and carbonization of biomass: a critical review

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HIGHLIGHTS

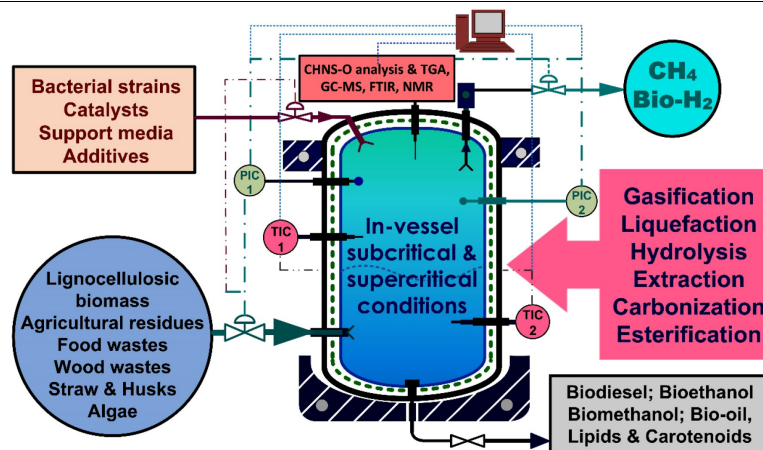
Advances of research trends in development of subcritical and supercritical water processes technologies are reviewed.

Essential aspects of sub- and supercritical water applied to extraction, hydrolysis, carbonization and gasification processes are discussed.

Equipment design, process parameters, and types of biomass used for sub- and supercritical water process are presented.

Bioactive compounds, reducing sugars, hydrogen, biodiesel, and hydrothermal char are the final products of sub- and supercritical water processes.

GRAPHICAL ABSTRACT



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ABSTRACT

This review summarizes the recent essential aspects of subcritical and supercritical water technology applied to the extraction, hydrolysis, carbonization, and gasification processes. These are clean and fast technologies which do not need pretreatment, require less reaction time, generate less corrosion and residues, do not use toxic solvents, and reduce the synthesis of degradation byproducts. The equipment design, process parameters, and types of biomass used for subcritical and supercritical water process are presented. The benefits of catalysis to improve process efficiency are addressed. Bioactive compounds, reducing sugars, hydrogen, biodiesel, and hydrothermal char are the final products of subcritical and supercritical water processes. The present review also revisits advances of the research trends in the development of subcritical and supercritical water process technologies.

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1. Introduction

Currently, our society is partially based on the concept of bioeconomy. Here, the term “bioeconomy” refers to the “sustainable production and conversion of plants into food, fibers, health and industrial products, and energy” (Yamamoto et al., 2014). Biomass-derived fuels have potentials as viable alternatives to petroleum-based fuels in the short to medium terms (Prado et al., 2016). Several techniques have been designed and evaluated for the recovery of bioactive compounds and sugars from natural feedstocks and to produce biogas, biohythane, or valuable carbonized solids from different types of biomass. However, comprehensive experiments and simulations are needed to optimize process parameters before the economic viability may be achieved at industrial scales. For liquid biofuel production, the most pressing challenge is to achieve more effective and benign bioconversion of biopolymers into sugars, since this step requires breaking down the lignocellulosic complex via energy-intensive processing steps.

Conversion of wastes into bioenergy products is especially promising as a method to increase value and minimize the environmental and ecological footprints of existing industrial processes. However, the utilization of renewable or even waste feedstocks does not guarantee that a process is either sustainable or green. To be both sustainable and green, processes must use benign catalysts, solvents, and auxiliary chemicals. Due to the quantities used, the selection of green solvents is especially important for achieving process sustainability. Here, benign solvents include especially those identified as Generally Regarded As Safe (GRAS), a category that includes water, ethanol, CO₂, and combinations (Clark and Pfaltzgraff, 2012; Vardanega et al., 2015; Timko et al., 2016a). Different techniques have been developed to streamline and enhance solvation intensity as well as the power and effectiveness of these solvents, including the use of high pressures and (sometimes) high temperatures (Vardanega et al., 2015).

Solvent selection is important for sustainable extraction and reaction processes. Subcritical water, supercritical fluid, and ultrasound-assisted processing are some of the emerging green extraction techniques receiving renewed and sustained research interest among many research groups worldwide. For recovery of sugars from biomass feeds, subcritical and supercritical water hydrolysis have been studied as alternatives that reduce the cost and chemical use of enzymatic, acid, and alkaline processing (Rostagno et al., 2015). The objective of supercritical water gasification is to transform wet biomass to a hydrogen-rich biogas. Supercritical water gasification process is effective at temperatures above its critical point, often around 600 °C (Lachos-Perez et al., 2015) and the introduction of a catalyst permits operation at reduced temperatures.

Extraction, hydrolysis, and gasification often co-generate substantial quantities of a carbonaceous char material. Valorizing this material as a co-product is necessary to achieve favorable economic performance for the overall process. In fact, recent works have shown that processes designed to maximize the yield of solid carbon products (processes that are collectively termed “hydrothermal carbonization” (HTC)) may have economic benefits as stand-alone technologies. Unlike pyrolysis, HTC is suitable for both wet and dry feedstocks and HTC of the former can result in superior energy balance compared with pyrolysis. The hydrothermal char product of HTC has shown

promise in many applications (Libra et al., 2011), including power generation as a “renewable coal” (Mumme et al., 2011), water purification (Regmi et al., 2012) electrochemistry (Wei et al., 2011), and catalysis (Karagöz et al., 2005). This review emphasizes on a fresh perspective of the application of subcritical and supercritical water conditions as environmentally-benign methods to extract, hydrolyze, gasify, and carbonize biomass to produce bioactive compounds, sugars, biogas, and other valuable solids.

2. Biomass

The term “biomass” can be defined as the total mass of living or recently dead (unfossilized) organic matters within a given environment. More practically, biomass attributes to all forms of organic matter potentially-recoverable from a variety of renewable sources such as dedicated energy crops and trees, agricultural crops, animal wastes, crop wastes from agricultural activities, wood and municipal wastes, etc. (Olanrewaju, 2012). Most of the biomass used comes from agro-industrial residues, because these are renewable and could be obtained at low-cost or in some cases no cost especially when the raw material is of residue nature. Main residue types are, for example, molasses, bagasse, and maize milling by-products (Pedras, 2015).

Cellulose, hemicellulose, and lignin are the components constituting lignocellulosic biomass. Cellulose is a regular, linear, homopolymer consisting of D-glucose monomers linked by β-(1,4) glycosidic bonds. Cellulose is the dominant structural polysaccharide. Plant cellulose is composed of two parts: a crystalline structure (organized) and a non-organized amorphous structure, also called para-crystalline structure. Individual cellulose polymers are “bundled” together as cellulose fibrils, which are usually independent and weakly connected by hydrogen bonds (Hendriks and Zeeman, 2009). Hemicellulose is a polysaccharide consisting of various sugar monomer units such as xylose, galactose, mannose, arabinose, and also glucose; unlike cellulose, hemicellulose is branched and amorphous. The function of hemicellulose is to bind cellulose and lignin. Lignin is a random, three-dimensional polymer consisting of phenyl-propanoic sub units. Lignin is naturally made of coniferyl alcohol, sinapyl alcohol, and p-coumaryl alcohol, arranged in an irregular structure and is the main source resistance against enzymatic degradation (Pedras, 2015).

For biofuels production, the most economically and technologically significant barrier is conversion of biomass into sugars readily available for microbial action, a process that requires cleaving and dismantling the lignocellulosic complex. Biopolymer breakdown is usually performed via energy intensive processing of the cellulose and hemicellulose fractions contained in the biomass into sugars; while subsequent fermentation processes convert the simple sugars into fuels and/or chemicals. The complex polymer composition of biomass, including cellulose, hemicellulose, and lignin polymers, makes direct and efficient conversion to bioenergy particularly difficult (Zhu et al., 2016). The combination of elevated temperatures and favorable solvent properties makes subcritical/supercritical processing a promising alternative to conventional

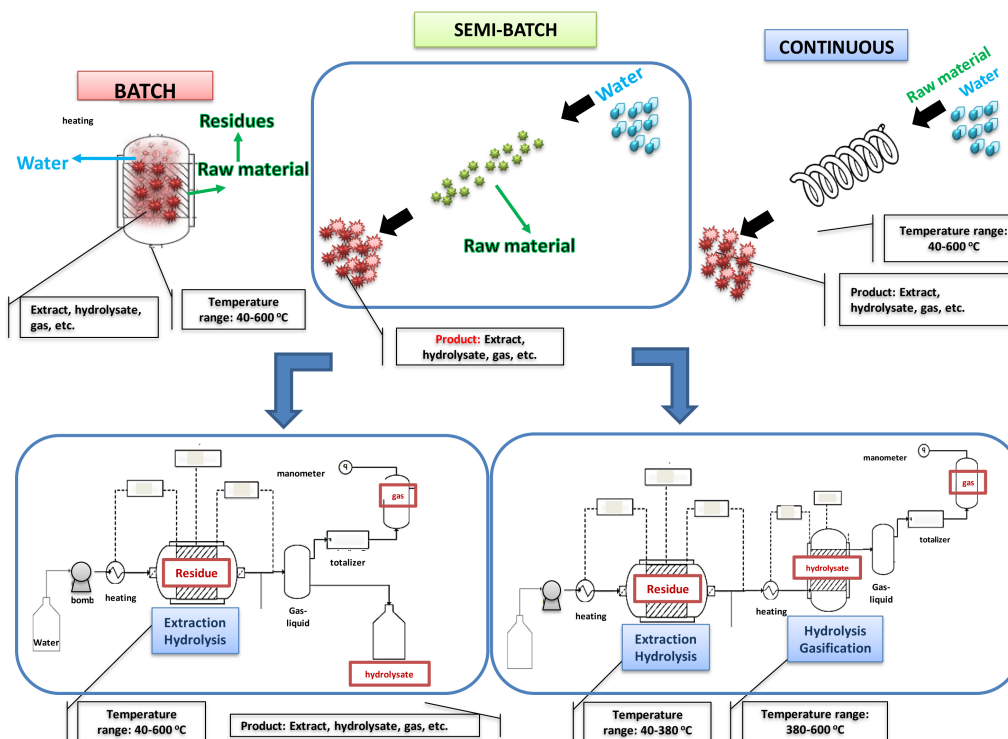


Fig.1. Sub/supercritical water hydrolysis performed in batch, semi-batch, and continuous systems.

biological and chemical processes for decomposition of the lignocellulosic complex (Rostagno et al., 2015).

In addition to the aforementioned biopolymers (cellulose, hemicellulose, and lignin), biomass may also contain proteins, simple sugars, pectins, phenolics, glycosides, saponins, fats, waxes, alkaloids, gums, resins, terpenes, starches, essential oils potassium, sodium and calcium (Yu et al., 2008). These minor components have potential as flavors, fragrances, pharmaceuticals, biomaterials, and nutraceuticals, all of which are more valuable than liquid fuels. Valorization of these minor components can therefore, be an important strategy for improving overall process economics of an integrated biorefinery.

On the other hand, it should be noted that although lignocellulosic biomass is abundant and inexpensive; commercial-scale conversion of lignocellulosic biomass into fuels requires regular delivery of a consistent raw material, a difficult logistic and supply challenge. In fact, overall economics of bio-ethanol production depend heavily on the cost of the feedstock (Davis et al., 2015). Thus, economically viable production of bioethanol requires careful process logistics and supply-chain consideration.

3. Subcritical and supercritical water conditions for biomass processing

The properties of any pure substances are dependent on temperature and pressure. When a pure substance enters the supercritical state, it is in fact heated and pressurized to temperatures and pressures greater than its critical point. For water, the critical temperature is 374 °C and the critical pressure is 22.1 MPa (Taylor et al., 2001; Elliott et al., 2015). Industrial applications that use water at the critical temperature and critical pressure are generally suffering from very high costs due to the high-pressure equipment and the energy to be applied. For this reason, careful engineering experiments and design are required to optimize processes based on supercritical water in order to reduce capital and operating costs. The motivation to study subcritical and supercritical conditions stems from the fact that such processing conditions possess some of the advantages embodied in the green chemistry and green chemical engineering concepts, namely, better energy efficiency and energy savings, minimization of wastes generation, improved atom economy, and better interphase mass transfer coefficients.

Subcritical/supercritical water extraction, hydrolysis, gasification, and carbonization can be carried out in batch, semi-batch and continuous systems (Fig. 1). When the raw material(s) (biomass) and reaction solvent (water) are placed inside a close reactor, the process is defined as batch. On the other hand, when biomass is brought into contact with a continuous flow of the reaction medium, the process is known as a semi-batch. In the continuous process, both the biomass feed and the solvent are continuously entering and exiting the reactor. Rapid reaction rates achievable by operation at high temperatures can be advantageous for continuous processing (Williams and Onwudili, 2005). For example, Elliott et al. (2015) reported yield improvements when converted a batch process to continuous operation. Since the carbon and energy recovery efficiency can be favorable, a considerable deal of interest exists for commercial application of supercritical water technologies in the continuous mode. On the contrary, the technical difficulties associated with pumping biomass slurries has made most studies focus on subcritical and supercritical processes that are performed using batch or semi batch systems. As result, many technical hurdles need to be addressed to determine the optimal scale of continuous systems. Furthermore, integration of several semi-batch processes into a simulated continuous operation at the industrial level may be preferred over batch or continuous operation.

In addition to the type of reactor (batch, continuous, or semi-continuous), several other factors also influence the performance of subcritical and supercritical water hydrolysis, chiefly; feedstock properties, solvent properties, reactor configurations, time-temperature behavior of reacting particles, as well as the use of catalysts and other reagents. Some of these factors will be discussed later.

4. Subcritical water extraction technology

Plant materials contain many useful compounds such as flavors, fragrances, pharmaceuticals, and dietary supplements. To use the compounds present in the biomass, they must first be separated from the rest of the raw materials. The typical extraction process involves using a solvent (liquid or gas) to selectively remove and/or dissolve target

compounds from the raw material matrix (i.e., the biomass). The process can be performed using different types of extraction systems and several variables will affect the efficiency and selectivity of the process, including raw material and target compounds characteristics, temperature, extraction solvent, solvent to feed ratio, etc.

Solvent characteristics play a major role in the selectivity of the process affecting both target compound selectively and – to a lesser extent – mass transfer rates. Water alone or as part of a mixture of miscible solvents is primarily used for extracting polar to moderately polar compounds. Water is used as a solvent for several extraction processes focusing on the recovery of useful and potentially valuable compounds from diverse biomass types. Due to their polarity, antioxidants, phenolic compounds, and carbohydrates are among the most common compounds extracted using water as solvent (Table 1). In general, an increase in the extraction temperature increases extraction rate by increasing diffusion constants, increasing solubility, and swelling the biomass matrix. The last stage of the extraction process is controlled by diffusion and can be most effectively improved the most by increasing extraction temperature (Rostagno and Prado, 2013). Solubility of compounds in the solvent is also affected by temperature. It has been shown that the solubility of gallic acid, catechin, and protocatechuic acid in water would increase by more than 200 times when the temperature was increased from 25°C to 142°C (Srinivas et al., 2010).

When using water as solvent for extraction processes performed at ambient pressure, extraction temperature is limited to the normal boiling point of water (100°C). In contrast, in pressurized systems, the process can be performed above the boiling point of the solvent. Usually high-pressure extraction processes using water are performed using temperatures up to 150°C. Increasing extraction temperature greater than 100°C affects the characteristic of water as a solvent, modifying its dielectric constant and viscosity. As a result, the water solubility of mid-polar compounds increases with increasing temperature, allowing water to replace or reduce the amount of organic solvent such as methanol and ethanol used for extraction (Çam and Hışıl, 2010).

The scope for increasing process temperature to improve extraction efficiency depends on the thermal stability of target compounds. Polyphenols, a class of compounds with high antioxidant capacity and biological effects, are an example of temperature-sensitive natural products. For recovery of phenolics from pomegranate peels, extraction temperature should not be greater than 40°C, as this temperature optimizes solubility and extraction rates while minimizing thermal degradation (Çam and Hışıl, 2010). Sugarcane bagasse is another example. Bagasse contains many compounds of potential value, including polyphenols which must be extracted at conditions which minimize thermal degradation (Zhao et al., 2015). In contrast, temperatures as great as 190°C can be used for the extraction of non-cellulosic heteropolysaccharides composed of xylose, glucose, galactose, mannose, arabinose, and smaller amounts of 4-O-methylglucuronic acid compared with sugarcane. The interest in the recovery of these compounds is to use them as water-soluble polymers to replace synthetic polymers in food packaging, wound dressings, and drug capsules (Jayapal et al., 2013; Banerjee et al., 2014).

For thermally-stable compounds, the scope for increasing extraction temperature to improve extraction efficiency and reduce extraction time is greatly increased compared with thermally labile compounds. In fact, subcritical water is employed in the extraction of several classes of phenolics from different biomass, including citrus peel, pomegranate seed residues, flaxseed meal sticks, sour cherry pomace, and onion skin among other examples (Chienthavorn and Insuan, 2004; Adil et al., 2008; Ko et al., 2011; Cheigh et al., 2012; Kanmaz, 2014). Subcritical water has also been used for the extraction of antioxidants from eucalyptus biomass, canola meal, onion peel, winery wastes, grape pomace spent coffee grounds, and silver skin, just to name a few examples (Kulkarni et al., 2008; Hassas-Roudsari et al., 2009; Aliakbarian et al., 2012; Narita and Inouye, 2012; Vergara-Salinas et al., 2013; Lee et al., 2014; Zeković et al., 2014; Xu et al., 2015). For many compounds and raw materials, subcritical water extraction efficiencies and yields are usually greater than what can be obtained with organic solvents using conventional techniques.

In some applications, acids have been used to modify water to improve extraction efficiency for some compounds. For example, anthocyanins, a valuable class of compounds present in blackberry residues, are extracted most efficiently using acidified water and temperatures between 60 and 80 °C. The remaining phenolics of blackberry residues could then be extracted by increasing the temperature and by using alcohol/water mixture as the

extraction solvent (Machado et al., 2015). This example implies the importance of the optimization of acidity for recovery of a specific target compound.

5. Subcritical and supercritical water hydrolysis technology

Decomposition of cellulose and hemicellulose into pure sugar streams is the major technical and economic bottleneck limiting commercialization of biofuels. Conventional technologies to convert biomass into sugars, including dilute acid treatment, steam explosion, and enzymatic hydrolysis, have been extensively studied in recent years (Agudelo et al., 2016; Jiang et al., 2016; Li et al., 2016b; Romero-García et al., 2016; Kapoor et al., 2017; Qin et al., 2017). Currently, acid and enzymatic hydrolysis processes are used in the synthesis of second-generation bioethanol. However, acid hydrolysis requires neutralization of the medium afterwards, and the use of enzymes is restricted due to their high cost and the operational processing steps (Li et al., 2016a). Compared with dilute acid pretreatment, hydrothermal technologies, especially those based on subcritical and supercritical water, could be used for decomposition of biomass into simple sugars with high yields (Shitu et al., 2015). Due to their environmentally-benign characteristics and abundance, water and CO₂ are mostly used in reactions at subcritical and supercritical conditions for agricultural biomass residue processing.

Hydrothermal processing can be divided into two categories – those that are performed at supercritical conditions and those that are performed at subcritical conditions. Subcritical water hydrolysis is usually conducted in a temperature range of 100 to 374°C under sufficient pressure to keep water in the liquid state (Yoshida et al., 2015; Lachos-Perez et al., 2016). Subcritical water treatment aims at utilizing the waste biomass to generate raw materials for new products and a concomitant reduction in waste streams volumes. Supercritical water processing is performed at temperatures greater than 374°C and typically at pressures greater than 25 MPa. At these conditions, water behaves as a single non-condensable phase, with a density close to a liquid and transport properties similar to a gas (Marrone and Hong, 2009).

Hydrothermal treatment offers several advantages, including rapid reaction rates and replacement of acids/bases with a more environmentally-acceptable solvent. In addition, many feeds of interest are moist and the water contained in the raw material and/or organic residue may be used as the reaction medium; compatibility with moist feeds eliminates the need of a drying step used in conventional methods.

Despite the existing potentials, the application of supercritical fluid technology to agricultural waste is still under development. A particular challenge is that hydrolysis rates and sugar yields depend on the characteristics of the residues, composition and structure of the cell wall, and the type of the monosaccharides present in the feed. As a result, each raw material must be studied individually, each new feed representing a new set of technological challenges (Prado et al., 2014).

The three main components of biomass respond differently to hydrothermal treatment. Hemicellulose is the most readily hydrolyzed fraction. Kim et al. (2014) found that 60-70% of the pentose content of hardwood could be recovered at mild conditions (<200°C), but that recovery of the remaining pentose content required more severe treatment. Piñkowska et al. (2011) studied hydrothermal decomposition of xylan as a model compound for hemicellulose. They reported the maximum soluble sugar yield at 220-235°C and within the shortest residence time studied (0 min, i.e., heating the reactor to reaction temperature followed by immediate cooling). Increasing the temperature or residence time decreased sugar yields, as sugar decomposition and re-combination became increasingly important.

Cellulose is generally more recalcitrant to hydrolysis than hemicellulose. Sasaki et al. (2000) studied dissolution and hydrolysis of cellulose in supercritical water, arguing that at 400°C cellulose was mainly decomposed to form hydrolysis products but at temperatures from 320 to 350°C, primary hydrolysis products were decomposed. The same group of authors studied cellulose dissolution using a diamond anvil cell, finding that individual cellulose particles became gradually smaller with increasing reaction time at T < 280°C but rapidly disappeared at T > 320°C. Sakaki et al. (2002) reported nearly 100% cellulose decomposition after 12 min at 295°C, resulting in a product consisting of a water soluble fraction (81 wt.%) and

Table 1.
Highlights of the results on biomass application for the production of bioactive compounds under subcritical water extraction.

Raw material	Target compounds	Extraction technique	Highlights of results	Reference
Blackberry residues	Polyphenols and Antioxidants - Anthocyanins	Solvent: water, acidified water pH = 2.5, ethanol and ethanol + water 50% (v:v) Temperature: 60, 80, and 100 °C Pressure: 7.5 MPa	Recovery of phenolics was significantly enhanced at higher temperatures. Higher extraction yields recorded for anthocyanins with acidified water at 60 and 80 °C.	Machado et al. (2015)
Pomegranate peels	Polyphenols and Antioxidants - Punicalagin and Ellagic acid derivatives	Solvent: water Temperature: 40,65, and 90 °C Extraction time (static): 5, 15, and 30 min Pressure: 102.1 atm Flush volume: 5-100 mL	Temperatures higher than 40 °C, longer extraction times, and larger particles reduced extraction yield. Pressurized water augmented the yield in comparison with methanol, ethanol, and acetone.	Çam and Hışıl (2010)
Potato peel	Phenolic compounds, Gallic acid, Chlorogenic acid, Caffeic acid, Protocatechuic acid, Syringic acid, p-hydroxyl benzoic acid, Ferulic acid, and Coumaric acid	Solvent: water Temperature: 100 to 240 °C Pressure: 6 MPa Flow-rate: 2 mL/min Residence time: 30-120 min	Best extraction yields at 160 to 180 °C, 6 MPa, and 60 min. Chlorogenic acid and gallic acid were essential components extracted at 180 °C.	Singh and Saldaña (2011)
Sugar cane bagasse	Hemicellulose components (arabinoxylans)	Solvent: water Temperature: 170, 180, 190, and 200 °C Extraction time: 15 min Pressure: not specified	Increasing temperatures increased release of polymeric hemicellulose but decreased lignin extraction.	Banerjee et al. (2014)
Pomegranate seed residues	Total phenolic compounds (antioxidant capacity)	Solvent: water (high pressure); water methanol, ethanol and acetone (low pressure) Extraction time: 15–120 min Temperature: 80–280 °C; Solid to water ratio: 1:10–1:50 (m/v) Pressure: 6.0 MPa	Increasing extraction temperatures increased the total phenolic content in extracts. Optimum extraction occurred at 220 °C for water to solids ratio of 40.	He et al. (2012)
Citrus peel	Phenolic compounds - Flavanones hesperidin and narirutin	Temperature: 110–200 °C Extraction time: 5–20 min Pressure: 100 atm.	Peak extraction yield at 160 °C for extraction time of 10 min.	Cheigh et al. (2012)
Onion skin	Phenolic compounds - Flavonol quercetin	Solvent: water (high pressure); water methanol and ethanol (low pressure): Temperature: 100–190 °C Extraction time: 5–30 min Ratio of the mixture sample and diatomaceous earth: 0.5:3.5–2:2 Pressure: 90–131 bar.	Peak extraction yield for quercetin obtained at 165 °C, and for 15 min of extraction time. Extraction yield with water was significantly greater than those recorded with methanol, ethanol and water-at-boiling-point	Ko et al. (2011)
Flaxseed meal	Lignan secoisolariciresinol diglucoside (SDG), Total phenolics and total flavonoids	Solvent: water Temperature: 160, 170, and 180 °C Extraction time: 5, 15, 30, and 60 min	Higher extraction temperatures of 170 and 180 °C decreased yields by less than 10% but impacted on extraction time reductions much more significantly. Total phenolics and total flavonoids were best extracted at 180 °C for 15 min.	Kanmaz (2014)
winery wastes	Total polyphenols and flavonoids	Solvent: water Temperature: 100, 120, and 140 °C Pressure: 8, 11.5, and 15 MPa	Extraction yield potentially to reach its maximum at 140 °C and 11.6 MPa. Subcritical water gave much higher yields than ethanol and water under atmospheric conditions.	Aliakbarian et al. (2012)
Grape Pomace	Phenolic compounds - tannins, anthocyanins, and croanthocyanidin	Solvent: water Temperature: 50–200 °C Extraction time: 5-30 min	Optimum extraction for anthocyanins obtained at 100 °C. Higher temperatures and longer extraction times considerably lowered extraction yields of phenolics. Proanthocyanidin was extracted only below 100°C.	Vergara-Salinas et al. (2013)
Apple pomace and citrus peel	Pectin	Solvent: water Solid to liquid ratio of 1:30. Temperature: Apple pomace: 130 -170 °C Citrus peel 100 - 140 °C Extraction time: 5 min	Optimum extraction temperature was 120 °C for citrus peel. With apple pomace substrate, optimum extraction was obtained at 150 °C.	Wang et al. (2014)

a solid deposit (18 wt.%). Sasaki et al. (2004) later studied cellulose decomposition in a continuous flow microreactor and successfully reproduced their data using an empirical kinetic model. Ehara and Saka (2002) studied supercritical water hydrolysis of microcrystalline cellulose in batch and flow reactors, finding that the flow system decreased sugar degradation but that

glucose yield was maximized in the batch reactor. Later, Ehara and Saka (2005) suggested sequential supercritical and subcritical water treatment to maximize cellulose hydrolysis and minimize sugar degradation. More recently, Cantero et al. (2013) studied ultra-fast reaction conditions (< 0.1 s) for cellulose hydrolysis, reporting >96% yield of total mono/oligo

saccharides at 400°C; with minimal (5 ppm) production of 5-hydroxymethylfurfural degradation product.

Lignin is the most recalcitrant of the three main biomass polymers and its hydrothermal decomposition has been studied mainly at temperatures greater than 300°C (Ma et al., 2016). For example, Yong and Matsumura (2012) studied decomposition of lignin in a flow reactor over the temperature range of 390 to 480°C and at residence times from 0.5 to 40 s, claiming complete decomposition within 5 s. Piñkowska et al. (2012) studied hydrothermal treatment of alkali lignin over the temperature range of 280 to 390°C. The authors found the greatest yields of stable phenol and cresol products at 280°C Barbier et al. (2012) performed a detailed analysis of the products of lignin decomposition in sub- and supercritical water (370-390°C) and concluded that the mechanism consisted of a complex network of parallel and sequential fragmentation and re-condensation reactions. In their studies of model lignin compound decomposition, Kanetake et al. (2007) found that guaiacol completely was decomposed within 100 min (at 380 to 400°C), producing catechol as the main product. Yong and Yukihiro (2013) studied guaiacol decomposition at short residence times (0.5 to 40 s) and under conditions of rapid heating. They confirmed rapid guaiacol decomposition, leading to char, gas, phenolic, and benzene production. At temperatures greater than the critical point, Yong and Yukihiro (2013) observed formation of polycyclic aromatic hydrocarbons.

The majority of studies on sub- and supercritical hydrolysis have focused on different types of whole biomass. Most studies on hydrolysis suggest that (1,4)-glycosidic linkages contained in cellulose break most rapidly under supercritical conditions, resulting in higher yields of mono- and oligosaccharides than under subcritical conditions. The main hydrolysis products are water-soluble oligomers (celohexose, celopentose, celotetraose, cellotriose, and cellobiose), monomers (glucose and fructose), and decomposition products of these monomers (1,6-anhydroglucose, glyceraldehyde, erythrose, glycolaldehyde, dihydroxyacetone, 5-hydroxymethyl-furaldehyde (5-HMF), and organic acids). The generation of soluble sugars from rice bran was reported by Pourali et al. (2010), who applied hydrothermal process conditions to decompose rice bran at different reaction temperatures and times in a batch reactor. They observed the greatest yields of water-soluble sugars at 220°C, and these sugars were primarily oligomers and monomers. Likewise, Shimanouchi et al. (2014) recovered reducing sugars from *Carya cathayensis* Sarg Peel (CCSP) under subcritical water at different reaction temperatures, and also reported that the optimal temperature for formation of reducing sugars was 190°C. Mohan et al. (2015) studied the conversion of bamboo to total reducing sugars by hydrolysis in subcritical water using a batch reactor at temperatures of 170 to 200°C for 40 min, obtaining a maximum yield of 42.21% at 180°C after 25 min of reaction. Prado et al. (2014) studied the conversion of several agro-industrial residues in a semi-continuous reactor (50 mL) by hydrolysis with subcritical water (208 and 257°C) for 30 min at a flow rate of 33 mL/min and pressure of 20 MPa. Their results indicated that for palm fiber hydrolysis, increasing the temperature reduced the yield of raffinose (0.1%) and increased the yield of glucose (0.7%), and 5-HMF (0.8%). However, the yield of sugars from coconut husk in this work did not change with temperature, and in the case of grape seed, the yield of sugars was calculated to be about 1.0%. All of these studies indicate that subcritical/supercritical water hydrolysis processes should be evaluated individually for each raw material.

Selecting reactor conditions to optimize sugar yield is important in order to balance biopolymer hydrolysis rates and sugar degradation rates, both of which increase with increasing temperature. For example, Lin et al. (2015) studied the competitive reactions involved in sugar production and degradation from rice straw substrates at concentrations of 2.5 and 10 wt.% in a batch reactor containing subcritical water at temperatures from 250 to 300°C, at pressures ranging from 12 to 20 MPa, and stirring speeds between 100 and 300 rpm. In their study, the greatest yield was 0.346 g/g of rice straw and least sugar breakdown was obtained at 280°C, 5% w/w, 20 MPa, and 200 rpm. In addition, increasing the temperature to 300°C decreased the yield, which the authors attributed it to the degradation of primary sugars to form acetic acid and 2-methyltetrahydrofuran (Lin et al., 2015). Zhu et al. (2016) studied the conversion of corn ear to reducing sugars by hydrothermal treatment at 190-320°C. Their results showed complete degradation of hemicellulose and cellulose, with sugars yields varying between 5.15% and 13.31%. These results indicated that hemicellulose was hydrolyzed most readily, and once hemicellulose was depleted, the hydrolysis of the cellulose started; however,

degradation of the produced reducing sugars was faster than the degradation of the cellulose. The combination of supercritical conditions as first stage and subcritical conditions as second stage showed better results than those obtained in separate sub- or supercritical treatments and greater control of product degradation was achieved (Ehara and Saka, 2005; Li et al., 2016a).

Another strategy to tune reaction rates independently of temperature is to adjust the pH of the solution phase. Carbon dioxide (CO₂) can be added to acidify subcritical and supercritical water to increase reaction rates. CO₂ reacts with water to form carbonic acid, releases protons to acts as a catalyst for hydrolysis reactions (Rogalinski et al., 2008), as shown in :



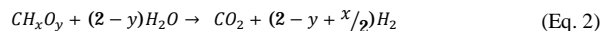
The addition of CO₂ as acid catalyst is advantageous as the acid is released during de-pressurization and does not require a neutralization step which would generate waste. Investigations on the addition of CO₂ showed that it increases hydrolysis rates, increases the yield of monomers, decreases the molecular weight distribution of the product, and apparently decreases the formation of degradation products (Miyazawa and Funazukuri, 2005; Schacht et al., 2008; Liang et al., 2016; Prado et al., 2017).

6. Supercritical water gasification technology

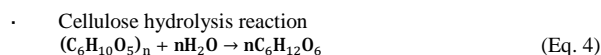
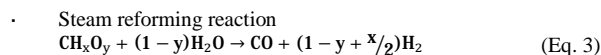
Gasification with supercritical water can break large biomass molecules into smaller molecules such as carbon monoxide (CO), methane (CH₄), hydrogen (H₂), and CO₂ because supercritical water is an adequate reaction medium for the hydrolysis reaction and subsequent gasification. The overall reaction is endothermic at temperatures greater than 680°C and is slightly exothermic at temperatures less than 680°C (Castello and Fiori, 2011). Hydrogen is generally the target product of biomass gasification. Hydrogen is considered entirely clean as a fuel, given the fact that its combustion produces water only. Hydrogen production from steam gasification is highly economic and effective with low environmental impacts.

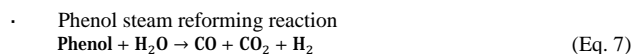
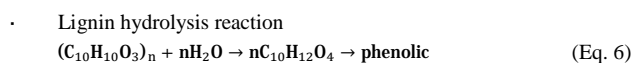
Supercritical water gasification is a relatively new process. Treatment of a variety of agricultural wastes at temperatures near 600°C and in the presence of supercritical water produces a gas rich in hydrogen (recently termed as 'biohythane') (Peterson et al., 2008). One of the main characteristics of supercritical water gasification is the reduced coal and tar formation compared with conventional technologies which has aroused initial interest in supercritical water gasification. In addition, supercritical water gasification is associated with relatively higher reaction efficiencies and yields as compared with conventional gasification methods, mainly with respect to hydrogen production due to the presence of water in the medium, without the need for a biomass drying step. Therefore, the conversion of moist biomass containing 90% of water in the gasification process seems to be a sustainable technological option (Calzavara et al., 2005).

Some of the vital reactions that take place in supercritical water biomass gasification are summarized in Equation 2 (Guo et al., 2010; Reddy et al., 2014)



where x and y are the elemental molar ratio of H/C and O/C in the biomass, respectively. The product of the reaction is synthesis gas, whose quality depends on x and y (Guo et al., 2010). In addition to Equation 2, other intermediate reactions may also occur during gasification of biomass in supercritical water (Eqs. 3-11):





Reducing the biomass particle size, increasing the reaction temperature, or increasing the steam-to-biomass ratio could promote H₂ yield and increases gasification rates. Many experimental studies have shown that temperatures from 500 to 700°C have a significant impact on yields and compositions of gases evolved, but values above the critical point have significantly much less influence on gas compositions. Pressure and residence time are other important control parameters of the supercritical gasification process. With increasing pressure, the ionic product of the water increases, and consequently the rate of hydrolysis also increases. In addition, high pressure was found to improve the steam change reaction, but reduce the rate of decomposition reactions (Guo and Faghri, 2007). The optimization of H₂ generation from processes conducted under supercritical gasification regimes using water and corncob biomass was investigated using the orthogonal experimental design technique by Lu et al. (2012). They found that temperature yielded a greater influence on the process compared with pressure, concentration of feedstock, and addition of an oxidizer. Acid hydrolysis of the feedstock increased H₂ yield in contrast to the addition of an oxidizer, which increased the carbon gasification efficiency but not hydrogen yield.

Temperature is a very important parameter and has significant effect on the biomass gasification in supercritical water, particularly when there are no catalysts involved. Lee et al. (2002) studied the gasification of glucose in supercritical water conditions and observed increasing H₂ and CO₂ yields with increasing temperature. In another work, a 30% increase in the reaction temperature to 650°C, increased the carbon efficiency and gasification efficiency by 167% and 300%, respectively (Hao et al., 2003).

Lu et al. (2006) studied the production of hydrogen as a function of increasing pressure to 30 MPa, and the results obtained showed that carbon and gasification efficiency were independent of pressure. Williams and Onwudili (2005) studied glucose gasification in supercritical water, and reported 90% conversion after 120 min. On the other hand, Basu and Mettanant (2009) demonstrated that increasing residence time of supercritical water gasification (650°C and 30 MPa) of rice husks increased hydrogen yield from 7 to 14 mol kg⁻¹. Lee et al. (2002) studied the influence of residence time on gas yield from gasification of 0.6 M glucose at 28 MPa and 700°C, showing a high yield of hydrogen regardless of the residence time, provided that the residence time was greater than 10.4 s. Safari et al. (2016) gasified almond shell, wheat straw, and walnut shell in supercritical water for hydrogen production, and observed that increasing the reaction time up to 30 min increased the hydrogen yield and gasification efficiency.

Subcritical and/or supercritical processing conditions can also enable the formation and potentially recovery of monomers and high-value chemicals from the gasification of agricultural residues (Table 2). Near the critical temperature, catalysts are required and a gas containing CH₄ is generated. At critical and higher temperatures, the generated gas will be rich in hydrogen if the concentration of the agricultural wastes feedstock is low and if the concentration of the biomass in water does not decrease. At these conditions, the product tends to contain more hydrocarbons and become less amenable for biomass conversion (Yusman, 2007).

Composition of the feed plays a role in H₂ yields through gasification. Safari et al. (2016) found that wheat straw yielded more H₂ than walnut or almond shell on account of its high lignin content; the corresponding H₂ yields from wheat straw, almond shell and walnut were 7.25, 4.10, and 4.63 mmol g⁻¹ at 10, 15, and 20 mins, respectively. Yoshida et al. (2009) pre-treated sewage

Table 2. Selected agricultural waste biomass used to generate biofuel(s) under supercritical water gasification conditions.

Feedstocks	Temperature (°C)	Pressure (MPa)	Reference
Corn starch, Potato starch and waste	600	22-34.5	Peterson et al. (2008)
Oily waste water	500-650	25-41	Zhiyong and Xiuyi (2015)
Timothy grass	450-650	23-25	Nanda et al. (2016a)
Eucalyptus grandis	450	27	Louw et al. (2016)
Rice straw	Less than 600	25	Yoshida et al. (2004)
Beet residues	450-600	30	Ondze et al. (2015)
Peanut shell	600-800	25	Lu et al. (2007)
Corn cob	600-800	25	Lu et al. (2007)
Fruit pulp	400-600	25	Elif and Nezihe (2016)
Chicken manure	620	30	Cao et al. (2016)
Sugarcane bagasse	400	-	Barati et al. (2014)
Sewage sludge	400-600	24.6-49.6	Acelas et al. (2014)
Wheat straw	650	26	Kang et al. (2016c)
Empty fruit bunches of oil palm	380	24	Sivasangar et al. (2015)
Sewage sludge	600	23	Sawai et al. (2014)
Food waste	400	22.1	Amuzu-Sefordzi et al. (2014)

sludge using sub-critical water hydrolysis and reported a two-fold increase in methane yield (after 3 d incubation) for the pre-treated sludge.

Table 3 tabulates studies on supercritical water gasification of model compounds for biogas production in recent years. Reddy et al. (2014) investigated the decomposition routes of cellulose and lignin under quasi-supercritical conditions and found that temperature, pressure, reaction time, catalysts, feed concentration, and reactor configuration all influenced H₂ production. These authors also indicated that around supercritical temperatures and pressures, hydrolysis rates could be enhanced based on ionic mechanisms and if reactors used for supercritical water gasification still had much scope for optimization. Demirbas (2010) found the generation of hydrogen under supercritical gasification with water highly attractive, although its cost of production was greater than hydrogen production from steam methane reforming. In this same work, increasing the temperature from 600-800°C at residence times of 2-6 s increased the H₂ yield from 53 to 73% by volume, while the effect of pressure was negligible beyond the critical pressure of water. Guo et al. (2012) investigated hydrogen evolution from supercritical water gasification of glycerol at 445-600°C, 25 MPa, and 3.9-9.0 s in continuous flow, and indicated that increasing the temperature greater than 487°C and/or increasing the glycerol concentration in the feed improved the gasification efficiency.

Supercritical biomass gasification can benefit from innovative reactor engineering approaches. Liao et al. (2013) studied supercritical water gasification of glucose and corncob using a novel solar thermal reactor. In this work, an increase in direct normal solar irradiation (DNI) caused an increase in the reactor temperature. Moreover, the elevated DNI and low feed concentrations increased H₂ yield, indicating the effectiveness of solar energy in supercritical water gasification systems. Later, Onwudili and Williams (2013) evaluated the potential of pre-treating sawdust using sub-critical water prior to supercritical water gasification and reported an increase in gas yields from 24.6 mol kg⁻¹ for untreated sawdust to 47.7 mol kg⁻¹ for pre-treated sawdust (neutral conditions).

Table 3.
Summary of supercritical water gasification of model compounds for biogas production.

Model compounds	Catalyst	Experimental condition	Experimental results	Reference
Glucose	Homogeneous organometallic catalyst and Raney nickel	Temperature: 310–350 °C Pressure: 10–21 MPa	homogeneous catalysts less effective than Raney nickel	Azadi et al. (2009)
Cellulose	Ru/C, Pd/C, CeO ₂ particles, nano-CeO ₂ , nano-(CeZr) _x O ₂	Temperature: 500 °C Pressure: 27 MPa	Catalyst used was Ru/C ₄ Pd/C ₄ nano-(CeZr) _x O ₂ ; nano-CeO ₂ ; CeO ₂ particles. With sodium carboxymethylcellulose, cellulose or sawdust can be completely gasified	Hao et al. (2005)
Xylan (Hemicellulose)	Ru/a-Al ₂ O ₃ /CaO	Temperature: 550 °C Pressure: 36 MPa	Hydrogen yield was of 10.7 mol kg ⁻¹	Onwudili and Williams (2013)
Glycerol	Ru/Al ₂ O ₃	Temperature: 700 – 800 °C	Ruthenium had high activity for C–C bond cleavage; H ₂ synthesis decreased when CH ₄ increased when glycerol levels were augmented to 40%.	Byrd et al. (2008)
Humic acid	-	Temperatures: 325–600 °C Feed concentration: 10–25 wt.% Reaction time: 30–90 min	High H ₂ yield of 0.79 mol kg ⁻¹ at 600 °C, 15 wt.% humic acid and 75 min without catalyst.	Gong et al. (2017)
Phenols	Ru/CeO ₂	Temperatures: 450 - 500 °C Feed concentration: 5 wt.% phenol	Carbon utilization efficiency rose to 90% in supercritical water gasification of phenol with Ru/CeO ₂ and 5 wt.% loading of phenol Gaseous yields had risen from 60% (no catalysis) 150% at 500 °C with catalyst.	Guan et al. (2016)
Methanol	Ni catalyst	Temperature: 500-550 °C Feed concentration: 10 wt.% methanol	Conversion rates significantly enhanced with Ni catalyst.	DiLeo and Savage (2006)
Oleic acid	Ru/Al ₂ O ₃ , Ru/AC, Pt/AC, Pd/AC, Ni/SiO ₂ -Al ₂ O ₃	Temperature: 400–500 °C, Pressure: 28 MPa Reaction time: 30 min	Higher temperatures and catalyst considerably improved yields.	Youssef et al. (2011)
Lignin	Ni/MgO	Temperature: 250–400 °C,	Higher nickel loadings on magnesium oxide augmented synthesis of gases. Highest yield was 78% with 20wt.% Ni/MgO catalyst (400 °C).	Sato et al. (2006)
Cellulose and lignin alkali	alkali catalyst (K ₂ CO ₃) and absence of catalyst	Temperature: 300 -600 °C Pressure: 9-41 MPa Reaction time 1 h	K ₂ CO ₃ favored gasification rates and restricted char generation.	Güngören Madenoğlu et al. (2016)
Fructose	KOH and NaOH catalyst	Temperature: 550 – 700 °C Residence time: 30 -75 s Feed concentration: 4 - 10 % Catalyst concentration: 0,2 – 0,8 % Pressure: 25 MPa	Gas synthesis yields, carbon gasification efficiency and hydrogen yields much improved at optimum conditions (700 °C, 60 s residence feed concentration of 4 wt.%).	Nanda et al. (2015)
Glucose	-	Temperature: 550 °C Pressure: 25 MPa Flow rate water: 1 -10 mL/min Conc. Solution: 50, 100, 150, 250 g/L	Biogas generation fluctuated from 100-200 L kg ⁻¹ glucose Biogas composition (vol./vol.) was: CO 40-50%, H ₂ 10-15%, CH ₄ 10-20%, C ₂ 2-8%, with finally CO ₂ 20-30%.	Molino et al. (2016)

The role of catalysis has also been regularly studied in biomass processing for biofuel production under subcritical and supercritical conditions using different liquids (namely ethanol, methanol, and water). Although the exact mechanistic pathways involved remain unclear, many studies have shown that the overall process performance and yield were enhanced when using specific types of metal-based (Azadi and Farnood, 2011) and/or zeolite-type catalysts (Fig. 2), while only a few studies have demonstrated that adequately satisfactory process metrics could be reached in catalyst-free reactions. Guo et al. (2010) provided an overview on the physicochemical characteristics of supercritical water gasification and confirmed that alkali metal catalysts enhance water-gas-shift reactions, but cause fouling and corrosion of equipment. Again according to Guo et al. (2010), transition metal catalysts promote methanation reactions, catalyze steam reforming reactions, and bond breakage. Yet, many catalysts are instable followed by damages of their support.

Process conditions influence gasification efficiency and H₂ yields. Kang et al. (2016a) conducted a process optimization study on the catalytic gasification of lignin and cellulose under supercritical condition with water using K₂CO₃ and 20 Ni-0.36 Ce/Al₂O₃ through Taguchi experimental design for process optimization. They found that temperature exerted the highest impact on the

process followed by catalyst type and loading, and finally the type of biomass used. They also found that H₂ yield was enhanced at the high temperatures of 650°C and high catalyst loading. Nanda et al. (2016b) probed the influence of nickel-laden feedstocks gasified in sub- and supercritical water conditions at varying temperatures, water-to-biomass ratios, pressures, and residence times, and thence found that nickel-laden biomasses yielded more hydrogen than non-catalytic ones with the optimal conditions for gasification observed at 500°C, a water-to-biomass ratio of 10 at 45 min and 23-25 MPa. Susanti et al. (2012) assessed supercritical water gasification of glucose in an updraft gasifier reactor under different temperatures, reaction time, feed concentration, and without a catalyst, and showed that the total gas and hydrogen yields increased with increasing temperatures. Moreover, the highest yields were achieved at 740°C and 1.8 wt.% of feed for 60 s, and carbon efficiency of 91% was recorded.

Catalysts enhance H₂ yields by favoring the reactions of the water gas shift process according to Parthasarathy and Narayanan (2014). Seif et al. (2016) studied the hydrothermal gasification of various industrial waste streams using different catalysts, temperatures and reaction times, and reported that Co₃O₄ was the most effective catalyst that could enhance the gasification efficiency and H₂ yields. Seif et al. (2016) also argued that

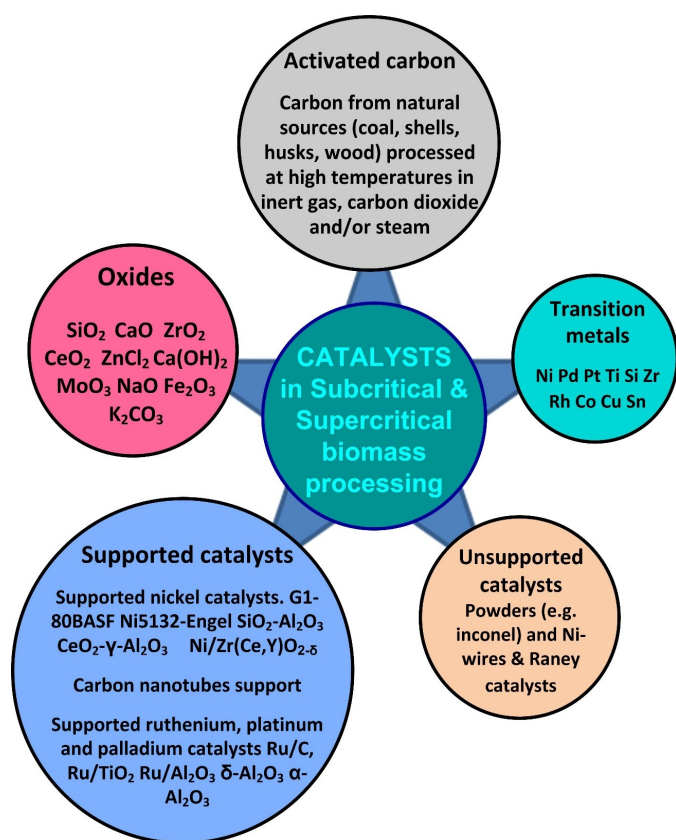


Fig.2. Broad classification of the main types of homogeneous and heterogeneous catalysts used in biomass processing for biofuel production under subcritical and supercritical conditions.

temperatures over 375°C and residence time of 45 min promoted H₂ generation, although catalysts were more effective at lower temperatures and longer residence time.

Gasification of fruit pulp in supercritical water catalyzed by Ru/C was investigated at varying temperatures, residence times, as well as biomass and catalyst ratios by Elif and Nezihe (2016), who demonstrated that H₂ yield increased by 400% at temperatures greater than 500°C. Huang et al. (2017) studied the catalytic supercritical water gasification of glucose over Ni/Zr(Ce,Y)O₂-δ catalysts at 500°C, 23–24 MPa, and feed concentration of 10 wt.%, and reported that carbon gasification efficiency was improved as Ni concentration was increased from 0.1 to 0.7. In this same work, a hydrogen yield of 22 mol kg⁻¹ was obtained using Ni_{0.5}Zr_{0.8}Y_{0.2}O_{2.8} (NZY582) catalyst which was 10 times greater than that of the catalyst-free conditions. Addition of Ni/CeO₂-γ Al₂O₃ catalyst to supercritical water gasification of biomass at 400°C, 24.5 MPa, and 9.09 wt.% glucose greatly boosted H₂ yield and selectivity according to Lu et al. (2010). They also deduced that coking and carbon deposits caused deactivation of catalysts and the presence of Ce in the catalysts inhibited this phenomenon.

Catalyst selection is also an important consideration, both in terms of activity and stability. Yamaguchi et al. (2009) investigated the generation of hydrogen under supercritical water gasification regimes of woody biomass with catalyst and observed that H₂ yield was heightened at shorter residence time and elevated temperatures. Palladium > ruthenium > platinum > rhodium > nickel catalysts over activated carbon and titanium favored lignin gasification. Amuzu-Sefordzi et al. (2014) demonstrated that nickel catalysts promoted steam reforming reactions (at 400°C and 22.1 MPa for 10 min) with minimum impacts on the water gas shift reaction compared with alkali catalysts (NaOH), which favored H₂ yield. Behnia et al. (2016) probed the influence of nickel and ruthenium metallic catalysts on CH₄ and H₂ generation from glucose subjected to supercritical water gasification at 500°C and reported the greatest H₂ yields and complete carbon conversion in glucose were achieved using Ni20%

Ru2%/γ-Al₂O₃ catalyst. Tar formation was inhibited and CH₄ formation was improved. Kang et al. (2016b) screened of 29 catalysts generated using 5 supports for the production of hydrogen by the water gasification of lignin under supercritical conditions, and finally ranked Ni-based catalysts in order of reactivity as follows: Al₂O₃ > TiO₂ > AC > ZrO₂ > MgO. Kang et al. (2016b) also showed that Ce improved H₂ selectivity by favoring dispersion of Ni and inhibiting Ni-Al₂O₃ interactions. In their study, the 20Ni-0.36Ce/Al₂O₃ catalyst exhibited a peak H₂ yield of 2.15 mmol g⁻¹. Li et al. (2011) observed that Cu improved the catalytic performance of Ni in reforming reactions to generate H₂, and that Cu also mitigated sintering of alumina whilst Co promoted Ni-based catalysis with respect to hydrogen selectivity. Madenoğlu et al. (2012) studied the sub- and supercritical gasification behavior of cotton and tobacco stalks with water as supercritical fluid at 300–600°C with addition of 10 wt.% of natural mineral catalysts, and found that Trona was most effective while Dolomite was least efficient. They claimed H₂ yields as high as 42.9% and 39.9% from tobacco and cotton stalks using Trona as catalyst at 600°C, respectively. The generation of hydrogen using subcritical water gasification of food wastes, glucose, and glutamic acid was studied by Muangrat et al. (2010) who examined the effects of adding NaOH, Ni/Al₂O₃, and Ni/SiO₂ catalysts. They found that glutamic acid yielded less hydrogen than glucose and the addition of NaOH increased H₂ production while the combined use of the different catalyst with NaOH resulted in a marginal increase in H₂ yield. An interesting feature of the work of Muangrat et al. (2010) was that NaOH was capable of preventing carbon deposition on the active sites of the catalysts.

7. Hydrothermal carbonization

7.1. Hydrothermal reaction mechanism

HTC comprises a complex network of reactions, and kinetics and details of each reaction are governed by feedstock, temperature, and pressure. A large number of chemical reactions occur during biomass conversion to hydrothermal char, and the full reaction network is not yet established. However, the conversion of biomass to biochar is believed to involve parallel and sequential hydrolysis, dehydration, condensation, and polymerization reactions (Funke and Ziegler, 2010). For example, Brunner (2009) suggested that the network consists of hydrolysis of glycosidic bonds to convert biomass polymers into sugars, followed by hydrolytic degradation of the simple sugars to produce compounds that act as building blocks to form hydrothermal chars. Similarly, Titirici et al. (2008) found that hexoses like glucose react to form HMF as an intermediate, while pentoses like xylose instead form furfural. Subsequent to biopolymer breakdown, the resulting simple carbohydrates and degradation products condense to form larger molecules (Titirici et al., 2007). Aromatization reactions convert the carbohydrate and furanic molecules into fully and partially aromatic structures in the hydrothermal char (Baccile et al., 2009; Sevilla and Fuertes, 2009a). Falco et al. (2011) reported that the aromaticity of the product char depends on the molecular structure of the carbohydrate feed; for example, xylose carbonization results in a more arenic product than does glucose carbonization. Throughout the process, decarboxylation and decarbonylation reactions remove carbonyl groups from the hydrothermal char, resulting in the production of CO₂ and CO while reducing the oxygen content of the hydrothermal char (Li et al., 2011). Timko et al. (2016b) reported a ball milling treatment that simultaneously decreased the oxygen content of a hydrothermal char and increased its aromaticity. The authors attributed their finding to the formation and recombination of carbon radicals during ball milling.

7.2. Hydrothermal carbonization process

Valorization of solid byproducts formed during gasification or hydrolysis of biomass feeds is key for improving overall process economics and maximizing environmental benefits of using bio-renewable feeds. In fact, the solids themselves may have sufficient value to justify HTC as a stand-alone process and in recent years the technology has been the subject of several reviews (Funke and Ziegler, 2010; Titirici and Antonietti, 2010; Libra et al., 2011). As a thermal process which is conducted in the presence of a liquid water phase, HTC offers a favorable energy balance compared

with pyrolysis or torrefaction for wet feeds. Moreover, the performance of the HTC process can be tuned by adjusting many operating parameters including: the design of the reactor, the reaction thermal history (including the set point temperature, ramp rate, and cooling rate), pressure, time, and the feedstock itself.

In terms of reactor designs, HTC is usually performed in sealed batch reactors, with only a limited number of studies reported HTC under flow conditions (Elliott et al., 2013; Jazrawi et al., 2013). Large-scale batch HTC reactors have been reportedly built at industrial scale while design and operation of flow reactors are on-going topics of university and industrial research. In terms of pressure, most HTC processes are performed at the saturation pressure of water, though several studies have measured the pressure changes that occur during the HTC process (Heilmann et al., 2010). The effects of operating HTC at pressures greater than the saturation pressure of water are unknown, but are likely modest given the body of work on HTL.

Hydrothermal carbonization is typically performed at temperatures ranging from 150 to 300°C, as these temperatures maximize the char yield (Sevilla and Fuertes, 2009b). Reaction temperatures must be selected to optimize the overall energy balance (Funke et al., 2013) as well as to tune the char yield and/or composition. Gao et al. (2012) and Sevilla and Fuertes (2009a) showed that properties, such as particle size and yield of the hydrothermal char product are dependent on the reaction temperature. Furthermore, using nuclear magnetic resonance (NMR) spectroscopy, Falco et al. (2011) reported that increasing reaction temperature of hydrothermal carbonization increased the arene content relative to furan of the hydrothermal chars and decreased the carbonyl content in the same char (Falco et al., 2011).

Reaction time has been reported to have a small effect on the yield of hydrothermal char (Sevilla and Fuertes, 2009a; Sevilla and Fuertes, 2009b). However, the composition and properties of the material has been found to vary with time. Gao et al. (2012) examined the effect of residence time on the properties of hydrothermal chars made from water hyacinth, reporting that the oxygen content decreased from 20 wt.% to 13 wt.% after 4 h of reaction time. Thermal analysis indicated that chars recovered after 6 and 24 h of reaction time showed nearly identical derivative thermograms (DTG) graphs (Gao et al., 2012). Similarly, Falco et al. (2011) used NMR analysis and showed that the structure of hydrothermal char changed rapidly over the first several hours of reaction, and then stayed mostly constant.

As mentioned previously, HTC is suited to processing a wide range of wet and dry biomass feedstocks, including agricultural waste biomass (Sevilla et al., 2011; Xue et al., 2012) and municipal wastewater sludge (Berge et al., 2011). Wiedner et al. (2013) reported that carbonization of different whole biomass feedstocks produced hydrothermal chars with different properties; however, establishing a predictive link between hydrothermal char composition and the composition of the feed is a current knowledge gap (Kang et al., 2012). Despite the challenge, progress is being made to tailor char composition. For example, Demir-Cakan et al. (2009) co-carbonized glucose and acrylic acid to produce hydrothermal char enriched in carboxylic acids. Latham et al. (2014) used a nitrogen-enriched algal feed solution to produce a nitrogen-rich char. Likewise, Yang et al. (2012) carbonized chitosan, a acetyl functionalized polymer of d-glucosamine, to obtain a nitrogen-rich material that was easily made highly fluorescent (Zhao and Wu, 2006).

7.3. Hydrothermal char characterization

The variety of feedstocks and reaction conditions make hydrothermal carbonization a highly variable process, the result of which is a complex, heterogeneous molecule. Figure 3 shows three hydrochar model compounds proposed by Sevilla and Fuertes (2009a), Chuntanapum and Matsumura (2009), and Latham et al. (2017). Many different techniques have been deployed in attempts to better understand the structure and properties of hydrothermal char. Most commonly elemental analysis has been used to understand how it compares to more common thermal residues, such as pyrolysis char or soot. Hydrothermal chars generally show higher carbon contents and lower oxygen contents than their corresponding feeds (Sevilla and Fuertes, 2009a; Sevilla and Fuertes, 2009b), but also tend to have higher oxygen contents than pyrolysis chars (Bridgwater et al., 1999).

Vibrational spectroscopy, both infrared and Raman, is often used to characterize hydrothermal chars. Infrared spectroscopy indicates that the hydrothermal char surface consists of many different oxygen-bearing functional groups (Sevilla and Fuertes, 2009a; Liu et al., 2013). Because of

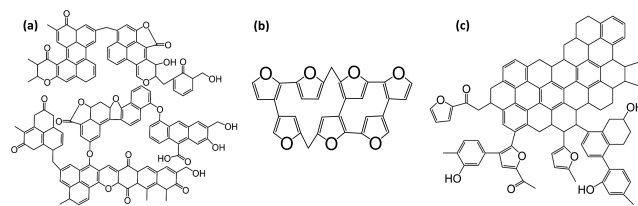


Fig.3. Hydrothermal char model compounds proposed in the literature. Molecular structures (a), (b), and (c) given here are redrawn based on the data from the following sources: Structure (a) is reprinted (adapted) with permission from Sevilla and Fuertes (2009a). Copyright© 2009; WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim [License number: 4061700558451]; Structure (b) is reprinted (adapted) with permission from Falco et al. (2011). Copyright© 2011; American Chemical Society; and Structure (c) is reprinted (adapted) with permission from Chuntanapum and Matsumura (2009). Copyright© 2009; American Chemical Society.

apparent similarities with the spectra of graphitic materials (Sadezky et al., 2005; Ferrari et al., 2006; Graf et al., 2007), Raman micro-spectroscopy of hydrothermal char suggests a defect-rich carbonaceous structure, consisting of polycyclic aromatic hydrocarbon (PAH) sub-units with 8-10 rings (Chuntanapum and Matsumura, 2009). However, Raman spectra of furan and furan-derived molecules (Kim et al., 2011) suggest that interpretation of hydrothermal char spectra may not be straightforward and that the presence of oxygen functional groups may shift band locations and intensities. Efforts to improve the interpretation of hydrothermal char Raman spectra are underway and may follow similar work performed for analysis of pyrolysis chars (Smith et al., 2016). In contrast with Raman micro-spectroscopy, NMR spectroscopy suggests that hydrothermal char is a highly furanic material (Baccile et al., 2009), consisting of PAH sub-units possessing approximately 1-5 rings on average. Carbon X-ray Absorption Near Edge Spectroscopy (C-XANES) spectra of hydrothermal char are also consistent with those of a furanic material, consisting of small PAH sub-units (Latham et al., 2017).

7.4. Hydrothermal char applications

As previously stated, hydrothermal chars are being investigated for a variety of applications that benefit from high surface areas (which can be achieved by post-reaction activation), high oxygen content of the hydrothermal char surface, or the ability of hydrothermal chars to be modified to include various heteroatoms or functional groups (e.g., carboxylic acids, amines, and sulfonic acids) (Fig. 4). Reported surface areas of hydrothermal chars range from approximately 10 m² g⁻¹ for chars synthesized from simple carbohydrates up to approximately 100 m² g⁻¹ for some biomass-derived chars (Sevilla and Fuertes, 2009a; Liu et al., 2010). Base treatments can increase the measured surface area of hydrothermal chars. For example, Li et al. (2011) and Sevilla et al. (2011) pyrolyzed a hydrothermal char in the presence of KOH to increase the surface area of the hydrothermal char from approximately 10 m² g⁻¹ to greater than 1200 m² g⁻¹. The increased surface area obtained after base treatment may be due to removal of acidic side chains that would block pore access (Li et al., 2011), as well as partial gasification and expansion of lattice structure of the aromatic islands that would form as a result of temperature treatment (Yoon et al., 2004). These increased surface areas were used by Sevilla et al. (2011) to produce high capacitance carbon electrodes with a specific capacitance of 236 F g⁻¹ (100 F cm⁻³) measured at a sweep rate of 1 mV s⁻¹. Sevilla et al. (2011) also showed that that these high surface area materials (Li et al., 2011) could be used for hydrogen storage; in fact, the 5 wt.% hydrogen storage capacity of hydrothermal char was very similar to the reported hydrogen capacity of carbon nanotubes (Cheng et al., 2001).

Given the success of pyrolysis chars for soil amendment and remediation applications (Sohi et al., 2010), soil amendment is an obvious application for hydrothermal chars. However, the behavior of hydrochars and pyrolysis chars are distinct from one another, and the two materials cannot be used interchangeably. For example, Eibisch et al. (2015) reported that pyrolysis char reduced the in situ availability of a model pesticide (isoproturon) by a

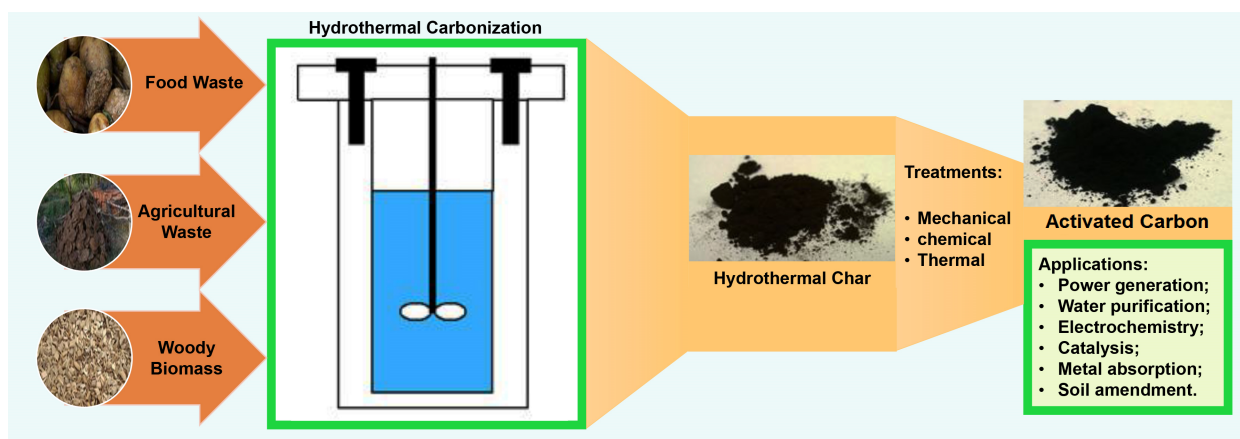


Fig.4. Hydrothermal char applications from agricultural waste, woody biomass and food waste.

factor of 10–2283 compared with 3–13 observed for hydrothermal char treatments. On the other hand, Ro et al. (2016) reported that the nutrient retention of hydrothermal char-amended soils was greater than what observed for pyrolysis char-amended soils, though the mechanism of nutrient retention could not be clarified. Malghani et al. (2013) showed that hydrothermal chars are less stable than pyrolysis chars in soil, as the carbon content of soils mixed with hydrothermal chars decreased by 60% after 105 d, while the carbon content reduction of soils mixed with pyrolysis chars was only 10%. Moreover, Busch et al. (2012) reported potential toxicity concerns with using hydrothermal char in soils, potentially a consequence of using raw hydrothermal chars that were not rinsed prior to use.

Hydrothermal chars have shown promises for adsorption of metal cations from aqueous solutions. Regmi et al. (2012) reported that the copper and cadmium adsorption capacities of switchgrass hydrothermal chars were comparable to those measured for Calgon WPH® activated carbon. Furthermore, an aqueous KOH post-treatment increased adsorption capacity by nearly 100% (Regmi et al., 2012). Similarly, Demir-Cakan et al. (2009) showed that hydrothermal chars co-carbonized with acrylic acid produced materials with lead and cadmium high capacities (approximately 350 mg g⁻¹ for lead and 988 mg g⁻¹ for cadmium). These extremely high adsorption capacities compared favorably with that measured for HNO₃ oxidized carbon nanotubes; the lead and cadmium capacities of oxidized nanotubes have been reported as 97 and 10.9 mg g⁻¹, respectively. Xue et al. (2012) found that H₂O₂ treatment increased the lead adsorption capacity of a peanut shell hydrothermal char from 0.88 mg g⁻¹ to 22.82 mg g⁻¹, a performance similar to that of an activated carbon.

8. Conclusions

Renewable energy is an area of active research which includes solar energy, wind power systems, geothermal power, and bioenergy. Renewable energy derived from biomass processing systems holds substantial promises and prospects for scale-up towards mass production of different types of bioenergy, namely, bio-ethanol and other liquid fuels, biogas, (or biohydrogen, biomethane, or biohythane), and hydrothermal chars. However, utilization of a renewable resource does not ensure an environmentally-sustainable process. For this reason, the principles of green chemistry and green engineering must be coupled with the utilization of renewable resources to yield environmentally-sustainable production of bioenergy. The application of subcritical and/or supercritical conditions for water extraction, water hydrolysis, water and hydrothermal carbonization using a variety of biomass embodies many principles of green chemical engineering. The core of green engineering principles encompassed by subcritical and/or supercritical processing for bioenergy generation is designing less hazardous and low-toxic chemical synthetic routes which may additionally be catalytically assisted and use benign/safer solvents. Moreover, these chemical schemes are intended to be more energy efficient using renewable feedstocks.

The present review also highlights three main areas of research. The first area is related to the significant impact and influence of the process fluid temperature(s) on the kinetics of the processes and on the thermal stability of the moieties involved. Conversely, the impact of pressure is less substantial than temperature, provided that the pressure is sufficient to maintain a liquid water phase. The second aspect pertains to the substrate-specific dependence of sub- and supercritical water processes making their development and optimization highly dependent on the feedstock used. As a result, there is an urgent need to comprehensively understand the underlying fundamentals required to design reactors suitable for processing a wide range of feeds, rather than single-feed reactors. The last aspect concerns the minimum throughput of feedstock needed to ensure a sustained supply-chain relationship in the overall network configuration and logistics which becomes relevant when attempting to scale up subcritical/supercritical biomass processing schemes.

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