Hydrothermal Reactions of Agricultural and Food Processing Wastes in Sub- and Supercritical Water: A Review of Fundamentals, Mechanisms, and State of Research

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ABSTRACT: Hydrothermal (HT) reactions of agricultural and food-processing waste have been proposed as an alternative to conventional waste treatment technologies due to allowing several improvements in terms of process performance and energy and economical advantages, especially due to their great ability to process high moisture content biomass waste without prior dewatering. Complex structures of wastes and unique properties of water at higher temperatures and pressures enable a variety of physical—chemical reactions and a wide spectra of products. This paper's aim is to give extensive information about the fundamentals and mechanisms of HT reactions and provide state of the research of agri-food waste HT conversion.

KEYWORDS: *hydrothermal reactions, subcritical and supercritical water, hydrothermal carbonization, aqueous phase reforming, liquefaction, supercritical water gasification, food waste, agricultural waste, bio oils, hydrogen, synthesis gas*

■ INTRODUCTION

The agricultural and food industries, as large manufacturing sectors, leave considerable amounts of residues each year, treated mostly as biowaste. Food and beverage production only resulted in annual waste in 2010 of approximately 90 million tonnes across the EU-27.[1] Reducing the amount of biowaste is a critical point of waste management strategy and a crucial step to meet targets related to reducing greenhouse gas emissions, increasing production of fuels and energy from renewable resources, and fulfilling environmental policy obligations, especially the European Union (EU) Landfill Directive to reduce the biodegradable waste amount going to landfills.[2,3] Despite many novel technologies for collection, separation, and treatment, reduction of waste biomass in the agricultural and food sectors is still case-limited. Reuse of waste, which remains after the primary utilization of plant or animal source, for production of value-added products such as biofuels, biomaterials, and chemicals is still inadequate.

Residues from agriculture and food processing industries result mostly from processing of herbaceous (lignocellulosic) and animal raw material to valuable foodstuff through extraction and/or separation of nutritionally valuable components of the raw material. Furthermore, these wastes emerge not only from food processing and consumption but also from their treatment and disposal (e.g., wastewater, sludge, H₂S). They are further used either as animal feed (e.g., spent grains, fruit and vegetable pulp and pomace, distiller's wash), fertilizers (solid sludge from wastewater treatment, filtration, etc.), or fuel (incineration of dry solid waste). Due to the low product value and net economics of these traditional methods, many novel technologies have been established in the past few decades as promising routes for waste biomass utilization (e.g., anaerobic digestion for production of biogas, composting, fermentation to alcohols, thermochemical conversions such as gasification and pyrolysis). Due to the fact that each individual agricultural and food industry generates different amounts of product-specific wastes, they vary considerably in chemical composition, consistency, water content, etc.[4] Nevertheless, such wastes typically consist of carbohydrates (sugars, cellulose, and starch), lignin, proteins, oils, and fats.[4] Moreover, many wastes contain large amounts of water, in some cases up to 95 wt % (e.g., animal blood, whey, sludges, wastewater).[4] This affects directly the selection of appropriate technologies for efficient utilization.

Wet biomass, containing >50 wt % water, is in most cases unattractive feedstock for further utilization due to increased transport costs, energy consumptive thermal separation prior to further processing (e.g., combustion), and also environmental considerations related to unpleasant odor, large numbers of pathogens including bacteria, viruses, and parasites, etc. For this reason, hydrothermal (HT) reactions have gained much attention during the past decades as potential conversion routes for wet biomass waste, especially for those of very high water content (>50 wt %). In general, HT reactions could be described as reactions in water media at higher temperatures and pressures (sub- and supercritical water). Regarding types (or phases) of products, they could be divided into four main processes: HT carbonization, aqueous phase reforming, liquefaction, and gasification. The main advantage over other processing methods includes ability to use wet biomass without prior dewatering. In these processes water has the role of reactant, solvent, and, as will be presented in further section, also catalyst. Also, reaction rates of biowaste feedstock conversions in water are relatively high (even a few seconds), and almost 100% conversions could be obtained. Furthermore, using mixed wastes with complex chemical composition (lignocelluloses, fats, proteins, inorganic) having different reactivities in water at higher temperatures and pressures enables production

Table 1. Review Papers Focused on HT Reactions Published in the Past Decade

authors	main interest of review[a]
N. Akiya and P. E. Savage, 2002[6]	roles of water as reaction medium
M. Möller et al., 2011[7]	properties of SubCW as reaction medium; reactions of model substances and formation of selected products in SubCW
H. Weingartner and E. U. Franck, 2005[8]	properties of water as solvent
A. Kruse and E. Dinjus, 2007[9]	properties of hot compressed water and synthesis reactions
G. Brunner, 2009[10]	properties of water; hydrolysis reactions in SubCW and SCW
Y. Yu, X. Lou, and H. Wu, 2008[11]	properties of water; hydrolysis reactions in SubCW and SCW and comparison with other hydrolysis methods
F. Jin and H. Enomoto, 2011[12]	acid−base-catalyzed reactions and reaction of oxidation
N. S. Kus, 2012[13]	review of chemistry and mechanisms of reactions in SubCW and SCW
A. A. Peterson et al., 2008[14]	biofuel production in HT media: structural components of biomass, chemistry of reactions and review of HT processes, aspects of inorganic components in biomass
M. Matsumura et al., 2006[15]	review of model biomass compounds reaction in SCW
J. A. Libra et al., 2011[16]	HT carbonization: chemistry, processes and application
B. Hu et al., 2010[17]	HT carbonization: engineering of carbon materials and their aplications
R. R. Davda et al., 2005[18]	aqueous-phase reforming: catalysis and factor controlling the selectivity of reactions
G. W. Huber and J. A. Dumesic, 2006[19]	aqueous-phase catalytic processes: production of alkanes and H_2
S. S. Toor et al., 2011[20]	HT liquefaction chemistry of model compounds; modeling of HT liquefaction; pilot-plant units for production of liquid biofuels
J. Akhtar et al., 2011[21]	effects of process parameters on bio-oil yield in HT liquefaction
Y. Guo et al., 2010[22]	catalytic supercritical water gasification for hydrogen production: water properties and catalysis
Y. Matsumura et al., 2005[23]	SCW gasification current status and perspectives: reactor design, chemistry of reactions of model and real compounds, review of catalysts, engineering aspects
A. Kruse, 2009[24]	short summary in HT gasification: accomplishments and challenges
P. E. Savage, 2009[25]	perspectives on catalysis in SubCW and SCW: synthesis reactions, waste destruction, and biomass processing

[a]SubCW, subcritical water; SCW, supercritical water.

of versatile chemicals and fuels in gaseous, liquid, or solid state. This provides processes for fuel or chemical production that are economically competitive with other biochemical or thermochemical processes.[5] Moreover, it enables integration of processes for production of versatile products (from high-value−low-quantity chemicals such as phytochemicals to low-value−high-quantity products such as platform chemicals, fuels) and energy on one location from waste streams through the principle of "biorefinery", which is the most interesting scenario for the future.

Hydrothermal reactions as a relatively novel way for conversion of biomass to fuels, energy, and chemicals have been described and discussed in several different reviews (Table 1). These previous reviews are focused on various aspects of HT reactions: from covering properties of subcritical and supercritical water and its roles and effects as reaction media,[6−9] to fundamentals of hydrolysis and other hydrothermal reactions in sub- and supercritical water,[10−13] to chemistry and engineering aspects of biofuel and energy production via HT transformations[14,15] and to reviewing separately each HT process such as carbonization,[16,17] aqueous phase reforming,[18,19] liquefaction,[20,21] and gasification.[22−26] Most of these reviews cover research on model substances such as cellulose, glucose, and lignin. From our knowledge, there is no review focused on the specifics of such various types of agriculture and food industry waste processing via different known types of hydrothermal reactions at one place. The experiments on real biomass mostly do not meet yields and selectivity as those done with model substances. Furthermore, the work with real biomass has many other engineering obstacles and challenges (solid feedstock delivery and loading, inorganic and other impurities in biomass cause scaling on equipment walls and catalysts, etc).[14]
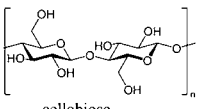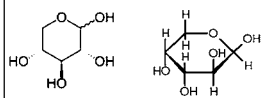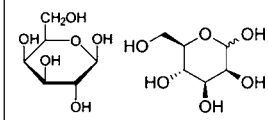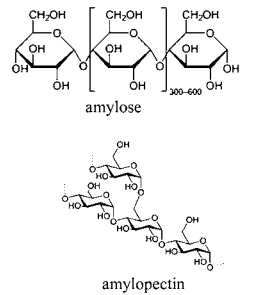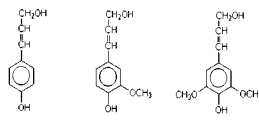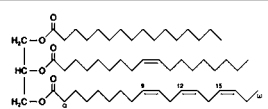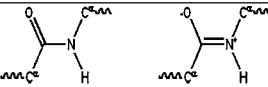
This review aims to cover a more extended view on experimental analyses performed on agriculture and food processing industry residues and wastes in sub- and supercritical water,

highlighting the products that could be produced during these reactions. The review is divided into three main parts. In the first part a short description of fundamental structural components of agricultural and food wastes and their properties is given. These properties affect the behavior of whole waste material during the hydrothermolysis in sub- and supercritical water. The second part gives a description of water properties in sub- and supercritical state as reaction media with the aim of providing a better understanding of HT reactions. The third part gives a detailed description of the chemistry and mechanisms of different HT processes, with specific interest in research focused on agriculture and food wastes and substrates that could be obtained from them. An overview of most the important efforts and achievements in the laboratory and at large scale (pilot and or/industrial) is given with the aim of stressing the key points, main obstacles, and perspectives from an engineering point of view.

CHEMICAL STRUCTURES AND PROPERTIES OF AGRICULTURAL AND FOOD WASTE BIOMASS

Agricultural and food processing residues are derived from processing of a particular herbaceous (lignocellulosic) or animal product. They include mostly wet materials such as molasses, bagasse, oilseed cakes, maize milling byproducts, brewer's waste, and crop residues (straws, stems, stalks, husks, shells, seeds, etc.), which come from cereals, fruits, coffee, olive, tea, etc., meat and fish production byproducts, slaughterhouse waste, wastewater and sludge, and many others. They are constituted of several main structural components (carbohydrates, lignin, lipids/fats, and proteins, mostly in animal sources) and several low-molecular-weight substances, arranged themselves in cross-linked three-dimensional resinous structure (extractives, inorganics, etc).[27] Table 2 presents the main structural components of wastes that originate from agriculture and food processing industries, their

Table 2. Main Structural Components of Agricultural and Food Wastes and Their Properties

Component	Chemical structure and monomers/oligomers formula	Main properties	The main sources in agro- and food industry waste
Cellulose	cellobiose $[C_6H_{10}O_5]_n$ n~100-10 000	Homopolymer of glucose units joined by β-1-4-glycoside bonds with crystalline ribbon-like structure. Cellulose is not soluble in water at standard conditions, but starts dissolving at 180°C and completely dissolves at around 330°C.	Cereals straw ,wine shoots, sunflower stalks, sugarcane bagasse, cotton stalks
Hemicellulose	$[C_5H_{10}O_5]$ xylose　　　arabinose $[C_6H_{12}O_6]$ galactose　　　mannose	Heteropolymer of pentoses (xylose and arabinose) and hexoses (glucose, galactose, mannose), highly substituted with sugar acids (acetic acid). Due to amorphous structure it is easily hydrolysed in water at temperatures above 160°C to monomers, which could be, at acid water conditions, further transformed to chemicals.	Sugarcane bagasse , corn cobs, sunflower seed hulls and stalks
Starch	amylose amylopectin	Polymer consisted from 10-35% of linear chain α-amylose (1,4 linked glucose chain) and 65-90% of branched chain α-amylopectin (branched chain of basic repeating units of 1,4 linked glucose with branches of 1,6 linked glucose). Hydrolyses very easily in hot water to glucose and further to chemicals (5-HMF, fufural, etc).	Potato, cereal grains
Lignin	p-coumaryl　coniferyl　sinapyl alcohols	Heteropolymer consisting of three hydroxycinnamyl alcohol monomers (C9) differing in their degree of methoxylation: p-coumaryl, coniferyl and sinapyl alcohols. Lignin is chemically the most resistant component of lignocelluloses. Dissolution and hydrolysis to monomers starts in near- and supercritical water.	Drup endocarp (coconut shell, walnut shell, olive shell, etc).
Lipids/fats	Triglycerides	Non-polar aliphatic compounds composed of triglycerides (TGAs)-esters of fatty acids and glycerol. They are insoluble in water at normal temperatures, but at HT conditions hydrolyse to fatty acids and glycerol and further to hydrocarbon like substances (higher alkanes, acrolein, etc).	Oilseed cakes, slaughterhouse waste, algae, meat food waste, etc.
Proteins	Peptide bonds [NHCH(R)C(O)]n n=50-2000, R-various side groups of amino acids	Built from amino acids linked together by peptide bonds. Not easily hydrolyzed by HT reactions, but degrade slowly to amino acids, which further rapidly degrade to hydrocarbons, amines, ammonia, aldehydes and acids.	Meat waste (blood, fats), fish waste, oil seeds...

chemical structures, and main properties regarding HT processing. Although ratios between components vary by feedstock types (grasses, grains, fruits, algae, etc.), carbohydrates are the major chemicals in plant biomass, representing almost 75% of biomass weight. The second most abundant chemical component is lignin (20−25% of biomass weight). Lignin is a complex, cross-linked polymer built of substituted phenols that form large molecular structures. It acts as a reinforcing agent, giving mechanical strength to biomass by gluing the fibers together between the cell walls. Therefore, plant biomass is commonly referred to as lignocellulose.[27,28] Minor parts are organic substances that have low molecular weight and are soluble in neutral solvents. Such organic substances are vegetable oils and fats, waxes, proteins, secondary metabolites (flavanoids, phenols, essential oils, sterols, alkaloids, tannins, etc.). Although plant biomass usually contains only limited amounts of these substances, they are important for the production of fine value-added chemicals (dyes, food additives, and nutripharmaceuticals).[29] The following section gives some basic information about the structure and most relevant properties of these components with the aim of understanding the main reaction pathways of these waste constituents during HT reactions.

Carbohydrates. The most abundant components of lignocellulosic type of waste are C_6- and C_5-sugars that form cellulose (a polymerized structure formed by glucose) and hemicelluloses (a polymer of glucose and xylose), commonly named carbohydrates. Cellulose is a linear biopolymer of β-glucopyranose interlinked by β-1,4-glycoside bonds. The basic repeating unit of cellulose polymer is cellobiose. a unit consisting by two glucose anhydrides (Table 2). Intermolecular and intramolecular hydrogen bonds between −OH groups within the same and surrounding cellulose chains arrange chains in parallel form and give cellulose a mostly crystalline ribbon-like structure. Most plant biomass has approximately half crystalline structure, the other half being amorphous.[30] Cellulose fibers constitute cell walls, giving strength to biomass. Due to its compact structure, cellulose is not soluble in water at standard conditions but partially dissolves in subcritical water and completely dissolves at temperatures >330 °C.[31] At these conditions, cellulose depolymerizes into oligosaccharides, which further hydrolyze and decompose to aqueous oligomers, monomers (glucose and fructose), and other byproducts of glucose. Chemical and thermal decomposition of monomers and smaller molecules leads to new molecular rearrangements, thorough ruptures, dehydration, and decarboxylation leading to various liquid, solid, or gaseous products depending on process conditions, which will be presented in detail in subsequent sections.

Hemicellulose is the second most common polysaccharide in nature and represents about 15−35% of lignocellulose, depending on type and source of biomass. Hemicellulose is a very important raw material for various transformations to biofuels and other products.[32−35] It is a short, highly branched polymer consisting of five-carbon (C_5) and six-carbon (C_6) sugars. Hemicelluloses are heterogeneous polymers of pentoses (xylose and arabinose) and hexoses (mannose, glucose, galactose), all of which are highly substituted with sugar acids. The branched nature of hemicelluloses makes them amorphous and more easily hydrolyzable to its constituent sugars in water at elevated temperatures, compared to cellulose. When hydrolyzed, the hemicellulose from, for example, hardwoods releases products high in xylose (a C_5-sugar) in contrast to softwoods, which yield more C_6-sugars. With further acid-catalyzed hydrothermolysis or enzyme

hydrolysis it converts to various building block chemicals such as weak carboxylic acids (succinic, fumaric, levulinic, glucaric acids, etc.), polyols (xylitol, arabitol, sorbitol), furfural. or lactones.[34] These platform chemicals could be additionally (bio)converted to a huge spectra of organic chemicals, of either low value and high volume (e.g., transport fuels, plastic) or low volume and high value (pharmaceuticals, food additives, cosmetics, and other).[35] With regard to relatively easy conversion to sugar monomers, production of basic chemicals from hemicelluloses in aqueous media on industrial scale is a well-known subject from the past century. One of the oldest and most important chemicals from hemicelluloses is furfural, mostly produced by acid hydrolysis of sugar cane bagasse, wood, corn stoves, cereals, and other biomass rich in pentoses, with annual production of over 142,000 tonnes.[36]

Starch is the most abundant storage reserve carbohydrate in plants, mostly found in seeds, fruits, roots, and other parts of plants. The composition and structure of starch vary considerably between different plants.[37] In general, it is a polymer consisting of 10−35% of linear chain α-amylose (1,4-linked glucose chain) and 65−90% of branched chain α-amylopectin (branched chain of basic repeating units of 1,4-linked glucose with branches of 1,6-linked glucose) shown in Table 2. The percentage of amylose is genetically determined, but could be increased through genetic modifications for various purposes.[38] In its native form, starch has a limited number of uses (mostly as a thickener or binder), but its physicochemical properties can be altered by chemical or enzyme modifications or chemical/physical treatments. Starch hydrolyzes more easily than cellulose at hydrothermal conditions at temperatures around 200 °C and depolymerizes to glucose and further to 5-HMF.[39−41] Nowadays, starch, with an annual market size of 60 million tonnes is a raw material for many purposes, from production of sweeteners for the food industry to production of ethanol. More than 80% of starch on the world market is produced from maize (most of this in the United States). The rest comprises wheat and potato starches, cassava, tapioca, etc. It has great potential as a renewable raw material in numerous industries such as paper, plastic, food, and building.[28]

Lignin. Lignin is a complex, highly aromatic polyphenolic material available in plants in different compositions, molecular weights, and amounts. The abundance of lignin in agriculture and food biomass is not so high as in woods, but some agriculture plants and parts, such as drupe endocarp (e.g., coconut shell, olive stone, walnut shell) could be a valuable source of lignin.[42] Other types of agriculture and food waste, such as straw, grasses, or animal materials, contain relatively low percentages of lignin. Lignin has a complex, branched structure mostly made from phenylpropane subunits of *trans-p*-coumaryl alcohol, *trans-p*-coniferyl alcohol, and *trans-p*-sinapyl alcohol (aromatic monomers).[43] Lignins from different types of plants are characterized by different percentages of corresponding alcohols and different final networks (subunit connections). For that reason, lignin does not have a regular structure like cellulose, but it is chemically and physically heterogeneous; even a final chemical structure is unknown. Nevertheless, it is usually assigned as a polyphenolic material having an amorphous structure with aromatic and C_3 chain parts. In general, two types of lignin are recognized nowadays: native lignin, present naturally in biomass; and technical lignin, which is isolated from biomass thorough various processes.[44] Large quantities of lignin without sulfur content could be isolated in various pretreatment processes for bioethanol production from

agriculture and food waste feedstock, where lignin and hemicelluloses are extracted to enhance saccharification and/or fermentation of cellulose to ethanol.[45] Nevertheless, the majority of technical lignin is produced by a chemical pulping process (Kraft pulping) in the paper industry.[44]

There is still little information about the real mechanism of lignin decomposition in subcritical and supercritical water, compared to knowledge about cellulose and hemicelluloses. Lignin decomposition in subcritical water is more difficult than that of other biomass components. The reason lies in the fact that lignin is chemically the most resistant component of lignocelluloses due to highly cross-linked phenol alcohol structure, bonded together with strong ether (C−O−C) and C−C bonds. Lignin could be liquefied by the addition of catalysts such as ethanol, phenol, or alkaline salts also at subcritical water conditions, but significant decomposition starts yet in supercritical water.[45−47] In near-critical and supercritical water, lignin hydrolyzes by cleavage of bonds between carbon and heteroatoms. More about lignin HT depolymerization in water at different temperatures is presented in the next section.

Vegetable Oils and Fats. Vegetable oils and fats are water-insoluble, hydrophobic substances in plants, which are products of esterification of one molecule of glycerol and three molecules of fatty acid and are commonly named triacylglycerides (triglycerides). Fatty acids account for 93−98% of the total weight of triacylglycerides, and their carbon chain length and the number of unsaturated bonds vary with plant type. The most common fatty acids in vegetable oils are lauric, myristic, palmitic, stearic, oleic, and linoleic acid, etc.[48] Although they are considered in minor concentrations in biomass (mostly in seeds, nuts, fruits), oils and fats are one of the most important raw materials for agriculture and food industries. Most of them are used for food and animal feed, and a minor amount is used for the chemical industry (relative share of 8−10% with tendency of increasing). Nevertheless, the increased use of vegetable oils is observed in the past decade for bioenergy and biofuel (biodiesel) production. The use of vegetable oils for chemicals includes palm oil, soybean oil, sunflower oil, coconut oil, and rapeseed oil, making them very attractive and widely abundant raw materials in the countries of Europe, Southeast Asia, South America, and India. The main waste product from biodiesel production is glycerol.

Vegetable oils and fats are insoluble in water at ambient temperatures. The increase in temperature results in increased solubility due to the decreasing dielectric constant of water, as is discussed in a further section. At supercritical conditions of water, they become completely miscible with water. During hydrolysis in subcritical water, lipids hydrolyze to fatty acids and glycerol. King et al. studied hydrolysis of soybean oil in subcritical water at 330−340 °C and 13.1 MPa and found 90−100% conversion to fatty acids. In an optically accessible flow cell they observed that two phases become completely miscible.[49] Similar observations were presented by Alenezi et al., who studied noncatalytic hydrothermal hydrolysis of sunflower oil in a tubular reactor at 270−350 °C.[50] Fatty acids and glycerol, as a product of triglyceride (TGA) hydrolysis, undergo further degradation at HT conditions. The degradation of glycerol at HT conditions at 200−400 °C without catalysts produced acetaldehyde, acrolein, allyl alcohol, and other unidentified products, depending on temperature conditions.[51] With the use of catalysts, glycerol could be in subcritical water reformed to hydrogen or alkanes.[18,19] Free fatty acids are relatively stable, but start to degrade significantly to long-chain

hydrocarbons at higher reaction temperatures and longer reaction times with the addition of alkaline catalysts, which can be used for the production of biofuels. Therefore, conversion of lipid- and fat-rich agricultural and food wastes, such as slaughterhouse waste, oilseed cakes, and some algae, at HT conditions will lead to bio-oil rich in fatty acids and their degradation products.

Proteins. Proteins are important constituents of animal (meat, blood, etc.) and fish food waste. Proteins are built from amino acids linked together with peptide bond. A peptide bond is a linkage between carbonyl and amine groups in amino acids, which is more stable in HT reactions than gycosidic bonds in cellulose and starch. Rogalinski et al. studied hydrolysis of some biopolymers (starch, cellulose, and proteins) in subcritical water and observed that proteins were most stable.[39] Only 3.7 wt % of amino acids was produced at 250 °C, 25 MPa, and 300 s of reaction time. With the addition of CO_2 as catalyst, the yield of amino acids was 15 wt %. For this reason, during HT reactions of protein-rich wastes significant concentrations of amino acids could be expected.[52,53] However, amino acids undergo rapid degradation at HT conditions, primarily by deamination and decarboxylation reactions, leaving hydrocarbons, amines, aldehydes, and acids in liquefied products (bio-oils) as the main degradation products of amino acids at these conditions.[54]

PROPERTIES OF SUBCRITICAL AND SUPERCRITICAL WATER

Interest in the use of hot compressed water (HCW) or water at temperatures and pressures above its boiling point as a reaction medium for conversion of waste biomass to chemicals has been drastically increased in the past two decades. The main reason for this lies parallel to increased interest in waste biomass usage as a renewable resource for sustainable development and also parallel to extending knowledge about water's unique thermophysical and chemical properties in recent years. As was mentioned in the Introduction, subcritical water (SubCW) is pressurized water at temperatures above its boiling point at ambient pressure and below the critical point (T_c = 374 °C, pc = 22.1 MPa, ρ = 320 kg m^{-3}).[7−9] Within a region close to critical conditions (near-critical or subcritical region), system properties become more sensitive to pressure and temperature changes. For example, with increasing temperature, the density of the liquid decreases and that of vapor increases. The properties of both phases become more similar and finely identical at critical point. Water above the critical point is named supercritical water (SCW) and its properties vary between liquid-like and gas-like with changing temperature and pressure without any phase transition.[7−9]

To understand hydrothermal reactions of biomass, it is crucial to know water behavior as a solvent, as a reactant, or as a catalyst. The most relevant properties of water are those that could be manipulated during reactions to enhance reaction selectivity to desired products, such as density, miscibility, solvent dielectric constant, ionic product, electrolytic solvent power, transport properties (viscosity, diffusion coefficients and ion mobility), and hydrogen bonding.[9,55] These properties are strongly influenced by temperature and pressure, as can be seen from Figure 1. Subcritical water differs not only from ambient water (water at room conditions) but also from supercritical water. The nature of the reactions of biomass degradation and conversion in SCW hence depends on changes of SCW properties with temperature and pressure. The dielectric constant
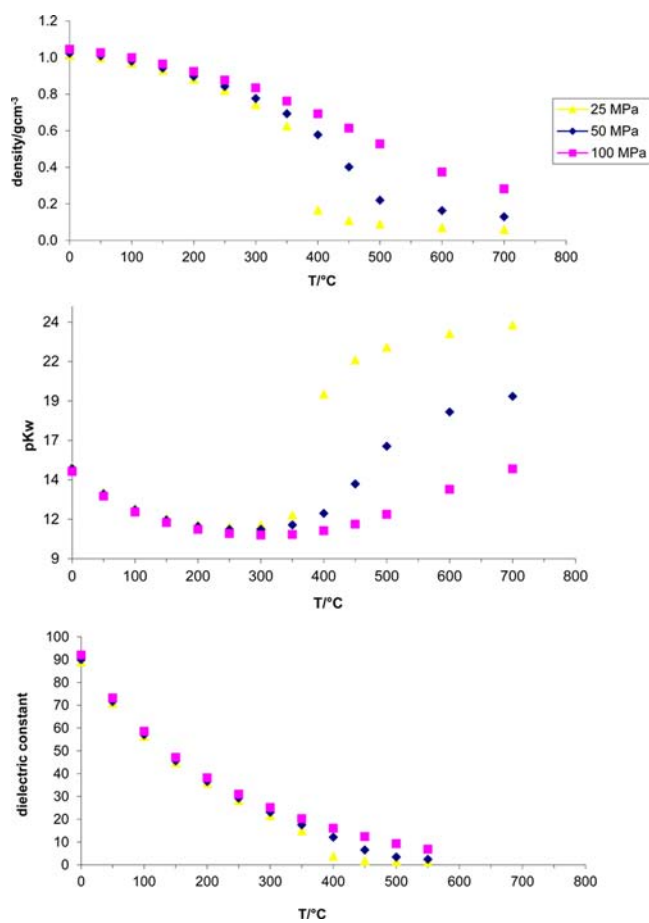
Figure 1. Changes in water density, ionic product, and dielectric constant in the range of 0−800 °C for 25, 50, and 100 MPa.

decreases from 78.5 Fm^{-1} at 25 °C and 0.1 MPa to 14.07 Fm^{-1} at 350 °C and 25 MPa[20] (comparable to some polar organic solvents at normal conditions, e.g., acetone and ethanol) so the solubility of hydrophobic organic compounds in subcritical water is increased, as is reviewed by Carr et al.[56] SubCW acts as a good reaction medium for various synthesis reactions, enhancing the ionic (heterolytic) reactions, as is summarized in a review by Kruse et al.[9] With increasing temperature of the SCW, the dielectric constant decreases to a value of 2 Fm^{-1} at 500 °C, resulting in water that behaves as a nonpolar solvent, favoring homolytic (free radical) reactions, for example, C−C bond splitting reaction during the pyrolysis and/or gasification.[56] Ionic species such as inorganic salts are poorly soluble in SCW, whereas permanent light gases such as O_2, N_2, NH_3, CO, CO_2, and hydrocarbons are fully miscible in SCW, making SCW a good reaction medium also for homogeneous reactions of organic compounds with gases (e.g., the oxidation of organic compounds with oxygen and air as a very interesting technology for hazardous waste treatment).[57] The ionic product of SubCW ($K_w = [H^+][OH^-]$) increases with temperature and is greater by 1−2 orders of magnitude than at ambient temperature (pK_w is 11.2 at a temperature of 250 °C and a pressure of 5 MPa), due to the endothermic nature of water self-dissociation.[9] At temperatures around 300 °C it reaches the maximum and afterward it decreases with further increase of temperature. Above the critical point, the ionic product drastically decreases due to decreasing ion solvation with decreasing density at higher temperatures. At a temperature of

400 °C and a pressure of 25 MPa it reaches a value of pK_w = 19.4.[9] According to these changes of ionic product, SubCW has an important role in acid- and base-catalyzed reactions, which is of great interest in biomass hydrolysis reactions, as will be discussed in following sections.

The unique behavior of SubCW and SCW could be also seen from transport properties, that is, high diffusion coefficient and thermal conductivity (maximal at critical state) and low viscosity, making them more similar to gases than liquids.[8−10] Due to enhanced mass and heat transfer processes, increasing reaction rates in processes with hot compressed water are increased, which is especially important in heterogeneous systems. Due to excellent potential to manipulate the type of reaction and selectivity by changing some of these water properties by changing the temperature and density, conversions of wastes in SubCW and SCW are some of the most promising routes for production of a wide variety of both low-quantity high-value and also high-quantity low-value chemicals.

In the context of hot compressed water properties, also the main disadvantages or technical challenges of the usage of this medium for biomass conversions should be mentioned. Biomass contains also small concentrations of various inorganic salts, the solubility of which in subcritical or supercritical media could be drastically decreased.[36] That causes salt deposition on reactor walls and other parts of equipment. Furthermore, processes with SubCW and SCW have process characteristics (acidic and oxidizing conditions, extreme pH values, sharp pressure changes, etc.) that favor corrosion process, which could be a huge problem regarding design consideration and safety.[57] High-temperature- and high-pressure-resistant materials such as Ni alloys with the addition of Cr and Mo are sufficiently resistant to corrosion in subcritical water and should be used in equipment construction.[58]

■ HYDROTHERMAL REACTIONS OF AGRICULTURAL AND FOOD PROCESSING WASTES

Hydrothermal reactions of complex agricultural and food processing wastes comprise a wide spectrum of physical and chemical reactions of main and minor components, mentioned in the previous section, and water in subcritical and supercritical states. In general, hydrothermal reactions of wastes could be divided into four main processes: hydrothermal carbonization, aqueous phase reforming, hydrothermal liquefaction, and SCW or catalytic gasification. This review does not cover separation processes with subcritical water (e.g., hydrothermal extractions of valuable phytochemicals from waste food industry streams) but is concentrated only on chemical reactions to new products. This section gives a more detailed description of the basic mechanisms of HT reactions with extended studies done on real agri-food industry waste in the past few decades.

Hydrothermal Carbonization (HTC). HTC of waste biomass has gained renewed interest during the past few decades due to great opportunities to produce valuable carbon materials with specific properties and applications.[16,17] It comprises, in general, the mildest reaction conditions compared to all other hydrothermal conversions. Most frequently, temperatures up to 250 °C, autogenous pressures up to approximately 2 MPa, and reaction times between 1 and 12 h are applied. This process simulates a long-time carbonization process at lower temperatures for coal production, producing a carbonaceous material named commonly "hydrochar".[16] Alternatively, also higher temperatures (even up to 900 °C) are applied, with or without catalyst addition. Although hydrothermal carbonization and

production of the carbonaceous solid product hydrochar take place in parallel also during the other hydrothermal conversions of biomass (liquefaction and gasification), mostly as an undesired side reaction that decreases contents of other favorable products (bio-oils, gases, etc.), here, HTC indicates a process for the production of charred solid material as a main product. Besides production of a solid fuel with a coal-like high heating value (HHV), this carbonaceous material has found many other potential applications, in environmental engineering,[59−61] catalysis,[62−65] energy storage,[66−68] the sensor industry,[69,70] medicine,[71] etc. During the treatment of waste material or waste originated substrates (e.g., saccharides such as glucose, sucrose, starch) in aqueous media at higher temperatures and pressures, the waste undergoes changes in its structure by numerous reactions such as hydrolysis, dehydration, decarboxylation, aromatization, recondensation, and depolymerization, occurring parallel in system.[16,72] They are always initiated by hydrolysis of macromolecules, which degrade to form a mixture of liquid, gaseous, and solid products, the characteristics and composition of which vary with reaction conditions, primarily with temperature. By comparison of product distribution from different hydrothermal conversion processes, it is shown that during the hydrothermal carbonization (at temperatures between 180 and 250 °C) even 80 wt % of initial biomass could be converted to hydrochar, whereas gasification or liquefaction (processed at temperatures between 300 and 800 °C) yielded only 10−35 wt %.[16] This is an indication that temperature remains the decisive process parameter in hydrothermal conversions of biomass.

High- and Low-Temperature HT Carbonization Processes. In general, there are two different reaction mechanisms of hydrothermal carbonization: high-temperature and low-temperature hydrothermal carbonization processes.[17] A high-temperature HTC process is based on wet pyrolysis of wastes at temperatures between 300 and 800 °C. At the high-temperature and high-pressure water conditions (supercritical water) reactive gases are produced parallel with other pyrolysis products (mostly bio-oils). Reacting together they could make various carbon structures (nanotubes, films, microspheres, fibers, activated carbon materials, etc).[17] For example, carbon nanotubes, which are well-defined and uniformly tubular structures with high specific surface properties (e.g., pore volumes, specific ion-exchange capacity), could be produced either as single-walled (SWNTs) or multiwalled (MWNTs) nanotubes.[73] Also, other three-dimensional carbon structures have been successfully synthesized from waste biomass originated compounds by high-temperature HTC. For example, Mi et al. have prepared microspheres from glucose solution at a temperature of 500 °C and a reaction time of 12 h.[74] These carbon materials possess various functional groups on their surface with high adsorption capacity, so the most important application of materials made through high-temperature HTC is their utilization as advanced activated carbon sorbents. For these purposes, various agricultural and food originated wastes could be used such as sewage sludge,[75−77] agro-industry waste,[77−80] animal manure,[81] and wood waste,[81,82] with or without activation with other chemicals to improve the functionality of carbon material.[82,83]

Despite many advantages, use of low-temperature HTC instead of high-temperature HTC processes is more favorable, especially for biochar for fuel production. Compared with a high-temperature HTC process, a low-temperature HTC process is carried out at temperatures up to 250 °C. Synthesis of carbonaceous materials with controllable morphology and surface functionality occurs through similar reactions as are in

high-temperature HTC processes but with different intermediate product distribution (and aggregate state) involved in particle formation. Sevilla et al. have described the mechanism of low-temperature carbonization of model substances: cellulose (220−250 °C)[72] and saccharides (170−240 °C).[84] They found that water-soluble organic compounds such as organic acids (lactic, acetic, levulinic, formic), furan-like compounds (5-hydroxymethylfurfural, furfural, 5-methylfurfral), aldehydes and phenols are first formed. Only minor concentrations of water-insoluble compounds and gases (composed mainly from CO_2) are produced. After that, these water-soluble compounds undergo polymerization and/or condensation and further aromatization of formed polymers to form aromatic clusters by intramolecular dehydration or keto−enol tautomerism. Nucleation starts when the concentration of clusters reaches the supersaturation point by diffusion of nuclei toward the surface of species present in solution resulting in nucleation growth. Growth is a result of linking of these species to microspheres via reactive oxygen groups (hydroxyl, carbonyl, carboxylic, etc.) present in both the outer surface of the microparticle and in reactive species, generating the stable oxygen groups of ether or pyrone (hydrophobic highly aromatic nucleus). Once the reaction stops, the surface of microparticles contains reactive oxygen groups and a hydrophilic shell has been formed.[84] Morphology and yield of products are defined by reaction temperature (aqueous solution behavior) and the concentration of substrate. It was observed that the diameter of microspheres and their yield increase with reaction temperature and concentration of solution.[84] Furthermore, by tailor controlled dehydration it is possible to obtain nanostructures with specific morphology and surface functionality (reactivity), making them attractive for use in various fields such as for catalysis, energy storage, drug delivery, and enzyme immobilization.[16,17]

In Table 3 recent research in the field of hydrothermal carbonization of various agricultural, food, and other waste-originated feedstock, at both low- and high-temperature regimens, is reviewed. The main properties of carbonaceous solid material with proposed application are also given. Produced micro- and nanospheric carbonaceous material has been tested mostly as a solid fuel or low-cost adsorbent for wastewater or for soil-conditioning applications.

Industrial HTC Plants. The major industrial application nowadays of HTC processes is in the production of carbonaceous solid biocoal with application as a fuel. The first demonstrative industrial scale HTC plant worldwide (HTC-0) was introduced into operation in 2010 in Karlsruhe (Germany) by AVA-CO₂ Co. and was developed in cooperation with Karlsruhe Institut for Technology (Gremany).[87] The multibatch process is able to convert waste organic biomass with low heating value (LHV) containing 20−75% water to biocoal in an economically and environmentally feasible way on aq scale of 8600 tonnes of biomass/year. In 2012, the company built an industrial (HTC-1) plant in Relzow (Germany) with a capacity of 10,800 tonnes of dry biomass/year. It is able to achieve >90% carbon efficiency and to produce biochar with >30 GJ/t. They stated the net energy efficiency of >70%.[88] From our knowledge, these industrial processes are still pioneers in HTC industrialization; however, they are very promising processes in agriculture and food industry waste treatment, a rapid increase of research activities and commercialization of HTC is expected soon.

Aqueous Phase Reforming. Aqueous phase reforming (APR) was proposed by Antal et al. as a promising route for

Table 3. Studies of HTC of Various Agricultural and Food Wastes or Substrates Originated from Them

waste material	experimental conditions	carbon material specifics	purposed application	ref
sugar beet tailing	$T = 300\ °C$, $t = 2$ h	biochar with functional groups, reduction of Cr(VI) to Cr(III), and electrostatic sorption of Cr(III) on biochar	Cr(VI) removal from wastewater	60
rice husk (hydrolysate)	$T = 95\ °C$, $t = 6$ h	sphere-like carbon material (500 nm size) with large specific capacitance (220 $F^{-}g$)	electrochemistry, catalysis, separation and absorption, medical industry	64
microalgae	$T = 200\ °C$, $t < 1$ h, $p < 2$ MPa	bituminous hydrochar with coal quality	producing syngas, conversion to chemicals and fuels, soil nutrient amendment	67
anaerobically digested maize silage	$T = 190–270\ °C$, $t = 2–10$ h	amorphous macro-sized particles HHV 25–36 MJ/kg	alternative fuel, soil conditioner	68
swine manure	(1) $T = 250\ °C$, $p = 3.4–9.0$ MPa, $t = 20$ h (2) $T = 620\ °C$, $t = 2$ h (pyrolysis)	hydrochar and pyrochar with different characteristics (functional group) regarding process conditions	soil fertility	85
sacharrides (glucose, cellulose, starch)	$T = 170–240\ °C$	uniform micrometer-sized spheres of tunable diameters (0.4–6 μm)	NA	84
olive oil waste, hazel nutshell	$T = 180\ °C$, $t = 4$ h	sphere-like particles of aromatic structure	NA	89
carbonated beverage (Sprite)	$T = 200\ °C$, $t = 3h$, with and without CO_2	microspheres of diameters 100–800 nm (600–800 nm in case of CO_2 addition)	NA	90
empty palm fruit bunches	150–350 °C	biochar (HHV = 25.8 MJ/kg)	solid fuel	91
	150–350 °C	biochar (HHV = 25.8 MJ/kg, 350 °C)	solid fuel	92
peanut hull	300 °C, $t = 5$ h (H_2O_2 activation)	biochar with high adsorption capacity for heavy metals	removal of heavy metals Pb^{2+}, Cu^{2+}, Ni^{2+}, and Cd^{2+}	93
pine sawdust and cellulose	$T = 200\ °C$, reactions done in acidic media, $t = 60–240$ min, microwave assisted	hydrochar 50% higher carbon content than raw material	NA	86
alginate	$T = 200\ °C$, Ca-assisted	carbon microspeheres (1–2 μm) with unique surface morphology	biochemistry, drug delivery, catalyst supports	63
sucrose	suspension of sucrose with In_2NO_3, $T = 180\ °C$, $t = 24$ h, followed by $T = 500\ °C$ for 2 h (conversion into thin and thick shells)	In_2O_3–carbon hollow spheres with gas sensing characteristics	gas sensors for C_2H_5OH	69
rice husk	$T = 800\ °C$, $t = 1$ h	carbon material with high adsorption capacity for Au(III) ions (0.76 mol/kg)	separation of Au(III) from wastewater and recovery of Au	61
barley straw	$T = 800\ °C$, $t = 1$ h	carbon material with high adsorption capacity for metals	separation of metals (Au, Pt, Pd, Cu, Fe, Ni) from wastewater.	61

processing waste biomass sugars and biomass-derived oxygenated hydrocarbons (C:O = 1:1) in aqueous media to hydrogen as a value-added chemical with wide application.[94] It is a process in which biomass carbohydrate or biomass-derived alcohols (methanol, ethylene glycol, glycerol, and sorbitol) convert over appropriate heterogeneous catalysts at temperatures of 220–250 °C and pressures typically of 1.5–5 MPa to produce primarily H_2 and CO_2. The overall reaction is presented in eq 1:

$$C_xH_{2x+2}O_x + xH_2O \xrightarrow{\text{catalyst, 220−250 °C, 1.5−5 MPa}} (2x + 1)H_2 + xCO_2 \tag{1}$$
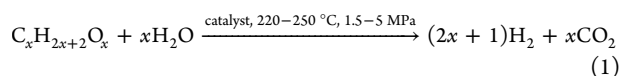
Due to a lower process temperature than is applied in the conventional processes, APR has several advantages over conventional steam reforming of methane such as lower energy consumption (elimination of the need to vaporize both water and hydrocarbon stream), increased safety (nonflammable and nontoxic feedstock), operational benefits (possibility to produce hydrogen with low CO concentration (100–1000 ppm) in a single-step process due to applied temperature and pressures favoring the water-shift reaction), effective purification using pressure-swing technology or membrane technologies and effective separation of CO_2 for further purposes, and fewer undesired decomposition reactions due to low applied temperatures.[18] Nevertheless, the process still has important challenges to improve the selectivity of H_2 production by this method. Due to the thermodynamic instability of the formed H_2 and CO_2 at low temperatures, they are highly reactive for methanation and Fischer–Tropsch reactions in which alkanes (especially CH_4) are formed.[18] An additional concern is related to detection of several side reactions that occur at these temperatures, especially during the sugar use as feedstock. Those are hydrogenation of CO and CO_2 to produce alkanes and dehydration reactions of intermediate hydrocarbons to acids, aldehydes, and other liquid or solid products.[18,94]

Oxygenated hydrocarbons with great potential for APR are methanol, ethylene glycol, glycerol, and sorbitol. Glycerol is probably the most interesting feedstock for APR, because it is available as high-quantity byproduct in the production of biodiesel.[95] In contact with a metal surface, oxygenated hydrocarbons undergo dehydrogenation steps in which intermediates are adsorbed on the metal surface by preferred metal–C bonding, subsequently causing C–C bond cleavage in hydrocarbons and formation of CO and H_2. CO reacts further with water to produce CO_2 and H_2 in the water-gas shift reaction (CO + H_2O → CO_2 + H_2).[18] However, parallel methanation and Fischer–Tropsch reactions proceed between CO and/or CO_2 and H_2, leading to methane and water formation. Furthermore, in cases of poor catalyst performance also undesirable alkanes could be formed by adsorption of hydrocarbon intermediates on metal surfaces by metal–O bonds, causing preferably C–O bond cleavage in hydrocarbons and formation of alcohols instead of H_2 and CO.[96] Another competitive reaction is cleavage of C–O bonds through dehydration caused by interaction with acidic sites on catalyst supports such as SiO_2–Al_2O_3 or by protons in the aqueous solution, followed by hydrogenation reactions on the catalyst. Organic acids could be also produced in dehydrogenation catalyzed by metals, followed by rearrangements in solution or catalyst. All of these side reactions decrease selectivity for hydrogen.

Identifying and improving the catalysts and catalyst support to increase hydrogen yield are major concerns of a great number of research teams throughout the world.[18] Research on aqueous-phase reforming of ethylene glycol with silica-supported group VIII metal catalysts performed by Davda and co-workers[97] at 210 and 216 °C suggests that Pt and Pd and Ni–Sn alloys show highest selectivity to hydrogen production and low tendency for alkane formation. On the contrary, silica-supported Ru, Rh, and Ni were very selective for alkane formation and were poorly active for hydrogen production. Ni catalysts show also some deviation during use, probably due to metal sintering.[97,98] Furthermore, it was observed that addition of other metals to catalysts could improve catalyst selectivity to H_2 formation and the water-gas shift reaction. Bimetallic catalysts PtNi, PtCo, PtFe, and PdFe supported on Al_2O_3 show significantly higher activity to hydrogen production from glycerol and ethylene glycol than monometallic catalysts under the same conditions.[98,99] The H_2 selectivity and stability of Ni catalysts can be improved by the addition of Sn to the Raney-Ni catalyst, decreasing significantly the rate of methanation.[98] The nature of the catalyst support also influences the selectivity of the APR process by catalyzing parallel dehydration pathways and formation of alkanes, as was described above. It was observed that a more acidic catalyst, such as SiO_2–Al_2O_3, leads to high selectivity of alkane formation, whereas the more basic/neutral support (e.g., Al_2O_3) favors hydrogen production.[18,97,100] Furthermore, catalytic activity decreases with reaction duration by carbon deposition on the catalyst surface so the addition of alkali metals (1 wt % of Na) exhibited both catalyst activity toward hydrogen formation and stability.[101] Along with the acidic/basic nature of the catalyst/support, also the pH in the reaction solution, originating from compound formation during the reaction, affects the selectivity of APR. Neutral or basic solutions promote hydrogen generation, so the addition of even 1% of KOH to feedstock solution could increase both glycerol conversion and hydrogen yield.[102]

The nature of the feedstock has also a strong influence on reaction selectivity. Cortright et al. have researched various biomass-derived hydrocarbons (methanol, ethylene glycol, glycerol, sorbitol, and glucose) in liquid water and have found that polyols (e.g., sorbitol) are the most suitable for hydrogen production.[103] By increasing the carbon number of the feed, as, for example, in the case of glucose, the selectivity for H_2 decreases due to the higher number of undesirable decomposition reactions due to complex chemical structures of sugars.[103] Although sugars (glucose) are not the most suitable feedstock for aqueous phase reforming due to low H_2 selectivity, a proper reactor design (e.g., more stages) could overcome this problem. Glucose could be first hydrogenated in a first reactor over the metal (Pt and Ru) catalyst supported over γ-Al_2O_3 or SiO_2–Al_2O_3 at temperatures from 170 to 200 °C and a pressure of 50 bar into sorbitol and mannitol.[104] A maximum yield of 31% was obtained with Pt/γ-Al_2O_3 catalyst at 190 °C and a pressure of 50 bar after 24 h of reaction. The sorbitol could be further reformed to hydrogen and/or alkanes at reduced pressure and temperatures of 200–220 °C.[104,105] Also, many other catalysts are proposed and tested for efficient sugar conversion to sorbitol such as Ni-containing carbon nanofibers,[106] carbon-supported Ru clusters,[107] and Ni_2P/AC catalyst.[108]

As was mentioned before, production of alkanes from sugar alcohols as a parallel reaction on metal catalyst is a potential way for production of alkanes from renewable resources. By increasing the acidity of the catalyst, the APR process is more

selective for alkane production. Light $C_1–C_6$ alkane production from sorbitol by dehydration/hydrogenation of sorbitol over the bifunctional catalyst system (catalyst containing acid as $SiO_2–Al_2O_3$ or mineral acid and metals) has been studied by Huber and Dumesic.[19] Sorbitol is first dehydrated over acid sites of catalysts and then hydrogenated on a metal catalyst (Pt and Pd, etc.). Hydrogen needed for hydrogenation could be produced in situ (cleavage of C–C bonds and water-gas shift reaction) or can be added to the reactor separately. The selectivity for production of alkanes could also be varied by type and composition of catalysts, reaction conditions, and reactor design, similarly as in the case of hydrogen production.[18,19] Nevertheless, hexane is the largest compound that could be produced by aqueous phase dehydration and hydrogenation of sorbitol and possess a low value as a fuel additive due to its high volatility. To produce larger liquid alkanes ($C_7–C_{15}$), linking of several carbohydrate species together must be performed by C–C bonding (C number increasing) through aldol condensation prior to the dehydration/hydrogenation reaction. Compounds derived from, for example, acid hydrolysis such as furfural, hydroxymethylfurfural, and acetone, which could form large organic molecules through aldol condensation reactions at room temperature over the magnesium–aluminum oxide base catalyst, could be of special interest for the production of alkanes.[109] These compounds undergo dehydration/hydrogenation reactions over before-mentioned bifunctional catalysts (e.g., 4% $Pt/SiO_2–Al_2O_3$) in a specially designed four-phase reactor producing the $C_7–C_{15}$ alkanes.[19,109]

APR is a very promising route for the production of hydrogen and alkanes from organic feedstock derived from the agricultural and food industries, at relatively mild reaction conditions and with the possibility to achieve energetically neutral process or use little additional energy for reaction. The first commercial demonstration of the APR process already started with implementation of the BioForming Technology by Virent Energy System Co. in cooperration with Cargill, Coca-Cola, Shell, Honda, and other partners.[110,111] BioForming Technology is a combination of APR and modified conventional catalytic (petroleum) processing. It is able to use a wide variety of feedstocks, including cellulosic feedstocks such as bagasse, corn stover, grasses, sorghum, and wood as well as conventional feedstocks such as beet sugar, sugar cane, and corn starch to convert them into hydrocarbons and a full range of bioproducts identical to those made from petroleum including chemicals for plastics and fibers.[110,111] In Table 4 some recent research involved in hydrogen and alkane production by APR from various biomass originated feedstocks is presented. Nevertheless, APR is still under serious research challenges, primarily in the field of heterogeneous metal catalyst design and optimization of reactor performance.

Hydrothermal Liquefaction. The oldest and most investigated HT process of agricultural biomass and food biowaste conversion to valuable products and fuels is hydrothermal liquefaction (HTL). Despite the fact that biomass liquefies (hydrolyzes) in water also at lower temperatures (160–280 °C) and produces water-soluble products (e.g., sugars, carboxylic acids, furfural, etc.) as main products, the term of hydrothermal liquefaction (HTL) is mostly interpreted as biomass transformation processes in water media under medium temperatures and high pressures (280–370 °C, 10–25 MPa) to give primarily water-insoluble bio-oils as main products.

At HT conditions, biomass hydrolyzes and decomposes to unstable small components, which further repolymerize and produce highly viscous hydrophobic bio-oil (called also biocrude), water-soluble substances, char (solid residue), and light gases (e.g H_2, CO, CO_2, CH_4).[20] 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.[21] 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 HTL bio-oils. Zhang and co-workers have studied HTL of various wood and corn substrates and have found identical groups of compounds in all bio-oils: carboxylic acids, alcohols, aldehydes, esters, ketones, sugars, lignin-derived phenols, furans, etc., but in different percentages.[118] Bio-oil added value has been primarily recognized from a biofuels perspective as a replacement for petroleum oils, similar to the well-known pyrolysis-originated bio-oil. The produced bio-oil has a HHV between 30 and 36 MJ kg^{-1} and an oxygen content of 10–20% (oils from pyrolysis have typically much higher oxygen content and moisture and contain up to 80 wt % of polar compounds).[14] HT bio-oil could be directly used for (co)-combustion in coal- and oil-fired power stations or could be also further upgraded by various processes, for example, by catalytic hydrodeoxygenation, zeolite cracking, or steam reforming, to transportation fuels, hydrogen, etc.[119,120] The upgrading of bio-oil to transportation fuels (diesel) is necessary due to its relatively high oxygen content, high melting point, and high viscosity compared to the similar petrochemical-derived hydrocarbons. An extensive review of catalytic upgrading of bio-oil to biofuels has been recently presented by Mortensen.[121] The mechanism of biomass HT liquefaction is complex and still not completely understood. To better understand liquefaction of complex real waste feedstock, the mechanism of HT liquefaction has been studied extensively on models of major biomass constituents: cellulose, hemicelluloses, and, in fewer cases, lignin and proteins.

Cellulose. Cellulose conversion mechanisms in subcritical and supercritical water have been intensively studied by Sasaki et al.[122−124] and Minowa et al.[125] The study of product distribution and reaction kinetics of cellulose conversion at temperatures between 290 and 400 °C (sub- and supercritical water) and at a pressure of 25 MPa in continuous-flow type microreactors shows that cellulose depolymerizes by two main reactions: (1) hydrolysis of the glycosidic bond via swelling and dissolution of cellulose and (2) dehydration of the reducing end of glucose via pyrolytic cleavage of the gylcosidic bond in cellulose (partly retro-aldol reaction).[122−124] The latter takes place dominantly as the temperature or residence time increases and the pressure decreases, whereas the former becomes faster in high-density regions in near-critical and supercritical water where fast dissolution of the crystalline cellulose occurs.[124] From a products point of view, the cellulose first depolymerizes into oligosaccharides (DP = 2−6) and monosaccharides (glucose) by water diffusion to the cellulose surface and then glucose rearranges/decomposes itself to various decomposition (pyrolytic) products: fructose, 5-hydroxymetyhlfurfural (5-HMF), furfural, pyruvaldehyde, dihydroxyacetone, glyceraldehydes, glycolaldehyde, erythrose. At lower temperatures, rates of glucose and oligomer conversion are higher than the rate of hydrolysis (dissolution) of cellulose, so lower concentrations of sugar oligomers and glucose could be obtained at low temperatures. At the near-critical point of water, hydrolysis rate jumps for 1 order of magnitude and become higher than the rate

Table 4. Overview of APR Processes of Various Biomass Origin Substrates and Catalysts Applied

raw material	experimental conditions	catalysts	achievements	ref
ethylene glycol	10 wt % ethylene glycol, $T = 210–225$ °C, $p = 2.2$ MPa	silica-supported Ni, Pd, Pt, Ru, Rh, and Ir catalysts	• catalytic activity decreases as Pt > Ni > Ru, >Rh > Pd > Ir • silica-supported Ni, Ru, and Rh; low selectivity to H_2, high alkene selectivity • silica-supported Pt, Pd; higher selectivity for H_2 production	97
ethylene glycol	10 wt %, $T = 210–225$ °C, $p = 2.24–2.93$ MPa, $t = 6$ h	Pt/black and Pt supported on TiO_2, Al_2O_3 carbon, SiO_2, $SiO_2–Al_2O_3$, ZrO_2, CeO_2, and ZnO.	• activity for H_2 production: • high, Pt/TiO$_2$, Pt/black, Pt/carbon, Pt/Al$_2$O$_3$; moderate, Pt/SiO$_2$–Al$_2$O$_3$, Pt/ZrO$_2$; low, Pt/CeO$_2$, Pt/ZnO, Pt/SiO$_2$ • selectivity for H_2: high, Pt/Al$_2$O$_3$, Pt/ZrO$_2$; low, Pt/TiO$_2$, Pt/black, Pt/carbon Pt/SiO$_2$–Al$_2$O$_3$	100
sorbitol	5 wt %, $T = 225–265$ °C, $t = 6$ h	Pt-SiAl, Pd-SiAl, Pt–Al, and their mixture	• selectivity for producing of alkanes is increased with cofed H_2 • more acidic metal sites added to catalyst – higher selectivity to heavier alkanes	112
glycerol	10 wt % glycerol, $T = 230$ °C, $p = 3.2$ MPa, $t = 4$ h	Pt, Ni, Cu, Co supported on SAPO-11, activated carbon, HUSY, SiO$_2$, MgO, Al$_2$O$_3$	• increased activity: Co < Ni < Cu < Pt • activity of Pt catalyst increases as SAPO-11 < AC (active carbon) < HUSY < SiO$_2$ < MgO < Al$_2$O$_3$ • basic supports – more hydrogen • acidic or neutral supports – alkane favorable • carbon deposition on Pt catalysts, sintering occurs during reactions	113
glycerol	225 °C, autogenous pressure	Pt supported on Al$_2$O$_3$, ZrO$_2$, MgO and CeO$_2$	• all catalysts led to high hydrogen yields • higher yield gives Pt/ZrO$_2$ and Pt/MgO	114
glycerol	$T = 180, 200, 220$ °C	Pt/Al$_2$O$_3$ (0.3–1.2 wt %Pt)	• 0.9 wt % Pt – best performance for H_2 • higher T and p; higher H_2 and lower CH_4 yield • carbonaceous material deposition on catalysts (deactivation)	115
ethanol	1 wt % EtOH, $T = 200°, 230°, 250$ °C	Ni/hydrotalcite catalysts	• 65 wt % ethanol conversion at 230 °C • higher H_2 and lower CH_4 selectivity than alumina supported Ni	116
waste water with hazardous organics (phenol, aniline, THF, toluene, cyclohexanol)	$T = 200–270$ °C, $p = 2.5–5.6$ MPa	Raney-Ni, Sn-Raney-Ni, Pd/C	• good catalytic performance of Sn- Raney-Ni, Pd/C • 100% selectivity for H_2	117

of degradation or rearrangement of glucose, so higher concentrations of glucose, oligomers, and sugars could be obtained at higher temperatures.[122]

Study of microcrystalline cellulose hydrolysis by Kumar and Gupta in subcritical and supercritical water (temperature range of 302−405 °C, pressure of 27.6 MPa, residence time of 2.5−8.1 s) shows that 66.8% of crystalline cellulose can be converted to hydrolysis products (oligomers and glucose) at 335 °C and 27.6 MPa in only 4.7 s.[31] With increasing residence time or increasing temperature to supercritical conditions, a retro-aldol condensation becomes the dominant process and hydrolysis products start self-degradation to glycolaldehyde, fructose, 1,3-dyhydroxyacetone, anhydroglucose, 5-HMF, and furfural, increasing the overall conversion of cellulose to almost 100%. A similar effect is observed in the study of Minowa and co-workers.[125] They investigated cellulose decomposition in a batch reactor in the temperature range of 200−350 °C and pressure up to 3 MPa. At temperatures slightly higher than 200 °C only minor decomposition of cellulose occurs, producing water-soluble (sugar) products. At temperatures above 240 °C, sugars start to decompose to form also gases, oils, and char, whereas at temperatures above 300 °C almost 60% of char on the carbon basis is formed. A gas yield of 10% was also produced (mainly CO_2 and CO). Several studies of conversion pathways in sub- and supercritical water, which started from glucose, fructose, or cellobiose, as model compounds of sugar monomers or oligomers also confirm similar conversion pathways as were observed in cellulose liquefaction study.[125−128]

Hemicellulose. Sugar oligomers of hemicelluloses are degraded in hot water in a similar way as is cellulose. Hemicellulose is liquefied in subcritical water very easily. It has amorphous structure, and its decomposition starts even at 180 °C. This was confirmed in studies with D-xylose as a model of hemicelluloses. The mechanism of retro-aldol condensation was dominant in conversion of D-xylose in near-critical and supercritical water (360− 420 °C, 25−40 MPa, and 0.02−0.1 s) with main products of glycolaldehyde, glyceraldehydes, and dihydroxyacetone.[129] At lower temperatures, 180−220 °C, and 10 MPa, xylose has been converted to furfural and formic acid, as main products. This confirms the above-mentioned differences in kinetics and product distribution between conversion of biomass at lower and higher temperature.

Lignin. Wahyundiono et al. have studied liquefaction of lignin model compound guaiacol at 653−673 K and various pressures (water densities).[130] They have proposed detailed reaction pathways and reaction kinetics for production of main water-soluble and solid products (char). The main products were catechol (40.73 wt %), phenol (14.18 wt %), and o-cresol (4.45 wt %), the amounts of which increase with water density at the same temperature. Similar products are detected also using other types of lignins. Zhang et al. have produced 12−37 wt % of solids in liquefaction of Kraft and organosolv lignin at near-critical water (374 °C, 22 MPa, 10 min) and 58−79 wt % of liquids was formed.[131] Saisu et al. have studied the conversion of organosolv lignin with and without the presence of phenols at 400 °C in a tube bomb batch reactor at water densities up to 0.5 kg cm^{-3}.[132] It was demonstrated that lignin depolymerizes by hydrolysis and then dealkylation, yielding tetrahydrofuran-soluble phenol products, mostly syringol, guaiacol, and catehols. Their molecular weights decreased as water density was increased. During the HT liquefaction of lignin, also significant amount of solids (tetrahydrofuran insolubles) have been

produced, the yield of which decreased as the reaction time and water density were increased at 400 °C. Furthermore, addition of phenols decompresses the solids (char) formation, due to reactions of phenol and reactive sites on degradation products. This has been observed also in a study by Okuda and co-workers.[133] Liquefaction of lignin in the presence of a water/phenol (1:1.4 v/v) mixture resulted in only 1 wt % of char formation. Moreover, also addition of alkaline catalysts improves liquefaction and enhances the yield of water-soluble products.[134] The amounts of solids increase also if the reaction time or heating time increases.[135] As could be concluded, hydrothermal treatment of technical lignin wastes yields liquid oil, mainly produced from monomeric phenols and partly aldehydes. These compounds could be found in all liquids produced by hydrothermal treatment of lignin-containing waste biomass. It could be used as a platform raw material for chemical production or high-value fuel. To obtain fuels, it must be further upgraded, as was mentioned before.

Influence of Various Process Parameters on HTL. Temperature and pressure are not the only parameters influencing the reaction mechanism of HTL. Heating time, residence time, biomass particle size, type of feedstock, solvent density, catalysts, etc., also have a significant influence on biomass hydrolysis and product formation.[21] Residence times of the reacting mixture in reactor systems affect product distribution and the reaction mechanism. In batch reactors, biomass particles are mixed with HCW in the reactor. The residence time of the mixture is long, the same as that of liquid products. This results in secondary reactions of the hydrolysis products, increased yields of oil and char, and low yields of sugars or sugar hydrolysis products. On the contrary, in semicontinuous and continuous reactors the residence time is short (could be only few seconds). In the semicontinuous reactor, HCW flows through the biomass particle fixed bed, rapidly sweeping the liquid products out of the reactor, whereas in the continuous (flow type) reactor, the reaction mixture is pumped through the reactor, so reacting particles and products are rapidly swept out of the reactor. In a comparative study of cellulose HT liquefaction reactions in batch- and flow-type reactor systems performed at the same temperature, it has been detected that in flow-type reactors minimal pyrolyzed products (char and gases) occur, whereas in batch-type reactors significant yields of pyrolyzed products are detected.[136] For this reason, it is very important to investigate the fundamental reaction of biomass degradation in appropriate reactor systems and at conditions that would avoid secondary reactions of primary products. At high temperatures, sugar decomposition could be very fast. Only a few seconds is needed for decomposition of glucose at temperatures >300 °C.[137] Therefore, reactions at higher pressures and temperatures (supercritical water) are, in general, investigated in semicontinuous or continuous reactors.

Biomass particle size and heating rate have little influence on liquefaction because subcritical/supercritical water has a leading role as a heat transfer medium and extracting medium, making HTL relatively independent of the size of biomass particles or heating rates.[21] On the contrary, compositional variations in waste biomass cause variations in compositional product distribution, their yields, and physical and chemical characteristics (high heating value (HHV), oxygen content, viscosity, etc.). In general, the presence of a high amount of carbohydrates leads to higher yields of bio-oils.[118,138] High contents of lipids and proteins (animal and fish wastes or microalgae) also enhance bio-oil yield.[139] The presence of a

high amount of lignin contents enhances char formation as was demonstrated in a comparative study of various wood samples produced by Zhong and Wei.[140] For four wood samples, the highest bio-oil yield (31 wt %) at the same temperature conditions has been observed for *Fraxinus mandshurica* wood, which has a low lignin content (21.57 wt %).

Quite likely as in other chemical reactions, catalysts play a great role also in HT conversions of biomass. There is a huge number of scientific publications dealing with the impact of various catalysts on the liquefaction mechanism, yield, and product characteristics, which have been published in the past few decades. In general, both acids and bases catalyze liquefaction of biomass. In general, acids (inorganic acids: HCl, H_3PO_4, H_2SO; acid salts: $AlCl_3$, $Al_2(SO_4)_3$) enhance production of water-soluble products such as sugars, carboxylic acids, furfural, and 5-HMF, whereas alkali salts (e.g., Na_2CO_3, KCl, KOH) enhance bio-oil yield and reduce residue formation at subcritical conditions.[20]

All of these investigations with model compounds were useful in highlighting the reaction pathways of individual waste components, but interactions of these compounds in real wastes are not well understood. Fortunately, there has been much research in HTL of various types of agricultural and food industry wastes done in the past few decades. In Table 5 some recent research regarding the feedstock used, reaction conditions, and catalyst impact on product distribution, yield, and composition is summarized. Most of the studies were done at small laboratory scale and, in particular, do not stress the challenges of processing real waste biomass such as feedstock delivery, catalyst deactivation, heat exchange, tar formation, and separation of product streams.

Pilot and Semi-industrial HTL Processes. Several HTL pilot or semi-industrial plants have been demonstrated around the world using various agriculture and food processing wastes. Hydrothermal upgrading (HTU) process of a wide variety of wet agriculture wastes (sugar beet pulp, roadside grass, etc.), developed by Shell Research Laboratory from Amsterdam in the early 1980s, was demonstrated at a pilot plant scale of 100 kg h^{-1}. These wastes were liquefied at temperatures of 300−350 °C, pressures between 12 and 18 MPa, and residence time of 5−20 min and upgraded to diesel-like bio crude of high caloric value (30 MJ kg^{-1}) and oxygen content of 10−15 wt %. Predesign and cost estimation of a commercial demonstration plant with a capacity of 25000 tons/year on dry basis was carried out by Jacobs Engineering Nederland, and plans for realization of this first commercial installation in the near future are made.[119]

The CatLiq process, a hydrothermal liquefaction technology developed by the Danish company SCF Technologies A/S, operates at continuous 30 L/h capacity pilot plant and is optimized to convert wet low-value feeds such as sludge, algae, manure, and residues from food production into green oil, which is easy to store and transport.[141] It uses primarily dried distillers grains with solubles (DDGS) as a feedstock to produce bio-oil in the presence of homogeneous (K_2CO_3) and heterogeneous (zirconia) catalysts at subcritical conditions (T = 280−350 °C, P = 22.5−25.0 MPa). The bio-oil yield is normally in the range of 30−35%. CatLiq produces approximately 5 times more energy compared to biogas technology. Other products are gases (CO_2 and H_2) and water-soluble organic compounds (organic acids, ethanol, etc.).[20,141,142] At the beginning of 2011 Altaca Environmental Technologies & Energy from Turkey bought all IP rights including know-how and worldwide patents of the CatLiq technology and relocated

the pilot plant from Copenhagen to its own facilities near Istanbul. Altaca has very recently entered into an agreement with Astosan, and its subsidiary Dogasan, to construct a combined Biogas and CatLiq plant in Dogasan's dairy farm located in Gonen/Turkey at the end of 2012. This first commercial CatLiq plant will have a 200 tons/day feed capacity and will mainly use the manure from the Dogasan dairy farm and liquid wastes from Astosan's whey powder plant as its raw material.[143]

A thermal conversion process that used animal waste (turkey offal from ConAgra Butterball Co. in Carthage, MO, USA) has been developed by Appel and co-workers from Changing World Technologies Inc. (CWT).[144] A pilot plant was installed in 2005 in Carthage to convert 250 tons of turkey offal and fats per day in a two-stage process.[14] In the first stage, complex animal waste is heated with water to temperatures between 200 and 300 °C and pressurized to about 4 MPa. Solids (minerals) are separated from the mixture, and the liquid is flashed to separate water. In the second stage, the water-insoluble phase is reheated to 500 °C to form fuel gas, carbon, and diesel oil ($C_{15}-C_{20}$ hydrocarbons). Technology also offers production of fertilizers from solids (minerals) and ammonia from waste gases. Fuel gases are used for internal heat needs, and the coke (carbon) materials are sold as solid fuel.

Hydrothermal liquefaction seems to be also a promising technology for production not only of hydrophobic bio-oils as main products but also of some water-soluble platform chemicals at lower temperatures and pressures. A very promising and commercially improved technology is also used for the production of levulinic acid via HT hydrolysis of lignocellulosic waste at temperatures of 200−250 °C (Biofine technology) from agricultural waste (tobacco industry waste).[145]

Hydrothermal Gasification. Hydrothermal gasification is a process in which biomass waste reacts with water at high temperatures and pressures to form gaseous products, mainly CH_4, H_2, CO, CO_2, and C_1-C_4 carbon gases. As side products, also some bio-oil, char, and tar is formed, which decreases the yield of gases. This kind of gasification differs from the conventional one ("dry gasification"); in fact, water acts here as a reactant, solvent, catalyst, and hydrogen donor via various reactions and should not be separated (dried) from the wet biomass prior to gasification. For this reason, the method has gained much attention as an attractive method for the conversion of wet biomass waste to valuable gaseous products, primarily hydrogen, methane, and syngas. Especially interesting is biomass with high moisture content (>50 wt %) such as swine manure,[156] whey,[157] and wastewater.[158] Depending on the applied temperature, hydrothermal gasification could be divided in two main types: low-temperature or catalytic wet gasification (in sub- and near-critical water) and high-temperature gasification or supercritical water gasification (SCWG). The low-temperature gasification is generally performed at temperatures between 300 and 500 °C with the addition of catalysts, which must be applied to enhance the conversion rate of biomass to gases and increase selectivity to CH_4, as a dominant gas at lower temperatures. At temperatures >500 °C (SCWG), H_2 is the dominant gas in gaseous product and the rates of conversions are high, even without the application of catalysts. The third temperature regimen for producing gases from biomass (sugar alcohols derived from biomass) is aqueous phase reforming, which is described in detail as a separate process under Aqueous Phase Reforming.

Interest in hydrothermal gasification began in the 1970s with the research of Model and co-workers, whose experiments with

Table 5. Research Dealing with Hydrothermal Liquefaction of Various Agri-food Waste Biomasses

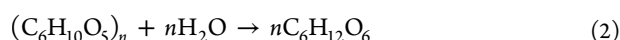| waste biomass	experimental conditions	catalysts	main products	achievements	ref
various corn parts (stokes, stover, pellets, etc.) and aspen pulp wood, pretreated aspen wood, aspen lignin	300–450 °C, t = 5–30 min, batch reactor	Na_2CO_3	• liquid phase: carboxylic acids, alcohols, aldehydes, esters, ketones, sugars, lignin-derived phenols, furans; • gaseous phase (mainly CO and CO_2, less H_2 and CH_4)	• liquids: 53.2–90.2%; gases: 5.2–21.5%; solid residue: 3.8–29.9%; • optimal residence time for liquid products = 10 min; 30 min for gases; • Na_2CO_3 increase yield of liquid from 68.2 to 72.2%	118
corn stalks	350 °C, 20 MPa, autoclave	acetic acid + sodium chlorite pretreatment	• bio-oil (water-soluble oil and heavy oil)	• maximum bio-oil, WSO, and HO yields from liquefaction of unpretreated cornstalk were 36.3% (260 °C), 26.8% (260 °C), and 13.8% (280 °C); • maximum bio-oil, WSO, and HO yields from liquefaction of the pretreated cornstalks were 39.6% (240 °C), 35.7% (240 °C), and 8.2% (260 °C)	146
wood (pine) sawdust	280 °C, 15 min, batch reactor	NaOH, Na_2CO_3, K_2CO_3	• mostly phenols • bio-oils were separated in three phase: 1. *ether soluble (oil 1):* major hydrocarbon was 2-methoxyphenol 2. *ethyl acetate soluble (oil 2):* 3-hydroxy-2-pentanone 3. *acetone soluble (oil 3):* major phenols were 3-methylphenol and 4-methylphenol	• overall oil yield from 10 to 16.7% catalysts; activity considering oil yield ranges K_2CO_3 > KOH > Na_2CO_3> NaOH • product distribution depends on type of base solution	135
phytomass (baby food)	330–410 °C, 30–50 MPa, 15 min, batch reactor	none	• gases: mainly CO_2 at $T > T_{crit}$ H_2 and CH_4 increased • liquids: phenols and cresols, organic acids (levulinic, acetic, formic, D-lactic), sugars (glucose, sucrose, fructose), furfurals, aldehydes • solid residue (char)	• maximum gas yield at 410 °C due to free radical reactions favorable in supercritical water • change of water properties from SubCW to SCW impact on reaction mechanism: SubCW dominancy of ionic reactions (low gases, furfural, and acids), SCW dominancy of free radical reactions (gas formation)	137
swine manure	300 °C, 10–12 MPa, 30 min, batch reactor	none	bio-oil: HHV = 34.7 MJ/kg; C:H:N:O:S = 71.2:9.5:3.7:15.6:0.12	bio-oil yield: 30.2 wt %	138
digested anaerobic sludge	300 °C, 10–12 MPa, 30 min, batch reactor	none	bio-oil: HHV = 32.0 MJ/kg; C:H:N:O:S = 66.2:9.2:4.3:18.9:0.97	bio-oil yield: 9.4 wt %	138
microalgae (*Spirullina*)	300 °C, 10–12 MPa, 30 min, batch reactor	none	bio-oil: HHV = 34.7 MJ/kg C:H:N:O:S = 68.9:8.9:6.5:14.9:0.86	bio-oil yield: 32.6 wt %	138
oil palm fruit press fiber	210–337 °C, batch reactor	10 wt % $ZnCl_2$, Na_2CO_3, NaOH	• bio-oil (benzene soluble, diethylether soluble, acetone soluble) • water-soluble • gases • char	• conversion increases with temperature to 75.8% at 337 °C • 10% $ZnCl_2$ added increases conversion slightly but gaseous products increase significantly, • 10% Na_2CO_3 and 10% NaOH addition increases bio-oil yield	147
cherry stones	200–300 °C, 0–30 min, batch reactor	none	light bio-oil (LBO): ether soluble	• highest total bio-oil yield was obtained at both 250 and 300 °C for the shortest residence time (0 min), whereas TBO yield was highest for the longest residence time (30 min) at 200 C • major identified compounds in the LBOs were furfurals, phenols, acetic acid, and vanillin • major components of HBOs contained furfurals, phenols, and fatty acids.	148

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Table 5. continued

waste biomass	experimental conditions	catalysts	main products	achievements	ref
shrimp shells (seafood processing waste)	90–250 °C, batch	none	amino acids (glycine and alanine)	• heating values of LBOs and HBOs increased with increase of temperature at the same holding time • yield of amino acids increases with temperature to 250 °C, after that, decreases	149
willow	diamond-anvil cell (DAC), semicontinuous reactor, 215–300 °C	none	not analyzed	• 95 wt % dissolution is achieved • increased dissolution with temperature till 300 °C, after that dissolution decreases due char precipitates on biomass	150
rabbit food	batch reactor: 200–400 °C; semicontinuous: 200–300 °C	none	batch reactor: water-soluble (WS) phase – major acetic and lactic acids	• batch reactor: maximal WS was 48% (250 °C, 50 s) and 51% (300 °C, 20 s) • max 2.6% (230 °C, 1200 s) of acetic acid and 3.2% (300 °C) of lactic acid • semicontinuous reactor: glucose yield decreases with temperature (max 11.5% at 200 °C)	151
cattle manure	270–350 °C, batch reactor purged with N_2, CO, H_2	red. gases, NaOH	bio-oil: C:H:N:O = 35.38:4.73:2.38:57.51 HHV = 15.16 MJ/kg	• max yield of bio-oil was 48.76 wt % in case of CO as process gas at 310 °C; after 310 °C, bio-oil yield decreases due to char formation and gases • CO and H_2 increase bio-oil yield • pressure, S/B ratio, and residence time increase bio-oil yield due to char and gases formation	152
swine manure	285–305 °C, 5.5–18 MPa, 5–180 min	CO as red. agent,	bio-oil: LHV = 34.94 MJ/kg	• bio-oil yield, 76.2 wt %; gas yield (CO_2 mainly), 16.9 wt %; and solids yield, 3.3 wt % of total volatile solids	153
microalga *Nannochloropsis* sp.	350 °C	(Pd/C, Pt/C, Ru/C, Ni/SiO_2–Al_2O_3, CoMo/γ-Al_2O_3 (sulfided), and zeolite) with and without H_2 pressure environment	bio-oil, gaseous products (H_2, CO_2, CH_4, lesser amount of C_2H_4, C_2H_6)	• bio-oil yield was higher in absence of H_2 (40–50 wt %), but was insensitive to presence and type of catalyst. • high-pressure H_2 environment led to lower gaseous yield than environment without H_2 • type of catalyst is irrelevant for bio-oil yield in both environments, but Ni and Ru give the highest yield of H_2	154
microalga *Enteromorpha prolifera*	220–320 °C	0–5 wt % of Na_2CO_3	• bio-oil (CH_2Cl_2 soluble fraction) – complex mixture of aldehydes, ketones, alkanes, fatty acids, phenols, esters, etc. HHV of bio oil: 28–30 MJ/kg • water-soluble (WS) – mostly acetic acid and glycerol • gases and solid fraction	noncatalyzed reactions: • WS product yield decreases with increasing temperature (from 34.3 to 45.2 wt %) • yield of bio-oil increases with temperature to 320 °C, after that decreases (gasification is enhanced) catalyzed reactions (5 wt % of Na_2CO_3): • slightly increases the yield of bio-oil to maximal 23 wt % at 300 °C and 30 min	155

maple wood sawdust in supercritical water represent pioneering research on supercritical gasification.[159] Over the past decades a few HT gasification research groups have been established around the world.[24,160−164] Despite their efforts and achievements, the chemistry of gasification is not fully understood yet. The reason lies, similarly to other hydrothermal reactions mentioned above, in the complex structure and chemistry of lignocellulose wastes and in the many different reactions covered under the term "gasification" (hydrolysis, dehydration, steam reforming, water-gas shift reaction, methanation, pyrolsis, etc). For these reasons, the most common efforts of researchers were directed to improving the desired gas yield and the economics of the overall process and solving the major technical and engineering challenges, instead of fully highlighting each reaction step.

The most common model substances used in predicting the behavior of agricultural and food processing waste biomass under the hydrothermal gasification are cellulose and glucose. Cellulose depolymerizes by hydrolysis to oligomers (cellobiose, cellotriose, cellotetraose, etc.) and monomers (glucose, fructose) through similar reactions as described in a previous section, describing the mechanism of hydrothermal liquefaction. Glucose and fructose undergo further fast decomposition to various compounds such as carboxylic acids, alcohols, aldehydes, and ketones.[137,165] All of these compounds are highly reactive and easily decompose to gases via decarbonylation and decarboxylation at higher temperatures. At lower temperature (subcritical water), at which ionic reaction mechanisms are preferable, furfural and phenol formation reactions compete with reactions of gas formation. At higher temperatures (supercritical water) free radical reactions are dominant, so formation of gases, mainly CO_2, CO, H_2, and CH_4, is preferable. HT gasification of lignin also starts by the same reactions of hydrolysis and forming of phenolic compounds by cleavage of ether and ester bonds. Nevertheless, efficient HT gasification of lignin is more difficult to obtain than that of cellulose and hemicelluloses due to high reactivity of low molecular weight lignin fragments (formaldehyde, syrngol, guaiacol, catehols, etc.) and repolymerization by cross-linkage reactions and formation of char and tar (detected as solid residue). To decrease tar/char residue and increase gasification yield at lower temperature, catalysts must be applied. Nevertheless, the gasification process could be divided into several reactions: biomass depolymerization and hydrolysis to oligomers and monomers, further decomposition of monomers, steam reforming (syngas formation), pyrolysis, tar formation, water-gas shift, and methanation. These could be expressed by further equations:[166]
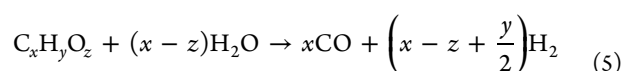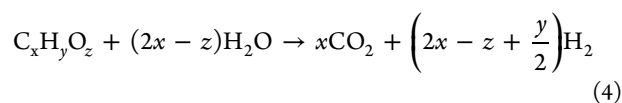
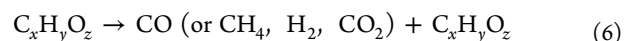(a) cellulose decomposition by hydrolysis

$$(C_6H_{10}O_5)_n + nH_2O \rightarrow nC_6H_{12}O_6 \tag{2}$$

(b) glucose decomposition

$$C_6H_{12}O_6 \rightarrow C_xH_yO_z \tag{3}$$

(c) steam reforming

$$C_xH_yO_z + (2x - z)H_2O \rightarrow xCO_2 + \left(2x - z + \frac{y}{2}\right)H_2 \tag{4}$$

$$C_xH_yO_z + (x - z)H_2O \rightarrow xCO + \left(x - z + \frac{y}{2}\right)H_2 \tag{5}$$

(d) hydrothermal pyrolysis for CO, CH_4, H_2, and CO_2 formation

$$C_xH_yO_z \rightarrow CO \text{ (or } CH_4, \ H_2, \ CO_2) + C_xH_yO_z \tag{6}$$

(e) char formation

$$C_xH_yO_z \rightarrow wC + C_{x-w}H_yO_z \tag{7}$$

(f) water-gas shift

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{8}$$

(g) methanation

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \tag{9}$$
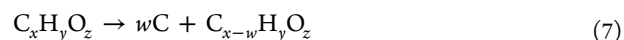
Kinetic models of gasification based on 11 various reactions and interactions between the species were first proposed by Resende and Savage.[166] They determined rate constants for 11 uncatalyzed cellulose and organosolv lignin gasification reactions in sub- and supercritical water and validated models with experimental data obtained in constant-volume quartz batch reactors to avoid unintentional contribution of catalysis by reactor walls. The models showed that the dominance of particular reactions and compounds was dependent on reaction times and temperatures. Reactions responsible for gas formation from intermediates (water-soluble products) are most important at short reaction times, whereas reactions that redistribute the different gases (e.g., water-gas shift) become the most important at longer residence time. Consequently, H_2 was primarily produced via steam reforming reaction (reaction c) at short residence time and via water-gas reaction (reaction f) at longer reaction time and higher temperature. CO, CO_2, and CH_4 were predominantly produced by hydrothermal pyrolysis reactions from various intermediate compounds (reaction d). Nevertheless, it is impossible to achieve complete conversion by gasification at low to moderate temperatures and short reaction times without proper catalysts. For this reason, the catalysis in sub- and supercritical water and the design of catalysts are some of the most challenging fields of research today.[25] A more detailed review of real agricultural and food waste gasification regarding temperature regimen and catalyst selection in connection with product distribution is given in the sections below.

Low- and Moderate-Temperature Catalytic Gasification. Low- and moderate-temperature gasification ranges from 300 to 500 °C, producing CH_4, CO_2, and H_2 as the main gaseous products. Although gasification at low temperatures and pressures is favorable due to lower energy input, catalysts must almost always be applied for efficient gasification. Their role is primarily to increase the rate of gasification and to increase the selectivity to desired products. They have the ability to enhance gasification by fast gasification of reactive intermediates produced by hydrolysis or dehydration, avoiding the repolymerization and formation of char/tar. This is especially important for aromatic (phenol) intermediates, for which a good catalyst must achieve a fast cleavage of the C−C bond in aromatic rings. Furthermore, the catalyst must enhance the dissociation of water, producing the $OH^{\bullet}$ and $O^{\bullet}$ reactive radicals, which will react with adsorbed $C_xH_yO_z$ fragments and release CO and CO_2. The adsorbed hydrogen from water splitting and this from cleaved $C_xH_yO_z$ fragments will combine to form H_2.[14] Catalysts for gasification are divided, in general, into homogeneous and heterogeneous ones.[22] Homogeneous catalysts are usually alkali salts (KOH, Na_2CO_3, $KHCO_3$, K_2CO_3, $NaOH$, etc.). In general, they act in a manner to lower the temperature

Table 6. Low- and Moderate-Temperature Catalytic Gasification of Various Agricultural and Food Processing Wastes

waste	reaction conditions	catalyst	reactor type	main products	refs
glucose	330 °C, 13.5 MPa, 120 min	H_2O_2 and NaOH	batch	H_2	170, 171
	330 °C, 60−120 min	NaOH, KOH, $Ca(OH)_2$, Na_2CO_3, K_2CO_3, $NaHCO_3$, H_2O_2	batch	H_2	173
corn	330 °C, 13.5 MPa, 120 min	H_2O_2 and NaOH	batch	H_2	170, 171
stalks and corncob	500 °C	Trona ($NaHCO_3 x Na_2CO_3 x 2H_2O$) and red mud		H_2, CO_2, CH_4, water-soluble products	174, 175
carrot (cooked)	330 °C, 13.5 MPa, 120 min	H_2O_2 and NaOH	batch	H_2	170, 171
bean (cooked)	330 °C, 13.5 MPa, 120 min	H_2O_2 and NaOH	batch	H_2	170, 171
beef meat (cooked)	330 °C, 13.5 MPa, 120 min	H_2O_2 and NaOH	batch	H_2	170, 171
mayonnaise	330 °C, 13.5 MPa, 120 min	H_2O_2 and NaOH	batch	H_2	170, 171
cat food	330 °C, 13.5 MPa, 120 min	H_2O_2 and NaOH	batch	H_2	170
mixed food waste	330 °C, 13.5 MPa, 120 min	H_2O_2 and NaOH	batch	H_2	170
glutamic acid (protein biomass model)	330 °C, 13.5 MPa, 120 min	H_2O_2 and NaOH	batch	H_2	170, 172
dairy waste (whey)	300−390 °C, 9.5−24.5 MPa, 120 min	H_2O_2 and NaOH	batch	H_2	157
mollase	330 °C, 60 and 120 min	NaOH, KOH, $Ca(OH)_2$, Na_2CO_3, K_2CO_3, $NaHCO_3$, H_2O_2	batch	H_2	170, 173
rice bran	330 °C, 60 and 120 min	NaOH, KOH, $Ca(OH)_2$, Na_2CO_3, K_2CO_3, $NaHCO_3$, H_2O_2	batch	H_2	170, 173
chicken soup	330 °C, 13.5 MPa, 120 min	H_2O_2 and NaOH	batch	H_2	170
cotton stalks	500 °C	Trona ($NaHCO_3 x Na_2CO_3 x 2H_2O$) and red mud	batch	H_2, CO_2, CH_4, water-soluble products	174, 175
tobacco stalk	500 °C	Trona ($NaHCO_3 x Na_2CO_3 x 2H_2O$) and red mud	batch	H_2 (mostly), CO_2, CH_4, water-soluble products	174, 175
sunflower stalk	500 °C	Trona ($NaHCO_3 x Na_2CO_3 x 2H_2O$) and red mud	batch	H_2, CO_2, CH_4, water-soluble products	174, 175
oreganum stalk	500 °C	Trona ($NaHCO_3 x Na_2CO_3 x 2H_2O$) and red mud	batch	H_2, CO_2, CH_4, water-soluble products	174, 175
vegetable tannery waste	500 °C	Trona ($NaHCO_3 x Na_2CO_3 x 2H_2O$) and red mud	batch	H_2, CO_2, CH_4, water-soluble products	174, 175
peanut shell	450 °C	Raney-Ni catalyst, $ZnCl_2$ or $Ca(OH)_2$	batch	H_2, CO_2, CH_4	176
straw	450 °C	Raney-Ni catalyst, $ZnCl_2$ or $Ca(OH)_2$	batch	H_2, CO_2, CH_4	176
dairy manure	350 °C, 20 MPa	Ru	batch, continuous flow stirred-tunnel reactor	CH_4, CO_2	179
DDGS	350 °C, 20 MPa	Ru	batch, continuous flow stirred-tunnel reactor	CH_4, CO_2	179
olive wastewater	400−600 °C, 25 MPa, 30−150 s	NR	tubular reactor	CH_4, CO_2	181
sugar cane bagasse	400 °C, $\rho = 0.33$ g cm^{-3}	Ru/C, Ru/TiO_2	autoclave	CH_4, CO_2	182

for biomass degradation, depress the reaction of intermediates (water-soluble compounds) to oils and tar/char, and improve CO conversion in the water-gas shift reaction to H_2 and CO_2. Additionally, stable metal catalysts such as Ru, Pt, or Ni, alone or supported on carbon, TiO_2, ZrO_2, or α-Al_2O_3 are mostly used.[14,22,23] Standard catalysts used in the petrochemical industry undergo poisoning, sintering, and oxidation in hot compressed water medium.[168] These phenomena are even more obvious in processes with real waste biomass, which contains nitrogen-containing compounds,[169] various salts, and sulfur.[156] A summary of catalytic low- and moderate-temperature gasification of some wet agricultural and food processing waste is presented in Table 6.

Muangrat et al. studied reactions of various food wastes with subcritical water in a batch reactor at 330 °C and 13.5 MPa. They used hydrogen peroxide and NaOH as catalysts to gasify sunflower oil, corn, carrot, bean, beef, mayonnaise, tropical fruit salad, cat food, and molasses as models for various types of food-processing wastes.[170,171] It was observed that hydrogen production was enhanced when both NaOH and H_2O_2 were used compared to reactions in which either NaOH or H_2O_2 alone was used. This was a result of H_2O_2-promoted decarbonylation reactions and production of more CO than by NaOH alone. Simultaneously, the consumption of CO in the

water-gas reaction to produce CO_2 and H_2 was enhanced. Additionally, NaOH captured CO_2 in the form of carbonate or bicarbonate, improved the purity of hydrogen gas in the effluent, and shifted the water-gas reaction in the forward direction. Carbohydrate-rich food waste (molasses, tropical fruit mixture, whey powder) produced higher H_2 gas yields than others (proteins and lipids). Lipid-rich samples were the most difficult to decompose into gasifiable intermediates and therefore produced the lowest H_2 yield. Similar results were obtained also with glutamic acid as a representative model for protein food waste with Ni-based catalysts in the presence of NaOH[172] and dairy industry waste (whey).[157] Furthermore, gasification of molasses and rice bran with other alkali catalysts such are KOH, $Ca(OH)_2$, $Na_2 CO_3$, K_2CO_3, and $NaHCO_3$ was also tested.[173] It was found that metal hydroxides produced more H_2 than carbonates and bicarbonates.

Yanik et al. have compared the gasification performances of Trona ($NaHCO_3 \cdot Na_2CO_3 \cdot 2H_2O$) and red mud (waste from Al production) as catalysts at 500 °C to those of an alkali metal and nickel catalysts in catalytic gasification of different organic waste (cotton stalks, tobacco stalk, sunflower stalk, corn stalk, corncob, oreganum stalk, and tannery waste).[174,175] The effect of these industrial byproducts as catalysts on gasification efficacy and H_2 yield was similar to those achieved with

commercial alkali salts. Hydrogen yields between 4.05 and 4.65 mol H_2/kg biomass have been obtained. The maximal hydrogen yield, 39.47%, was obtained from tobacco stalks, although tobacco stalks produced a relatively low gas amount.

Pei et al. studied gasification of peanut shell, sawdust, and straw at 450 °C in a batch reactor in the presence of Raney-Ni catalyst (with different concentrations of Fe, Mo, or Cr metals) alone or in a mixture with $ZnCl_2$ or $Ca(OH)_2$.[176] The yield of H_2 was higher in gases obtained with the presence of a mixture of Raney-Ni catalysts and $ZnCl_2$ or $Ca(OH)_2$. $ZnCl_2$ enhanced the depolymerization of cellulose and hemicelluloses as acid salts, and $Ca(OH)_2$ adsorbed CO_2 and produced carbonate on catalyst walls, increasing the yield of H_2.

Elliott at al. investigated extensively the stability of heterogeneous Ni and Ru catalysts supported on various materials, for example, silica, ceramics, carbon, zirconia or titania, and α-Al_2O_3, during the gasification process.[26] Of the many tested materials, the useful supports identified included carbon, monoclinic zirconia or titania, and α-alumina. Ni and Ru were found to be the most stable metal catalysts and give the highest yield of methane with many waste biomasses.[177] Furthermore, stable nickel catalysts impregnated by promoter (copper, tin, and silver) with stable lifetimes of >6 months were developed in laboratory testing and patented.[178] Similar Ni and Ru catalysts have been proposed and tested on real wet biomass waste also from other research groups, yielding high conversions, higher yield of methane, and long stability (>200 h).[23,168,179] There are also many other promising types of catalysts researched in systems with model or real biomass, such as active carbon catalysts[180] or some SCWG reactor wall materials (Inconel, Hastelloy C-276, etc.).[167]

High-Temperature Gasification or SCWG. Although low- and moderate-temperature gasification is energetically more preferable, in high-temperature or supercritical water gasification (SCWG) at temperatures from 500−800 °C wet biomass could be converted almost completely to gases rich in H_2. High gasification efficiency and H_2 yield are results of promoted free radical mechanism reactions (as was described in previous sections) and water-gas shift reaction at high temperatures, so catalysts could be avoided. Nevertheless, catalysts such as carbon, metals, or alkali salts are often used to increase gas yield in systems with real biomass.[23,183] This is of great importance for SCWG of protein-containing biomass, a very common type of agriculture and food industry residual (e.g., meat industry waste). Kruse et al. investigated differences in SCWG of phytomass (cooked vegetable baby food), zoomass (chicken meat containing baby food), and glucose in a continuous stirred tank reactor at 500 °C and 30 MPa.[184] They found that the addition of K_2CO_3 catalyst decreased the concentration of CO in gas products the same as it increases gasification yield, but protein-containing waste feedstock (zoomass) gave surprisingly small gaseous product. They explained that by inhibition of free radical chain reactions by the Maillard reaction (reaction between amines and aldose sugars into stable free radical ions), which is highly relevant for gasification. Similarly decreased and slow gasification was detected also with model systems for protein and amino acid food waste (aniline−glucose model system) in batch and tubular reactors.[185] Due to the Maillard reaction, difficulties in gasification of biomass feedstock containing proteins and amino acids could be expected, primarily by quenching of desired reaction pathways in the gasification process.

Recent investigations of high-temperature gasification with food and agriculture waste have pointed out several critical issues that affect the gasification efficiency, hydrogen yield, and, no less important, technological and engineering obstacles in relation with proper and stable reactor design. The most important challenge is probably plugging of reactor equipment with inorganic salts precipitating from biomass and carbonaceous product (char, coke, tar). Xu et al. studied SCWG of some sewage sludge bagasse liquid extract slurries (22 wt %) into flow-type tubular reactor.[186] Almost 100% conversion to high hydrogen yield gases was observed for all feedstocks at 600 °C and 34.5 MPa in the presence of various carbon catalysts and active carbon. However, deactivation of catalysts after <4 h without and 6 h with a swirl generator at the entrance in the reactor was observed. A problem with plugging of the reactor was observed also by Antal et al. during the gasification of corn- and potato-starch biomass.[187] They detected that the flow of feed into the reactor was halted by a buildup of coke and ash in the heat-up zone of the reactor. They suggest that the coke could be easily and quickly removed from the reactor by combustion in flowing air delivered from the other end of the reactor at 0.1 MPa.

Despite these technical obstacles, SCWG technology is recognized as prospective technology for agriculture and food industry waste reuse and is still under further development and optimization on various demonstration pilot plants. The pilot plant system "VERENA" installed in 2003 in Karlsruhe Institute of Technology, Germany, was the first completely equipped continuously operating plant worldwide for biomass gasification in supercritical water.[188] Total throughput is 100 kg/h of various agricultural wastes (corn silage, ethanol, and waste from the beverage industry) with maximum solid content of 20%. The plant was designed for a working pressure of up to 35 MPa and a maximum temperature of 700 °C. The stated gasification efficiency is very high (90−98%) with maximal successful operation duration of 10 h. The problem with salt precipitation was solved by preheating the feed stream (homogeneous slurry of biomass and water) with externally generated flue gases to temperatures below the critical point before entering the reactor. After the reaction, the liquid/gaseous stream is led to a separator, where gases are separated from the water phase by cooling (heat exchanger). Removal of CO_2 in the produced gases is obtained by water scrubbing. Such a down-flow reactor design with controlled water level enables also precipitation of inorganic salt at the bottom of the separator, avoiding downstream plugging issues.[188]

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