

# Thermochemical biofuel production in hydrothermal media: A review of sub- and supercritical water technologies

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Received 13th June 2008, Accepted 24th June 2008

First published as an Advance Article on the web 9th July 2008

DOI: 10.1039/b810100k

Hydrothermal technologies are broadly defined as chemical and physical transformations in high-temperature (200–600 °C), high-pressure (5–40 MPa) liquid or supercritical water. This thermochemical means of reforming biomass may have energetic advantages, since, when water is heated at high pressures a phase change to steam is avoided which avoids large enthalpic energy penalties. Biological chemicals undergo a range of reactions, including dehydration and decarboxylation reactions, which are influenced by the temperature, pressure, concentration, and presence of homogeneous or heterogeneous catalysts. Several biomass hydrothermal conversion processes are in development or demonstration. Liquefaction processes are generally lower temperature (200–400 °C) reactions which produce liquid products, often called “bio-oil” or “bio-crude”. Gasification processes generally take place at higher temperatures (400–700 °C) and can produce methane or hydrogen gases in high yields.

## 1. Introduction

This review deals with technologies for converting biomass into liquid and gaseous fuels in hydrothermal media, which we define

as a water-rich phase at temperatures above about 200 °C and at sufficient pressures to keep the water in either a liquid or supercritical state.† Hydrothermal processing offers a number of potential advantages over other biofuel production methods, including high throughputs, high energy and separation efficiency, the ability to use mixed feedstocks like wastes and

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† For pure water, if we are below its critical temperature at 374 °C, a liquid phase will exist when pressures are held above the vapor pressure; if we are above the critical temperature and above its critical pressure of 22.1 MPa, a supercritical fluid phase will exist. For aqueous mixtures, the pressure and temperature conditions of the critical point will vary with composition.

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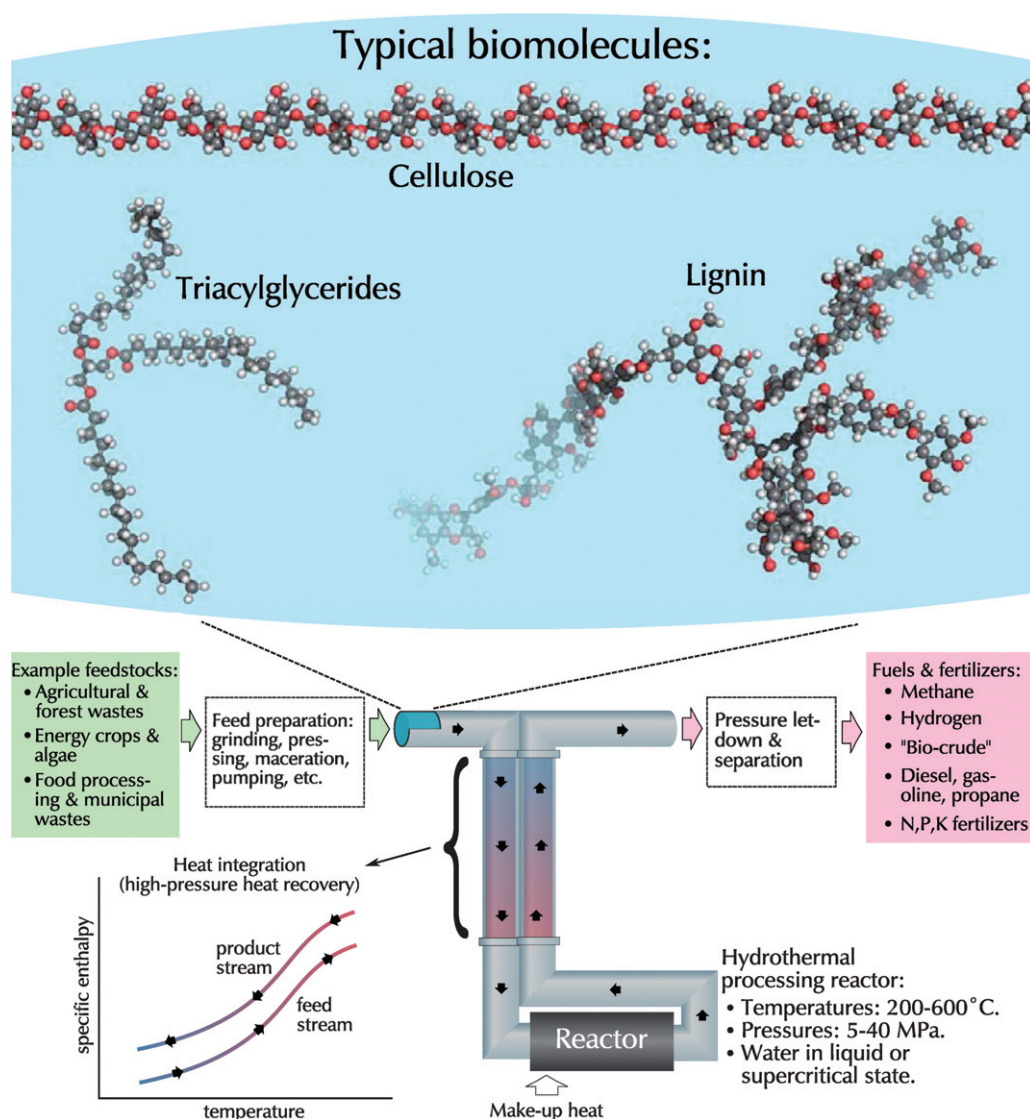
lignocellulose, the production of direct replacements for existing fuels, and no need to maintain specialized microbial cultures or enzymes. Hydrothermal processing also offers unique possibilities in coordination with other biofuel processing techniques, including as a pretreatment step or for post-fermentation reforming. In addition, because of the high temperatures involved, biofuels produced would be free of biologically active organisms or compounds, including bacteria, viruses, and even prion proteins. A schematic overview of hydrothermal processing is shown in Fig. 1.

However, many engineering challenges remain for hydrothermal processing. These include unknown or largely uncharacterized reaction pathways and kinetics, inadequate catalysts which do not withstand hydrothermal conditions, inadequate solid management practices that lead to precipitation of inorganic materials and can result in fouling and plugging issues, and a need for specialized materials to withstand the high-temperature, high-pressure, and often corrosive environments of hydrothermal media.

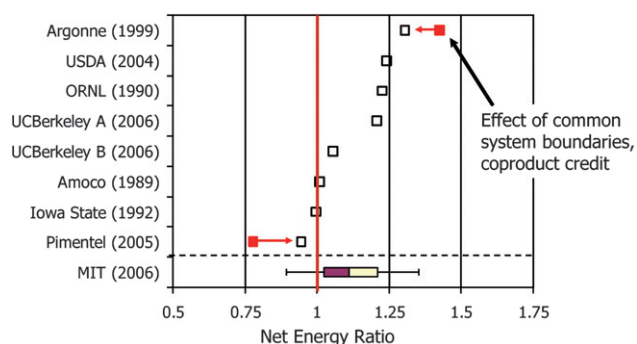
This review summarizes the state of knowledge with respect to biomass processing in hydrothermal media, including a review of characteristic chemical reactions and of the main processing methods employed for biomass conversion to liquid and gaseous fuels.

### 1.1. Biomass potential and availability

Recently there has been renewed interest worldwide in producing biofuels from a range of biomass feedstocks. Meeting today's energy needs of the transportation sector is particularly challenging as it requires liquid combustible fuels that can fit into our existing hydrocarbon fuel infrastructure. For many developed countries, including the U.S., Japan, and many European countries, crude oil and refined petroleum products must be imported in large amounts to meet transportation fuel demands. While the public tends to emphasize the economic and political stresses associated with imported oil, environmental issues surrounding emissions of carbon dioxide from vehicles creates



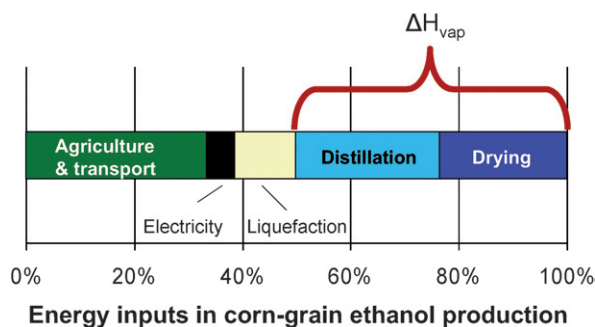
**Fig. 1** Conceptual schematic of hydrothermal processes. Biomass feedstocks (top), including cellulose, triacylglycerides, and lignin, are processed in the aqueous phase. The lack of a phase change (bottom-left) allows for increased heat recovery.



**Fig. 2** Net energy ratio for producing ethanol from corn grain. The net energy ratio is defined as the energy content of a unit mass of ethanol produced divided by the total energy inputs required to produce it. (Adapted from Johnson.<sup>1</sup> References: Argonne (1999),<sup>2</sup> USDA (2004),<sup>3</sup> ORNL (1990),<sup>4</sup> UC Berkeley A (2006) & UC Berkeley B (2006),<sup>5</sup> Amoco (1989),<sup>6</sup> Iowa State (1992),<sup>7</sup> Pimentel (2005),<sup>8</sup> MIT (2006).<sup>1</sup>)

challenges that are equally daunting given the large number of these mobile emission sources. Renewable and nuclear energy technologies are viewed by many as long term solutions, but only renewable biomass has the ability to directly generate hydrocarbon-based liquid fuels that could approach carbon neutrality.

The two major chemical pathways to biofuels that are commercially pursued today are fermentation of starches (primarily from corn grain or sugar cane) to ethanol and transesterification of fatty acids from soy, canola and other natural oils to biodiesel. In both cases, agricultural products are being produced as feedstocks for biofuels rather than as food for humans or feed for animals. The net energy balance and impacts on land and water resources across the full life cycle of these biofuels are variable and highly dependent on many factors, but are marginally favorable at best. For example, Fig. 2 shows the range of reported energy efficiencies for corn grain ethanol production reported in a recent MIT study by Johnson and co-workers.<sup>1</sup> They analyzed the statistical variance of crop production and biomass to ethanol conversion conditions in the U.S. and showed that net energy efficiencies for producing ethanol from corn grain varied from about +30% to -10% depending on the intensity level of farming (fertilizer, irrigation, and agricultural chemicals needed) and the efficiency of the conversion and separation processes used.



**Fig. 3** Distribution of energy requirements for producing ethanol from corn grain. Adapted from Johnson.<sup>1</sup> Distillation and drying, both related to the enthalpy of vaporization of water,  $\Delta H_{\text{vap}}$ , make up about half of the total.

Also as shown by Johnson *et al.* (in Fig. 3), only about 1/3 of the total energy consumed in producing ethanol is associated with the production of the corn (including planting, harvesting, irrigation, fertilizer, and transport); 2/3 of the energy needed is associated with the manufacturing plant that converts the corn to ethanol. Approximately 50% of the total energy requirements are consumed by two steps alone: distillation and drying. These two inefficient steps are primarily a result of the energy requirements to volatilize water. As will be further discussed in Section 1.2, hydrothermal technologies can largely avoid energetic sinks associated with the evaporation of water and can thus result in more efficient processing of biomass.

Given the limitations of using grain feedstocks for biofuel production, much research and development is currently focused on using residuals, wastes and low intensity energy crops (such as switchgrass, poplar, willow, and algae) as feedstocks. While this transition can increase the amount of biofuel that could be produced, transitioning to residuals can ideally also reduce energy inputs and reduce other environmental impacts. There are many challenges, from the production, harvesting, and storage of the biomass itself to its chemical transformation to a useful fuel. A major focus now is on developing economically acceptable processes for sustainable feedstocks that primarily consist of lignocellulose or fatty acids or oils, as shown in Table 1. Full life cycle analysis is now commonly used to evaluate the energetic and environmental efficiencies of proposed processes.

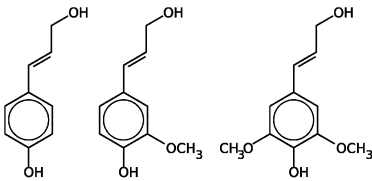
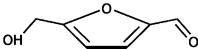
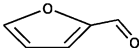
## 1.2. Suitability of hydrothermal technologies for mixed waste streams

A recent evaluation of biofuels production in *Science* suggested that supercritical fluids may be well-suited to enhance the chemical transformation of biofeedstocks to useful liquid and gaseous fuels.<sup>9</sup> The basic concept being pursued by many researchers is that reactions and separations in certain supercritical fluids might have advantages over conventional biochemical processing methods. Hydrothermal processing carried out near and above the critical point of water (374 °C, 22 MPa) is attractive for biomass conversion for three main reasons:

- 1. The presence of water.** Many biomass feedstocks, such as agricultural residuals, food processing wastes, and municipal and agricultural sludges, contain large amounts of water. In conventional processing, the water is typically thermally separated, by vaporization in pyrolysis, by distillation in biochemical processing, or by similar means in other processing approaches. These separation steps lead to large parasitic energy losses that can consume much of the energy content of the biomass. By carrying out reactions under pressure the phase change is avoided, providing possible efficiency advantages in hydrothermal processing.

- 2. Versatility of chemistry.** Feedstocks containing lignocellulose, fatty acids, and protein derivatives can be hydrothermally transformed to produce a range of gasified or liquefied fuel products such as methane, hydrogen, biocrude, biodiesel, and biogasoline that are usable at commercial scale in existing infrastructures.

**Table 1** Representative biomass feedstock chemical compounds and reaction intermediates encountered in hydrothermal processing

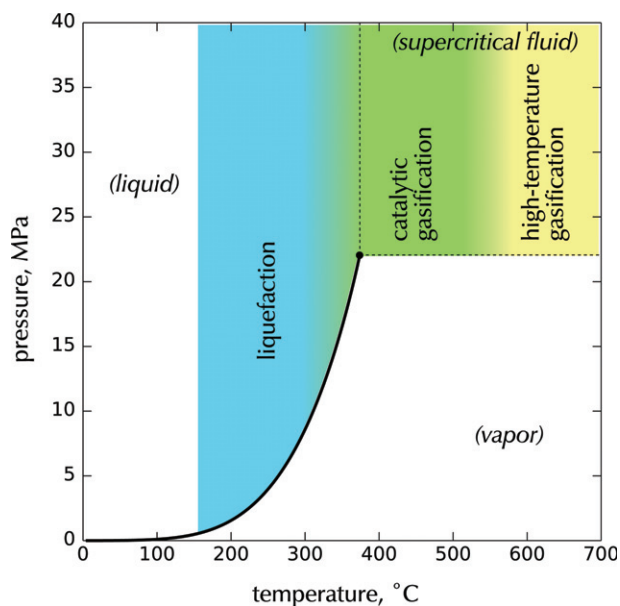
Substance	Chemical formula	Structural information
<b>Feedstocks</b>		
Cellulose	$[C_6H_{10}O_5]_n$	$n \approx 500\text{--}10\,000$ ; $\beta$ (1 $\rightarrow$ 4) linkages between glucose residues
Hemicellulose	Typical monomers: $[C_5H_8O_4]$ , $[C_6H_{10}O_5]$	Branched with variable monosaccharide residues; degree of polymerization $\sim 500\text{--}3000$
Lignin	Typical monomers: 	Polymer of aromatic subunits in random structure (see Fig. 1); molecular weight: $>10\,000$ Da
Triacylglycerides (fats)	$RCOO-CH_2CH(R'COO)CH_2-(R''COO)$	$RCOO$ , $R'COO$ , $R''COO$ are fatty acids with ester linkages to the glycerol backbone
Proteins	$[NHCH(R)C(O)]_n$	Monomer is amino acid residue with various side (R) groups; $n \approx 50\text{--}2000$
<b>Intermediates</b>		
Glucose	$C_6H_{12}O_6$	Exists as 6-membered ring, 5-membered ring, and open chain (see Fig. 9)
Xylose	$C_5H_{10}O_5$	Exists as 6-membered ring, 5-membered ring, and open chain
Amino acid	$H_2NCH(R)COOH$	R is the side group, varies from H to heterocyclic group
Fatty acid	$RCOOH$	R is an alkyl group, typically of 12–20 carbons with 0–4 double bonds
5-Hydroxymethylfurfural		
Furfural		

**3. Enhanced reaction rates and efficient separations.** Inter-phase mass transfer resistances are substantially reduced or eliminated by operating at hydrothermal or supercritical conditions. Furthermore, energy savings may result from carrying out reactions in a dense supercritical vapor or near-critical liquid phase system with both improved selectivity to more desirable energy products such as methane, hydrogen, and a range of liquid biofuel products. The considerable variations in the physical properties of water that occur with changes in temperature and pressure can facilitate efficient separations of product and by-product streams, which can reduce the energy consumption required to purify products. In the case of feedstocks that also contain inorganics such as sulfates, nitrates, and phosphates, hydrothermal methods can facilitate recovery and recycling of these chemicals in their ionic form, for eventual use as fertilizers.

An ancillary advantage of hydrothermal processing is that product streams are completely sterilized with respect to any possible pathogens including biotoxins, bacteria or viruses. In addition, temperatures and exposure times are usually sufficiently high—250 °C or greater for a few seconds—to destructively hydrolyze any proteins present so that even prions would be destroyed. (Research in the food industry shows 22D

destruction of prions in just 1 min at 160 °C.<sup>10</sup> D refers to a “decimal reduction”, meaning 90% of the infectious material is destroyed. For 22D destruction, hypothetically only 0.1<sup>22</sup> of the infectious material could survive the treatment.) This detoxification feature has also been demonstrated for complex mixed feeds from pharmaceutical production undergoing supercritical water oxidation.<sup>11</sup>

Hydrothermal processing can be divided into three main regions, liquefaction, catalytic gasification, and high-temperature gasification, depending on the processing temperature and pressure as shown in Fig. 4. The pressure-temperature phase diagram for pure water is superimposed to highlight the regions with respect to water's liquid-vapor co-existence behavior. Hydrothermal conversion *via* liquefaction pathways occurs generally between about 200 and 370 °C, with pressures between about 4 and 20 MPa, sufficient to keep the water in a liquid state. At near-critical temperatures up to about 500 °C, effective reforming and gasification generally requires catalytic enhancement to achieve reasonable rates and selectivity. At higher temperatures above 500 °C, homogeneous gasification and thermolysis often occur. Sections 3 and 4 of this article review hydrothermal technologies in these three thermal regions.



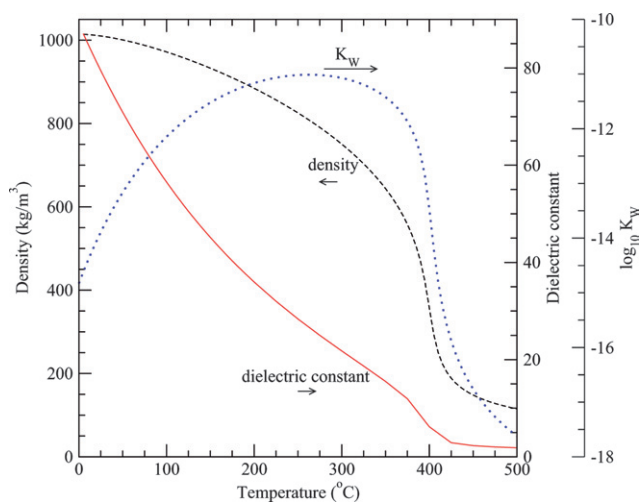
**Fig. 4** Hydrothermal processing regions referenced to the pressure-temperature phase diagram of water.

These three regions take advantage of substantial changes in the properties of water that occur in the vicinity of its critical point at 374 °C ( $T_c$ ) and 22 MPa ( $P_c$ ). By moving from subcritical to supercritical temperatures at pressures above  $P_c$  we can control both the rate of hydrolysis as well as phase partitioning and solubility of components so that more chemically and energetically favorable pathways to gaseous and liquid biofuels may be released.

In the region near the critical point, water is highly compressible. For example, the density decreases nearly two orders of magnitude without a change in phase from liquid-like (about 800 kg m<sup>-3</sup>) to dense gas-like (about 150 kg m<sup>-3</sup>) conditions as the temperature is increased from 300 to 450 °C. These changes in density correlate with other macroscopic properties to reflect changes at the molecular level such as solvation power, degree of hydrogen bonding, polarity, dielectric strength, molecular diffusivity, and viscosity.

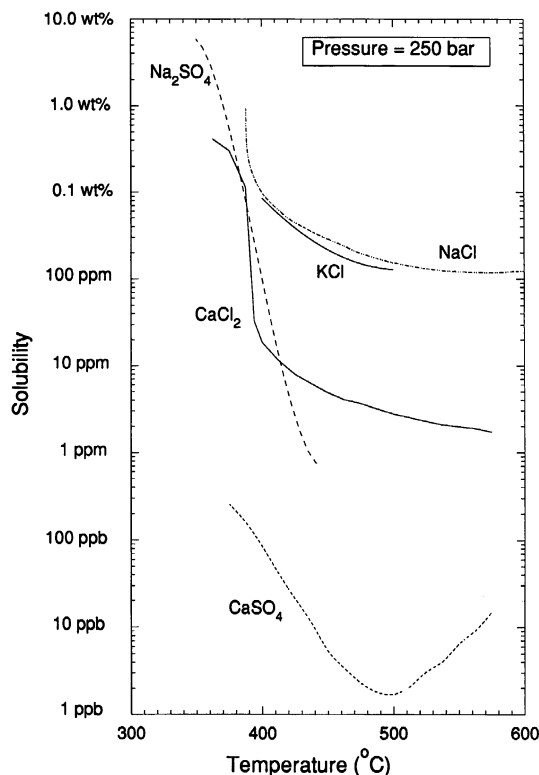
Fig. 5 illustrates the range of property variations that occur. For example, if we start with pure liquid water at 30 MPa and 25 °C and heat it to temperatures above its critical temperature of 374 °C, enormous changes in solvation behavior of water occur where it transforms from a polar, highly hydrogen-bonded solvent to behavior more typical of a non-polar solvent like hexane. Specifically, the dielectric constant decreases from about 80 at 25 °C to less than 2 at 450 °C, the ion product ( $K_w$ ) first increases from 10<sup>-14</sup> to 10<sup>-11</sup> just below 350 °C and then decreases by five orders of magnitude or more above 500 °C. The ion product, or self-ionization constant, is defined as the product of the concentrations of the acidic and basic forms of water,  $K_w \equiv [\text{H}_3\text{O}^+][\text{OH}^-]$ , in units of mol<sup>2</sup> kg<sup>-2</sup>.

Because we are avoiding a specific phase change when heating at pressures greater than  $P_{\text{vap}}(T)$  or  $P_c$ , the specific energy requirements needed to effect the isobaric expansion from liquid-like to gas-like densities are typically lower than what is needed when boiling occurs under subcritical pressures at an intermediate temperature to form a two-phase mixture.

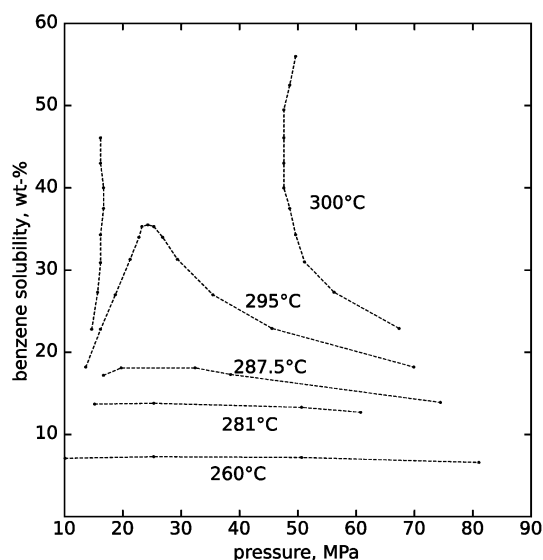


**Fig. 5** Density,<sup>12</sup> static dielectric constant<sup>13</sup> and ion dissociation constant ( $K_w$ )<sup>14</sup> of water at 30 MPa as a function of temperature. The dielectric constant of water drops drastically as water is heated, and approaches that of a (room-temperature) non-polar solvent at supercritical conditions.

Another aspect of hydrothermal processing that can have significant advantages over other biomass processing methods is in the area of separations. Because we have the ability to tune the solvation properties of water in the highly compressible near-critical region, partitioning of products or by-products into separate phases can be used to separate and purify products. Fig. 6, 7 and 8 illustrate the sensitivity of solubility to temperature at high pressures for inorganic ionic compounds, for simple organic compounds, and for lipids. Additionally, gases including



**Fig. 6** The solubility limits of various salts at 25 MPa. From Armellini.<sup>20</sup>



**Fig. 7** Benzene solubility in high-pressure water, as measured by Connolly.<sup>21</sup> At temperatures of 295 °C and below, a solubility limit exists at all pressures. At 300 °C and above, the phases become completely miscible between 17 and 47 MPa.

nitrogen,<sup>15</sup> air and oxygen,<sup>16</sup> carbon dioxide,<sup>17</sup> hydrogen<sup>18</sup> and methane<sup>19</sup> all exhibit complete miscibility with supercritical water. One can rapidly alter solubility and selectively phase partition, precipitate or dissolve certain components by changing temperature or pressure in the near-critical region.

### 1.3. Related processes in supercritical water

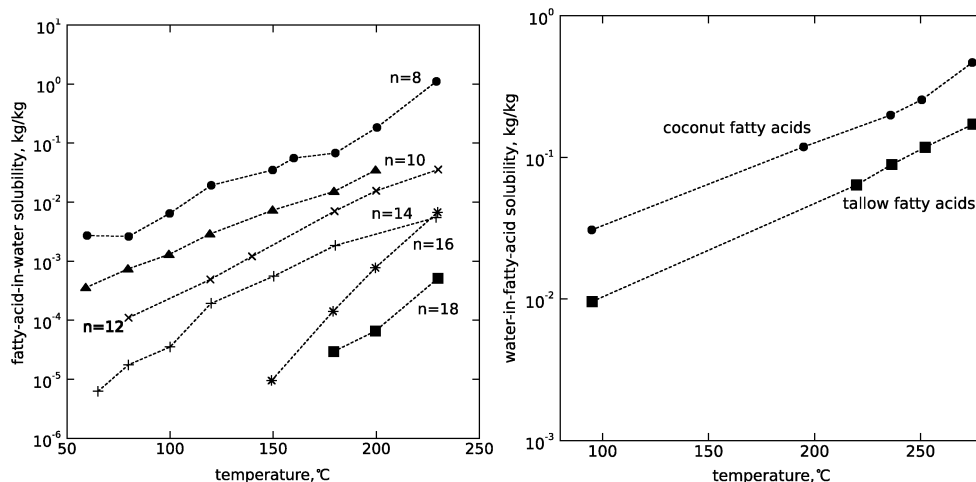
Much of the industrial processing knowledge in the field of hydrothermal processing comes from two application areas: (1) supercritical-water oxidation, and (2) supercritical-water power generation cycles.

Oxidation in supercritical water has been effectively employed to detoxify and remediate a wide range of organic and biological wastes. The original supercritical water oxidation (SCWO)

process was developed in the early 1980s<sup>22,23</sup> based on research at MIT by Modell and co-workers in the late 1970s and has been deployed at both pilot and demonstration scales commercially in the U.S., Europe, and Asia. SCWO has been shown to be very effective in industrial, military, and municipal waste treatment applications in achieving high destruction and removal efficiencies with very short residence times of 1 min or less; for dilute aqueous wastes containing 1 to 20 wt% organics. In principle, SCWO is not only more effective but also more environmentally acceptable and economical than incineration or selective absorption for many waste treatment applications. Because the oxidation process is carried out in water, SCWO does not require drying as is needed in incineration. Also because the supercritical process is fully contained, there are no vapor emissions or stack releases of products of incomplete combustion.

The basic approach of SCWO brings together water, oxygen, and organic compounds along with any heteroatoms that are present, such as N, S, P, or Cl, at supercritical temperatures of 400 °C or more and supercritical pressures greater than 22 MPa, typically about 25 MPa. Under these conditions, a single fluid reaction phase exists that can rapidly be oxidized or mineralized to form CO<sub>2</sub>, H<sub>2</sub>O and mostly molecular nitrogen (N<sub>2</sub>) with some N<sub>2</sub>O, but without forming NO<sub>x</sub> compounds, NH<sub>3</sub> or other toxic products of incomplete combustion. Sulfur, phosphorus, and chlorine heteroatoms are oxidized to form their inorganic acids—H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, and HCl—which can be neutralized to form salts using a suitable base. Above 450 °C and at 25 MPa, these salts become nearly insoluble and can be precipitated and removed from the fluid stream.

Because of these applications and other possible uses of supercritical water for synthetic transformations, a number of research groups have been active in characterizing and modeling phase and chemical reactions over a full range of scales from laboratory to demonstration plants. Interested readers can consult a number of excellent review articles, for example for general treatments of the SCWO process itself and related technologies, see Thomason and Modell, 1984;<sup>24</sup> Modell, 1989;<sup>25</sup> Shaw *et al.*, 1991;<sup>26</sup> Tester *et al.*, 1993;<sup>27</sup> Tester and Cline, 1999;<sup>28</sup> Gloyna and Li, 1998;<sup>29</sup> and Marrone *et al.*, 2007.<sup>30,31</sup> For reviews



**Fig. 8** (Left) The solubility of saturated fatty acids in water at 15 MPa, adapted from Khuwijitjaru *et al.*<sup>117</sup> *n* is the carbon number of each fatty acid. (Right) The solubility of water in fatty acids at the vapor pressure of the system, from Mills and McClain.<sup>118</sup>

specific to reaction mechanisms and kinetics in supercritical water see Savage *et al.*, 1995<sup>32</sup> and Akiya *et al.*, 2002<sup>33</sup> or for salt management technology see Hodes *et al.*, 2004<sup>34</sup> and Marrone *et al.*, 2004.<sup>35</sup>

Catalytic methane reforming in the presence of supercritical water has also been investigated in order to identify a single-step method for producing higher alkanes, a liquid product such as methanol, or hydrogen gas. A promising catalyst and reaction conditions have recently been identified in our laboratory at MIT that gave over 90% methane conversion to produce a hydrogen-rich gas with nearly stoichiometric CO<sub>2</sub> content at 14 second residence time.<sup>36</sup>

Supercritical and hydrothermal media may also be attractive for upgrading problematic unconventional fossil feedstocks such as heavy oils and tar sands. Again using the fact that the physical properties of water near its critical point vary significantly with temperature and pressure, water can act both as solvent and reactant in reforming processes.

Industrially, the largest use of supercritical water is in steam cycles for electric power generation; for a new coal power plant, a pulverized-coal/supercritical-steam cycle is “presently the choice of new coal-fired utility plant worldwide”.<sup>37</sup> Although chemical reactions are not taking place in these systems, much can be learned about engineering and materials of construction from power generation applications, which operate with water at conditions of up to about 590 °C and 35 MPa.<sup>38</sup>

#### 1.4. Other sources of information on hydrothermal biomass processing

A number of prior reviews and reports have been published on various aspects of hydrothermal biomass processing over the years.<sup>39–41</sup> Additionally, meetings sponsored by the International Energy Agency have been held every 3 to 4 years since 1981 that bring together scientists and engineers working on thermochemical methods of biomass processing; the published proceedings of these conferences have a wealth of information.<sup>42–46</sup>

Much of our understanding of chemical reactions and behavior in hydrothermal systems has resulted from research in other fields. For example, reactions of lignocellulose and related compounds in hydrothermal systems have been investigated by researchers in the forest products industry (see, for example, Bobleter<sup>39</sup>). The field of evolutionary biology has produced many insights into natural processes involving other biochemicals, such as amino acids and the synthesis of hydrocarbons, and is motivated by the discovery of and proposed origin of life around hydrothermal vents in the ocean floor (for example, Simoneit<sup>47</sup>). The geochemistry literature contains extensive information on reactions and behavior of both organic (for example, Katritzky *et al.*<sup>287</sup>) and inorganic (for example, Hack *et al.*<sup>48</sup>) compounds.

#### 1.5. Scope of the review

This review focuses on the underlying chemistry and engineering science associated with hydrothermal processing of a range of biomass feedstocks and processing conditions. Section 2 starts by describing major chemical structures and chemical reactions of biomass feedstocks in hydrothermal systems. Next we describe the major chemical processes that have been proposed or are

being developed for converting biomass into fuels. Section 3 focuses on technologies that produce liquid fuels, and Section 4 focuses on those that produce gaseous fuels.

Section 5 focuses on the role of the inorganic components of biomass, including their separation from supercritical water and their value as fertilizer. Finally, Section 6 covers the key issues that have prevented the widespread adoption of hydrothermal biomass conversion methods, and summarizes research opportunities that will help to address these issues.

## 2. Chemical reactions of biological molecules in hydrothermal systems

The chemistry behind reactions of individual biochemicals under hydrothermal conditions is well studied for a number of common materials, such as glucose and triacylglycerides. However, the chemical pathways of, kinetics of, and interactions between most other components of biomass at these conditions are largely uncharacterized. This section reviews hydrothermal reactions of biological materials, as well as some condensation reactions that may contribute to the formation of oils in hydrothermal systems under reducing conditions. The main focus of this section is on chemistry in the subcritical water zone, leading largely to extraction, depolymerization, fragmentation, and liquefaction, as supercritical-water chemistry tends to favor gas formation which is discussed more thoroughly in Section 4.

**Generalities of hydrothermal reactions.** In the early 1980s, many researchers expected altered or enhanced rates of chemical reactions occurring near the critical point of solvents such as carbon dioxide or water. However, it is now commonly accepted that no such enhancement takes place for water, as shown, for example, by Narayan and Antal<sup>49</sup> for the dehydration chemistry of 1-propanol. However, observed rates can be significantly enhanced by the loss of mass-transfer limitations (as most organic species become miscible with supercritical water) as well as the ability of supercritical water to sustain ionic as well as free-radical reactions.<sup>50</sup>

Generally speaking, in producing fuels from biomass, one overall objective is to remove oxygen; biomass feedstocks often contain 40–60 wt% oxygen and conventional fuels and oils typically have only trace amounts, under 1%. Oxygen heteroatom removal occurs most readily by dehydration, which removes oxygen in the form of water, and by decarboxylation, which removes oxygen in the form of carbon dioxide. Thermodynamically, since both water and carbon dioxide are fully oxidized and have no residual heating value, they can make ideal compounds in which to remove oxygen without losing heating value to the oxygen-containing chemicals removed.

Although an excess of water is present, dehydration reactions commonly occur in hydrothermal media at elevated temperatures and pressures. In fact, thermodynamics calculations for the alcohol/alkene equilibrium<sup>51</sup> show that, for a 1 M solution at 400 °C and 34.6 MPa, we would expect ethanol to equilibrate to a mixture of about 74 mol% ethylene/26 mol% ethanol, and *n*-propanol would equilibrate to a mixture of 97 mol% propylene/3 mol% propanol. The chemistry of cellulose and hemicellulose is dominated by their polyol structure (see Table 1 and Fig. 1), and degradation occurs by a mixture of dehydration and hydrolysis (fragmentation) reactions, as discussed further in Section 2.2.

Primary alcohols dehydrate *via* E2 eliminations, S<sub>N</sub>2 substitutions, and Ad<sub>E</sub>3 additions (involving the alkene product), as shown for ethanol<sup>51,52</sup> and *n*-propanol.<sup>51,49</sup> Tertiary alcohols' dehydration chemistry is dominated by E1 and Ad<sub>E</sub>2 (also involving the alkene product) mechanisms.<sup>53,54</sup> For secondary alcohols, the mechanism is less clear—for isopropanol, both E2 and E1 mechanisms give a good fit to the data.<sup>55</sup> In all three cases, ethers (which may be formed from alcohols *via* substitution reactions) play an important role in the dehydration chemistry. Generally, dehydration reactions are accelerated by the catalytic effect of a small amount of an Arrhenius acid such as H<sub>2</sub>SO<sub>4</sub>.

Decarboxylation reactions provide a second means of removing oxygen from biomass compounds; unfortunately, compared to dehydration reactions, fewer fundamental studies have been initiated. (Decarboxylation reactions are discussed for amino acids and fatty acids later in Section 2.4.2 and 2.3, respectively.) Decarboxylation reactions are attractive because they not only decrease the oxygen content of the feedstock, but because they also increase the H:C ratio, which typically leads to more attractive fuels.

Relative to water-free conditions, decarboxylation reactions in hydrothermal media can be suppressed<sup>56</sup> or enhanced,<sup>57</sup> and some suppressed reactions can return to similar levels with the addition of a catalyst such as KOH.<sup>58</sup> Goudriaan and Peferoen,<sup>57</sup> as well as Boocock and Sherman<sup>59</sup> have shown that under liquefaction conditions of 300 to 350 °C in liquid water, a large portion of the oxygen is removed from lignocellulose as carbon dioxide. However, the mechanism of this is unclear: deoxyhexonic acids, which are formed *via* the dehydration of many sugars, have not been found to undergo selective decarboxylation under hydrothermal conditions of 340 °C.<sup>60</sup>

Of course, in mixtures containing multiple functional groups, reactions and interactions (both inter- and intramolecular) between these groups can change chemical pathways. In acids such as lactic acid<sup>61</sup> and citric acid,<sup>62</sup> which contain both hydroxyl and carboxylic acid groups, a decarbonylation pathway (involving the loss of CO) is opened and can occur instead of dehydration or decarboxylation reactions.

## 2.1. Reactions of carbohydrates

**2.1.1. Monosaccharides.** All carbohydrates, including sugars, starches, cellulose, hemicellulose, and chitin, are fundamentally polymers of monosaccharides (see Table 1). As discussed in Section 2.2, cellulose breaks down to form glucose (and other products) under hydrothermal conditions, and hemicellulose breaks down to form a number of monosaccharides, the most prevalent being the 5-carbon sugar xylose. An understanding of the subsequent reactions of monosaccharides is important in hydrothermal reactions involving any of these large molecules, including cellulose pretreatment to produce glucose.

**Glucose and fructose.** When D-glucose dissolves in water, it exists in three forms: as an open chain, a pyranose ring, and a furanose ring. Similarly, when D-fructose dissolves in water, it can also exist as an open chain, a pyranose ring, and a furanose ring. Glucose reversibly isomerizes into fructose *via* the LBAE (Lobry de Bruyn, Alberda van Ekenstein) transformation.

Hence, when glucose or fructose is present in water, at least six forms of monosaccharide are present, and glucose and fructose will follow the same general reaction pathways in hydrothermal systems, as shown in Fig. 9.

However, the rate of inter-isomerization is slow relative to the rates of degradation of both glucose and fructose. Antal *et al.*<sup>65</sup> saw that, when starting with glucose (or fructose), the amount of fructose (or glucose) formed was quite small compared to the amounts of other degradation products formed. Fructose is reportedly more reactive than glucose; for instance, Kabyemela *et al.*<sup>70</sup> observed that the rate of glucose isomerization to fructose was important in hydrothermal media; however, the reverse reaction of fructose to glucose was not important. His observations are based on experiments in which glucose or fructose were the starting material at temperatures of 300 to 400 °C and pressures of 25 to 40 MPa. In agreement with Kabyemela *et al.*, Salak Asghari and Yoshida<sup>71</sup> have seen that despite the isomerization, fructose reacts much faster than glucose, at least in the presence of phosphoric acid: after two minutes at 340 °C fructose was 98% destroyed, but glucose was only 52% destroyed. They noted that at room temperature the more-reactive acyclic form of glucose is in much lower relative abundance than the acyclic form of fructose, and speculated the same principle may be driving the lower reactivity at hydrothermal conditions.

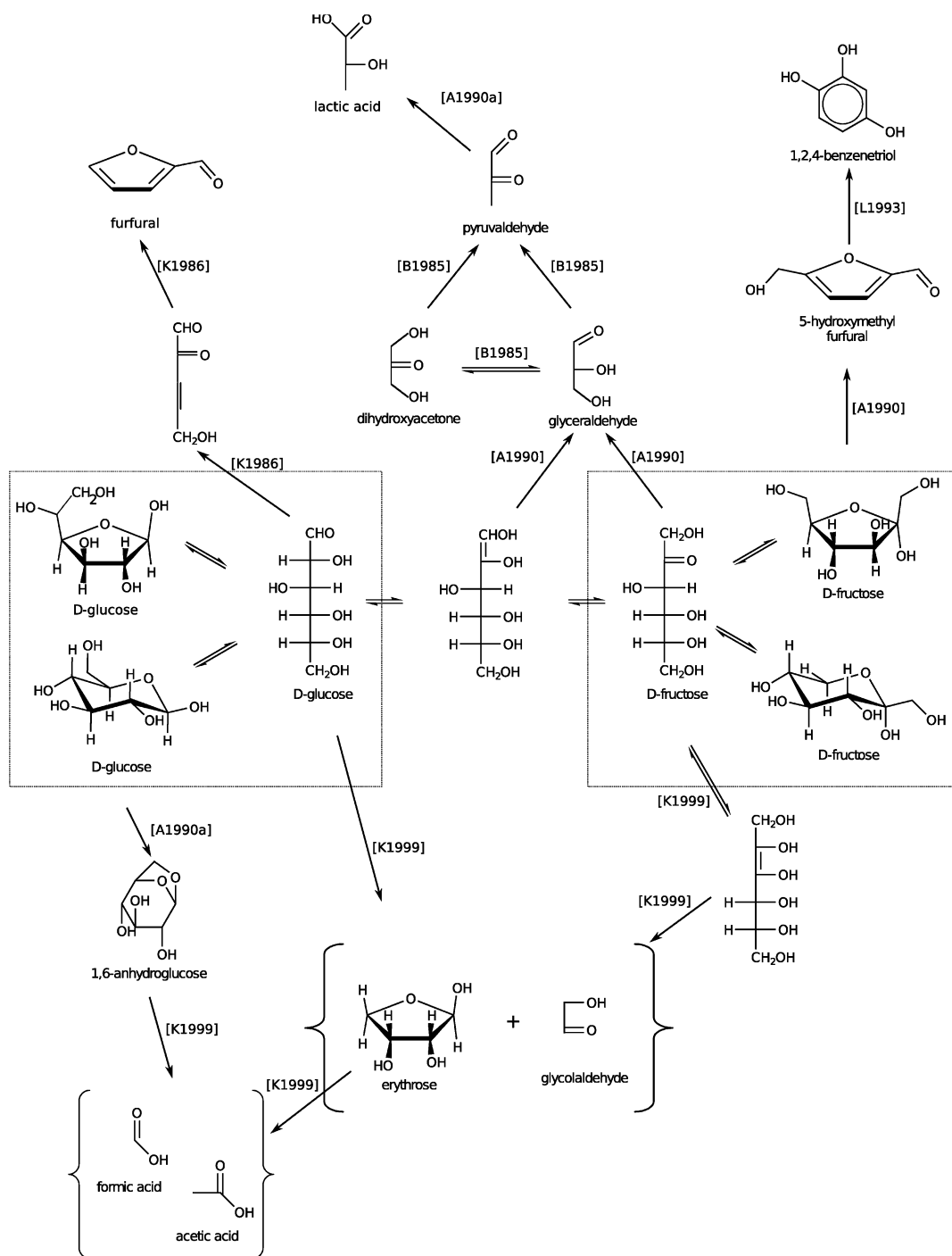
The hydrolysis of glucose and fructose has been studied for well over a century, and all confirm rapid degradation at hydrothermal conditions. Fig. 10 is an Arrhenius figure showing the glucose degradation rate as a function of temperature from a number of studies. Glucose destruction is drastic under hydrothermal conditions; for instance, Kabyemela *et al.*<sup>68</sup> saw 55% conversion of glucose after 2 s at 300 °C and 90% conversion after 1 s at 350 °C. Most researchers have assumed that glucose undergoes 1st-order degradation kinetics; however, Matsumura *et al.*<sup>72</sup> observed a reaction order of ~0.8 for temperatures above about 250 °C.

Table 2 shows common degradation products observed in six different studies. An overall degradation network for glucose under hydrothermal conditions is presented in Fig. 9, which has been compiled from a number of sources.

Because the rate of isomerization between glucose and fructose is slow relative to their degradation rates, different major products are observed when starting with glucose or fructose. While different reaction conditions and analytical techniques cause the products reported to differ, most publications agree that glucose degrades mostly to fragmentation products (glycolaldehyde, pyruvaldehyde, glyceraldehyde, *etc.*)<sup>75,78</sup> while fructose will react to a higher amount of the dehydration product 5-hydroxymethylfurfural (5-HMF).<sup>65,75,78</sup> (5-HMF has been proposed as an industrial building block chemical for bio-based products<sup>79</sup> and was the starting material for biomass-derived dimethylfuran, a bio-based gasoline replacement proposed by Dumesic and co-workers.<sup>80</sup>)

Interestingly, Luijckx *et al.*<sup>67</sup> reported that the aromatic compound 1,2,4-benzenetriol could be formed in significant yields from fructose. They determined that this compound was being formed in yields of up to 46% from 5-HMF (as shown in Fig. 9). This is noteworthy because in lignocellulosic pretreatments, aromatic compounds are often assumed to originate from the lignin portion. Thus Luijckx and co-workers' results show that





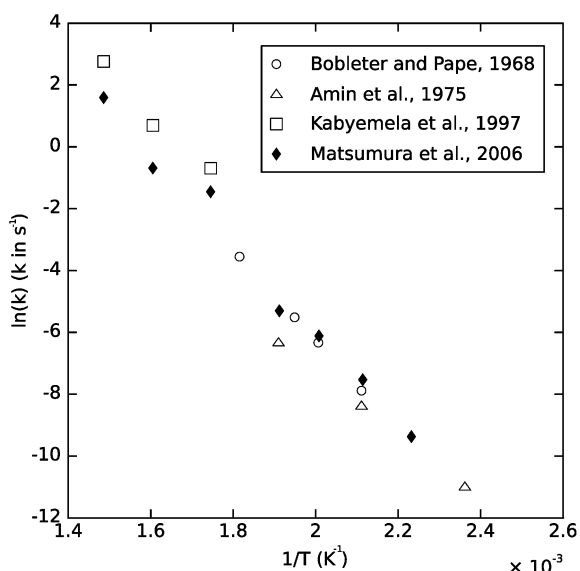
**Fig. 9** Pathways for the degradation of D-glucose and D-fructose. References for individual reactions are given in brackets. [B1985] = Bonn *et al.*, 1985;<sup>63</sup> [K1986] = Krishna *et al.*, 1986;<sup>64</sup> [A1990] = Antal *et al.*, 1990;<sup>65</sup> [A1990a] = Antal *et al.*, 1990;<sup>66</sup> [L1993] = Luijckx *et al.*, 1993;<sup>67</sup> [K1999] = Kabyemela *et al.*, 1999;<sup>68</sup> and [J2004] = Jin *et al.*, 2004.<sup>69</sup>

aromatics can also be formed from the cellulosic sugars. Indeed, Nelson *et al.*<sup>81</sup> reported, in 1984, the formation of aromatic compounds from hydrothermal reactions of pure cellulose at 250 to 400 °C.

Temperature can have a profound impact on the reaction pathway. The first studies of glucose hydrolysis over a range of temperatures including supercritical water, conducted in the 1970s,<sup>74</sup> reported that product spectra changed from char and

liquid organics below the critical temperature of water (374 °C) to gases, with little char, and liquid furans and furfurals above water's critical temperature.<sup>74,82,83</sup>

Various reactions within the pathways are sensitive to pH. Xiang *et al.*<sup>77</sup> studied the kinetics of glucose decomposition in dilute-acid mixtures at 180 to 230 °C in sealed glass ampoule reactors at unspecified pressures, and found, at 200 °C, that lower ambient pH solutions increased glucose destruction with



**Fig. 10** Assumed first-order Arrhenius plot of glucose degradation data. Data from Bobleter and Pape, 1968;<sup>73</sup> Amin *et al.*, 1975;<sup>74</sup> Kabyemela *et al.*, 1997<sup>70</sup> (40 MPa data), and Matsumura *et al.*, 2006<sup>72</sup> (25 MPa data).

the highest conversion being approximately 68% after 30 min at an (ambient) pH of 1.5. In experiments with fructose as the starting material at 250 °C, Antal *et al.*<sup>65</sup> noted that adding 2 mM

**Table 2** Glucose/fructose degradation products observed in various studies. Conditions given at end of table<sup>a</sup>

Compound	Study
Acetaldehyde	75,76
Acetic acid	65,70,75–77
Acetol (hydroxyacetone)	65
Acetone	75
Acetylacetone (2,5-hexanedione)	76
2-Acetylfuran	76
Acrylic acid (propenoic acid)	75,76
Arabinose	65
1,2,4-Benzenetriol	75
Cellobiose	77
Dihydroxyacetone	65,70,75,78
Erythrose	70
Formic acid	65,70,75–77
Fructose	65,70,77,78
2-Furaldehyde (furfural)	65,75,76,78
Glyceraldehyde	65,70,75,78
Glycolaldehyde	65,70,75,78
Glycolic acid	75
5-Hydroxymethylfurfural (5-HMF)	65,70,75–78
Lactic acid	65,75,76
Levulinic acid	65,77
Levoglucosan (1,6-anhydroglucose)	65,70,77
Mannose	65
5-Methylfurfural	76
Pyruvaldehyde	65,70,75,78
Solid precipitate (“humic solid”)	77
Gaseous products	77

<sup>a</sup> Sources: Bonn and Bobleter:<sup>78</sup> glucose/fructose at 220–270 °C, 5 s–15 min. Antal *et al.*:<sup>65</sup> fructose at 250 °C, 34.5 MPa, 1–95 s. Kabyemela *et al.*:<sup>70</sup> glucose at 300–400 °C, 25–40 MPa, 0.02–2 s. Xiang *et al.*:<sup>77</sup> glucose at 200–230 °C, unreported pressure (sealed in ampoules), 0.5–30 min, with weak H<sub>2</sub>SO<sub>4</sub>. Holgate *et al.*:<sup>76</sup> glucose at 425–600 °C, 24.6 MPa, 6 s. Srokol *et al.*:<sup>75</sup> glucose at 340 °C, 27.5 MPa, 120 s.

H<sub>2</sub>SO<sub>4</sub> significantly affected the degradation pathways of fructose, causing increased yields of 5-HMF and furfural and decreased yields of pyruvaldehyde and lactic acid, but had no measurable effect on the isomerization of fructose to glucose. Salak Asghari and Yoshida<sup>71</sup> worked to optimize yields of 5-HMF from fructose, and found phosphoric acid to be the best acid catalyst they tried, giving an optimal yield of 65% 5-HMF at 240 °C after 120 s using 0.05 M fructose in a phosphoric acid solution with an initial pH of 2. Rates were observed to decrease with increasing fructose concentration, concurrent with the build up of solid humin.

**Xylose.** Xylose is a five-carbon sugar that is one of the most common monosaccharide residues contained in hemicellulose. Industrially, most of the global production of furfural (2-furaldehyde) is produced from hemicellulose-derived xylose.

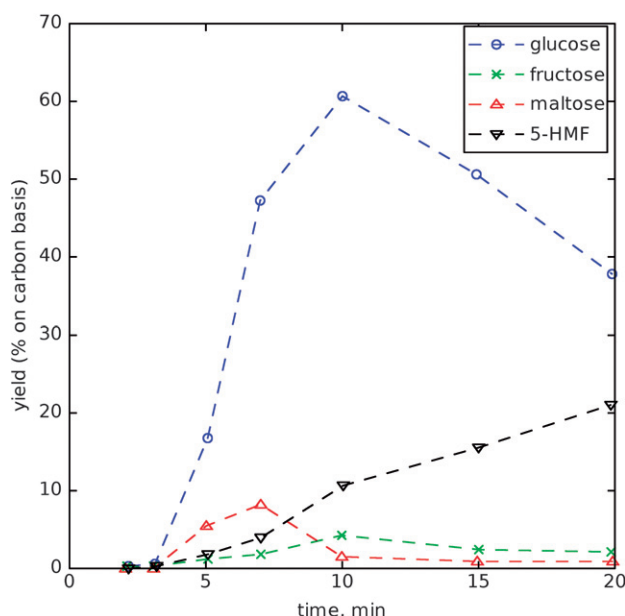
Xylose can exist in water as a pyranose ring, a furanose ring, or as an open-chain structure. Antal *et al.*<sup>84</sup> have proposed a mechanism for the conversion of xylose into furfural. Perhaps counterintuitively, furfural (itself a five-membered ring) was found to be formed from the pyranose ring form of xylose; the furanose ring was relatively stable to further chemical transformations under their test conditions. The open-chain form was found to produce glyceraldehyde, pyruvaldehyde, lactic acid, glycolaldehyde, formic acid, and acetol, which are fragmentation by-products in furfural production. The stability of the furanose ring, coupled with relatively slow rates of isomerization between the three forms of xylose, explained the presence of a small and enduring concentration of xylose in the products even after relatively long residence times at 250 °C. This mechanism was recently confirmed by *ab initio* molecular dynamics simulations by Qian *et al.*<sup>85</sup> at the National Renewable Energy Laboratory.

While Antal *et al.* showed how furfural is formed directly from xylose, Jing *et al.*<sup>86</sup> showed that furfural also degrades under hydrothermal conditions, but at a much lower rate than the xylose transforms into it. Sasaki *et al.*<sup>87</sup> saw, as the temperature rose higher into the 360–420 °C range, that the measured quantity of fragmentation products (glycolaldehyde, glyceraldehyde, pyruvaldehyde, and dihydroxyacetone) dominated the measured quantity of furfural after reactions with residence times of 0.1–0.25 s and pressures of 25–40 MPa.

Xylose is also capable of forming aromatic compounds in hydrothermal degradation, as observed by Nelson *et al.*<sup>88</sup> for acidic mixtures at 300 °C.

**2.1.2. Starch.** Starch is a polysaccharide consisting of glucose monomers bound with  $\alpha$ -(1 → 4) and  $\alpha$ -(1 → 6) bonds. Starches are easily hydrolyzed in hydrothermal conditions. However, while starches can be broken down rapidly without the addition of acids or enzymes, the reported yields of glucose are lower than those achievable with conventional enzymatic methods, presumably due to further decomposition of glucose or degradation of the starch into oligomers, like the ones produced in cellulose degradation, that cannot be further hydrolyzed to glucose.

Nagamori and Funazukuri<sup>89</sup> studied starch (from sweet potato) decomposition and quantified the yields of glucose, fructose, maltose, and 5-hydroxymethylfurfural (5-HMF) *versus* time at 180 to 240 °C in a batch reactor at unspecified pressures. They found their highest yield of glucose to be 63% (carbon basis)



**Fig. 11** Products from the degradation of starch at 220 °C. Adapted from Nagamori and Funazukuri.<sup>89</sup>

at 200 °C and 30 min. Fig. 11 shows product spectra *versus* time for reactions at 220 °C; a large amount of glucose is produced in the early period, but it is significantly degraded at longer residence times, primarily into 5-hydroxymethylfurfural (5-HMF).

Miyazawa and Funazukuri<sup>90</sup> report significantly lower yields of glucose from starch at similar conditions: 3.7% glucose yield after 15 min at 200 °C and unspecified pressures. However, they had a key finding that the glucose production increased drastically to 53% with CO<sub>2</sub> addition at the ratio of 0.1 g CO<sub>2</sub> per g H<sub>2</sub>O. The CO<sub>2</sub> was likely acting as an acid in hydrothermal media. The amount of glucose extracted increased approximately linearly with increasing CO<sub>2</sub> concentration, in the range of 0 to 0.1 g CO<sub>2</sub> per g H<sub>2</sub>O.

## 2.2. Reactions of lignocellulose

Lignocellulosic materials constitute the bulk of the dry weight of woody and grassy plant materials, and as such are amongst the most abundant biochemicals on earth. Lignocellulose is expected to be available at higher industrial yields than starch, by utilizing “energy crops” such as switchgrass, willow and poplar and from agricultural and forest-product residuals such as corn stover, wheat and rice straw, and wood waste.

Lignocellulose is composed of three primary components: cellulose, hemicellulose, and lignin. Garrote *et al.*<sup>91</sup> give typical cellulose, hemicellulose, and lignin fractions of various hardwoods, softwoods, and agricultural residues. These three chemical components of lignocellulose behave quite differently under hydrothermal conditions. For instance, in hydrothermal experiments with woody and herbaceous biomass at 200 to 230 °C without added acid or base, Mok and Antal<sup>92</sup> found that 100% of the hemicellulose was extracted over the span of just a few minutes, as compared to just 4–22% of the cellulose and 35–60% of the lignin over the same time period.

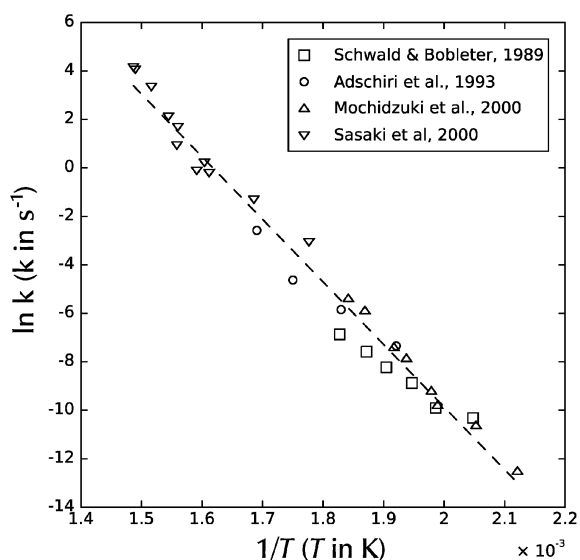
Hydrothermal media, often with the addition of acids and bases, have long been studied for the decomposition of

lignocellulose into monomers. See, for example, Bobleter’s excellent review article<sup>39</sup> and more recent updates by Mosier *et al.*<sup>93</sup> and Yu *et al.*<sup>94</sup> The monosaccharides produced can make suitable sugars for fermentative processes, such as the production of (cellulosic) ethanol and other biofuels and materials. (However, it is suggested that some aromatic compounds formed in hydrothermolysis may inhibit some fermentation products.<sup>88</sup>) Hydrothermal technologies can also liquefy and gasify lignocellulose. This section focuses on sugar extraction; liquefaction and gasification of lignocellulose are discussed in Sections 3 and 4, respectively.

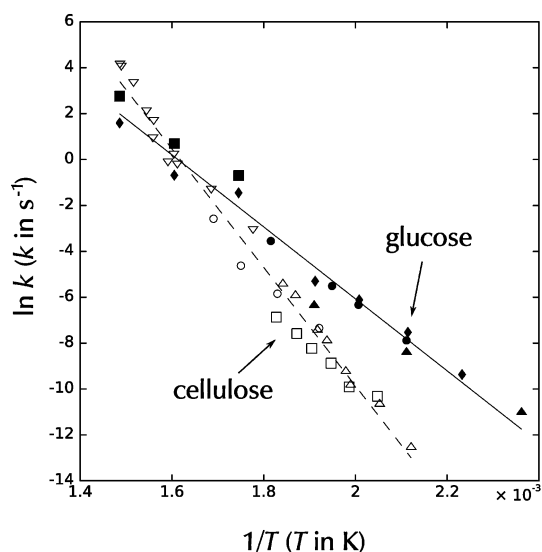
**Cellulose.** Cellulose, like starch, is a polysaccharide composed of units of glucose. However, unlike starch, the glucose monomers are connected *via* β-(1 → 4)-glycosidic bonds, which allows strong intra- and inter-molecular hydrogen bonds to form, and makes them crystalline, resistant to swelling in water, and resistant to attack by enzymes. Water at elevated temperatures and pressures can both break up the hydrogen-bound crystalline structure and hydrolyze the β-(1 → 4)-glycosidic bond, resulting in the production of glucose monomers. However, competing reactions hinder high glucose yields: glucose itself is subject to hydrothermal degradation (as discussed in Section 2.1) and cellulose has been found to also break down into oligomers, some of which can hydrolyze into glucose and some of which cannot.<sup>95</sup>

Cellulose from different biological sources has different properties, and both its physical (crystalline) and chemical structure can effect its behavior. Perhaps as expected, there is considerable variation in reported degradation rates for cellulose. Schwald and Bobleter<sup>96</sup> show classic first-order Arrhenius kinetics for cotton cellulose degradation with an activation energy of 129.1 kJ mol<sup>-1</sup> in the temperature range of 215 to 274 °C. However, in a semi-batch system, Adschiri *et al.*<sup>97</sup> showed a significantly higher activation energy of ~165 kJ mol<sup>-1</sup> on powdered cellulose of unspecified plant origin. In an experiment involving a hydrothermal thermogravimetric apparatus measuring loss-in-weight of a cellulose sample at isothermal conditions, Mochidzuki *et al.*<sup>98</sup> found an activation energy of 220 kJ mol<sup>-1</sup>. Meanwhile, Sasaki *et al.*<sup>99,100</sup> report a drastic acceleration of the reaction kinetics as water becomes near-critical, associated with a change in activation energy from 146 to 548 kJ mol<sup>-1</sup> as the system is heated past 370 °C! Sasaki *et al.*’s data<sup>99</sup> is plotted with Schwald and Bobleter’s, Adschiri *et al.*’s and Mochidzuki *et al.*’s in Fig. 12, which makes the apparent change in activation energy observed by Sasaki *et al.* appear less dramatic. If a best-fit line is fit to all of the data in Fig. 12, an activation energy of 215 kJ mol<sup>-1</sup> is obtained. For comparison, the activation energy for cellulose pyrolysis in the absence of condensed water is about 228 to 238 kJ mol<sup>-1</sup>.<sup>101</sup>

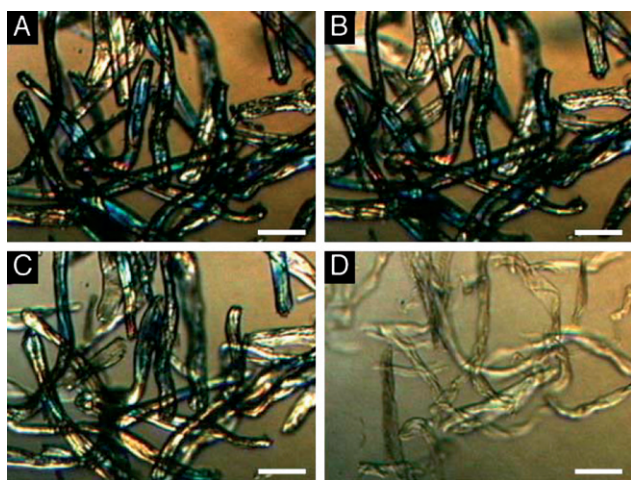
Other researchers have undertaken temperature scanning techniques to determine when the breakdown of cellulose becomes significant. Deguchi *et al.*<sup>102</sup> have used polarized light microscopy to observe the loss of crystallinity in cellulose fibers using similar techniques to those conventionally used to monitor starch gelatinization, namely a loss of birefringence which corresponds to a loss of crystallinity. When scanning at 11 to 14 °C min<sup>-1</sup> at 25 MPa, they observed a loss of birefringence at around 320 °C, indicating the cellulose crystallinity disappeared at these conditions. As illustrated in Fig. 13, they observed



**Fig. 12** Arrhenius plot of natural logarithm of pseudo-first-order reaction rate *versus* inverse temperature for cellulose decomposition. From Schwald and Bobleter,<sup>96</sup> Adschiri *et al.*,<sup>97</sup> Mochidzuki *et al.*,<sup>98</sup> and Sasaki *et al.*<sup>99</sup>



**Fig. 14** Arrhenius plot overlay of first-order decomposition rate constants for the degradation of glucose (filled data points) and cellulose (open data points). Data sources are identical to those in Fig. 10 and 12.



**Fig. 13** Cross-polarized light microscopy of cellulose being heated in high-pressure water. From Deguchi *et al.*,<sup>102</sup> used with permission.

breakup of the cellulose fibers very shortly after the loss of crystallinity, suggesting that the crystallinity was preventing breakdown of the cellulose.

As mentioned earlier, Sasaki *et al.*<sup>99</sup> reported that the cellulose degradation kinetics begin to have a much higher reaction rate as the reaction temperatures approached and entered the supercritical-water regime, and the hydrolysis proceeds at a much higher rate than glucose degradation at these conditions, above about 350 °C at 25 MPa. By making use of these phenomena, which they attribute to the swelling of cellulose, they claim yields of around 75% glucose. Regardless of whether the cellulose degradation kinetics start to follow a higher activation energy as water becomes near-critical, cellulose degradation appears to be more activated than glucose degradation in general. An overlay of the Arrhenius plots of cellulose and glucose decomposition kinetic constants shown in Fig. 14 clearly illustrates this. It

appears that cellulose destruction starts to proceed faster than glucose degradation at temperatures roughly at and above the critical point of water. This may warrant more research into high-temperature, short-time reforming of cellulose to maximize glucose yield. However, oligomers which cannot be hydrolyzed into glucose<sup>95</sup> may ultimately limit yields.

**Hemicellulose.** Hemicellulose is a heteropolymer composed of sugar monomers, including xylose, mannose, glucose, galactose and others, which can also have side chains. Garrote *et al.*<sup>91</sup> give typical hemicellulose sugar compositions of several hardwoods, softwoods, and agricultural residues. The ratios of these monomers can change quite dramatically for different feedstock sources. Given the lack of repeating  $\beta$ -(1 → 4)-glycosidic bonds and the random nature of the hemicellulose polymer, it does not form as crystalline and resistant of a structure as cellulose does, and thus is much more susceptible to hydrothermal extraction and hydrolysis. According to Bobleter,<sup>39</sup> hemicellulose is easily dissolved in water at temperatures above about 180 °C. Mok and Antal<sup>92</sup> found they could extract an average of 95% of hemicellulose as monomeric sugars at 34.5 MPa and 200 to 230 °C over a span of just a few minutes. Garrote *et al.*<sup>91</sup> also review reaction kinetics for hemicellulose degradation into sugars and subsequent degradation of the sugars into furfurals and other degradation compounds, and found that most studies reported hemicellulose extraction and recovery as sugars or oligomers at yields of 65 to 82%, although Mok and Antal's research was not included in their review.

**Lignin.** Lignin is a complex high molecular-weight compound with an even more random structure than hemicellulose. The three most prevalent monomers in lignin, all phenylpropane derivatives, are *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol, as shown from left to right in Table 1. A number of researchers have explored using hydrothermal processes to extract potentially valuable chemicals<sup>103–106</sup> from lignin as well as

for oil production<sup>107–110</sup> and gasification.<sup>111–114</sup> The density of water within the hydrothermal media has been found to be a key parameter. Many researchers have found that higher water densities increase the breakdown of lignin for the production of oils and gases, presumably by enhanced hydrolysis with the higher water density.<sup>107,108,115</sup> However, Sato *et al.*<sup>112</sup> found gasification efficiency to decrease when the density increased beyond  $0.4 \text{ g cm}^{-3}$ , possibly due to Le Chatelier's principle (the increasing pressure inhibits gas formation) or interference with the catalyst. In gasification reactions, the presence of lignin has been found to inhibit rates of gas formation.<sup>111,116</sup> More information on chemical transformations occurring during lignin gasification is found in Section 4.

### 2.3. Reactions of lipids

Fats and oils, which are non-polar compounds that in their chemical structures are similar to hydrocarbon fuels, can undergo reactions which can convert them into ready substitutes for conventional hydrocarbons as discussed in this section and Section 3.1.2.

The reactions of lipids and water are strongly influenced by their phase behavior. As noted in Section 1.2, the dielectric constant of water decreases drastically as water is heated isobarically, at pressures greater than its critical pressure, from room temperature to values above its critical temperature, causing the solvation properties of the water to more closely resemble organic solvents. Under these conditions, hydrogen bonding between water molecules becomes weaker allowing greater miscibility between lipids and water. The increase in temperature causes fats and oils to become increasingly soluble in water as its temperature rises under hydrothermal conditions, ultimately becoming completely miscible by the time the water has reached its supercritical state. Simultaneously, the amount of water that is soluble in the oil phase increases with the temperature. Both of these trends are shown in Fig. 8 for mixtures of fatty acids and water. The left plot shows the solubility of various saturated fatty acids in water as measured by Khuwijitjaru *et al.*,<sup>117</sup> showing an exponential increase in solubility with temperature. The right plot, measured by Mills and McClain in 1949,<sup>118</sup> shows the amount of water that is soluble in fatty acids derived from two types of oils: coconut oil and beef tallow. This also shows an exponential increase with temperature.

As the system continues to rise in temperature, the two phases eventually become miscible before the critical temperature of water is reached. Mills and McClain measured this to occur at  $293 \text{ }^\circ\text{C}$  for coconut-oil-derived fatty acids and  $321 \text{ }^\circ\text{C}$  for tallow-derived fatty acids. Using an optically accessible flow cell, King *et al.*<sup>119</sup> also observed the reactive system of soybean oil and water to become completely miscible by  $339 \text{ }^\circ\text{C}$ .

The solubility data presented are for fatty acids. Fats and oils in biological systems are typically in the form of triacylglycerides (TAGs), which consist of three fatty acids bound to a glycerol backbone (see Table 1). The TAG/water system is reactive, with water hydrolysing the TAGs to form fatty acids, as discussed below. Consequently, measurements are only possible for the solubilities of free fatty acids and water, not TAGs and water. In general, if they were stable TAGs would be expected to have much lower miscibility with water, since TAGs lack the polar

group of fatty acids. This was observed at  $100 \text{ }^\circ\text{C}$  by Lascaray,<sup>120</sup> who saw the solubility of water in tallow/free-fatty-acid mixtures to increase linearly from  $0.0027$  to  $0.0122 \text{ kg kg}^{-1}$  as the fraction of free fatty acid in the tallow/free-fatty-acid mixture was increased from  $0$  to  $100\%$ .

**Hydrolysis of triacylglycerides.** Triacylglycerides (TAGs) are the most common form of lipid in biological systems. As early as 1854, hydrothermal processes were reported to split fatty acids from oils,<sup>121</sup> and industrially, the Colgate–Emery<sup>122</sup> process was first implemented several decades ago to hydrothermally split TAGs to form free fatty acids and glycerol. The Colgate–Emery process takes place under similar conditions to hydrothermal processing:  $250 \text{ }^\circ\text{C}$  and  $5 \text{ MPa}$ , with a TAG : water ratio of approximately  $2 : 1$ .

Hydrolysis reactions occur primarily in the oil phase, and proceed to an increasing equilibrium level with increasing water-to-oil ratios. The equilibrium level attained has been found to not be a function of temperature. While the reaction is believed to be first-order within the oil phase, in practice, an induction period is usually observed, which is likely related to the relatively low solubility of water in TAGs as compared to fatty acids. As the reaction proceeds, more fatty acids are generated which increases the solubility of water in the oil phase and thus the observed reaction rate. Moquin and Temelli<sup>123</sup> provide a nice overview of this phenomenon in the introduction of their recent article on canola oil hydrolysis in supercritical media.

Fujii *et al.*<sup>124</sup> have confirmed that a first-order reaction drives the degradation kinetics of monoacylglycerides in the aqueous phase, and have shown a first-order reaction rate that follows Arrhenius kinetics, with activation energy of  $77.5 \text{ kJ mol}^{-1}$  and frequency factor of  $1.01 \times 10^5 \text{ s}^{-1}$ .

King *et al.*<sup>119</sup> found that they could achieve rapid hydrolysis of fatty acids in liquid water at temperatures of  $330$  to  $340 \text{ }^\circ\text{C}$  and water-to-oil ratios of  $2.5$  to  $5.0 : 1$ , giving  $90$  to  $100\%$  yields of free fatty acids. Using an optically accessible reactor, they found the phase behavior to be extremely important, and noted that the reaction quickly went to completion when the mixture became a single phase at  $339 \text{ }^\circ\text{C}$ .

**Fatty acids.** Free fatty acids have been shown to degrade in hydrothermal systems, and can produce long-chained hydrocarbons. Watanabe *et al.*<sup>58</sup> studied stearic acid ( $\text{C}_{17}\text{H}_{35}\text{COOH}$ ) decomposition to a maximum processing temperature of  $400 \text{ }^\circ\text{C}$  in a batch reactor at a fixed density of  $0.17 \text{ g cm}^{-3}$ . They found two major products,  $\text{C}_{17}\text{H}_{36}$  and  $\text{C}_{16}\text{H}_{32}$ . The authors compared this reaction in a hydrothermal system to pyrolysis reactions of neat (water-free) stearic acid. Although quantitative data was not given, the authors found that stearic acid decomposition was suppressed in the hydrothermal experiments, and more alkene was made than alkane. The production of hydrocarbons with fewer than 16 carbons was also suppressed in the hydrothermal experiments. However, when NaOH or KOH was added to the hydrothermal system, decomposition of stearic acid increased significantly and the alkane again became the dominant product, while lower hydrocarbons were still suppressed. KOH had a larger effect than NaOH.

The decarboxylation of formic<sup>125,289</sup> and acetic<sup>126,127</sup> acid in hydrothermal media has received more study than the

corresponding reactions of fatty acids, and can provide chemical insights. The decarboxylation reaction is strongly influenced by catalytic effects of reactor wall surfaces, in particularly stainless steel. Bell *et al.*<sup>126</sup> studied acetic acid and sodium acetate decomposition at 335 °C and 13.7 MPa. They found that numerous mineral surfaces increased reaction rates by around two orders of magnitude. Additionally, the sodium acetate form was found to decarboxylate more rapidly than the acid form.

#### 2.4. Reactions of proteins and amino acids

**2.4.1. Protein depolymerization.** Amino acids, the building blocks of proteins, have high commercial value (for use in feed, food, pharmaceuticals and cosmetics) relative to most other fractions of biomass. Therefore, a number of researchers<sup>128–131</sup> have explored the potential of hydrothermal technologies to extract amino acids from various protein-rich feedstocks, particularly marine waste in Japan. The structural bond that links amino acids together into proteins is the peptide bond, which is a C–N bond between the carboxyl and amine groups present in all amino acids. It is known that this bond will rapidly hydrolyze in hydrothermal systems. However, yields of amino acids are generally significantly lower than by conventional acid hydrolysis since amino acids produced by hydrothermal hydrolysis subsequently degrade. Most researchers have reported optimal yields at temperatures of around 250 °C; however, these yields are generally below about 10 wt%.

Some researchers have reported ways to enhance yields: Rogalinski *et al.* report that the yield of amino acids quadrupled with the addition of carbon dioxide<sup>129</sup>: at 250 °C, 25 MPa and 300 s residence time total amino acid yield increased from 3.7 to 15 wt%. Quitain<sup>130</sup> found that microwaves increased amino acid yields by an order of magnitude at 200 °C and 60 min, which increased their yield to about 12 wt%.

**2.4.2. Amino acid reactions.** The speculation that organic compounds, and possibly life itself, may have originated around hydrothermal vents on the ocean floor<sup>132</sup> prompted a spirited debate within the scientific community, which in part focuses on the stability limit of amino acids under these conditions, which is often around 250 °C in a pressurized liquid brine phase.

As such, a number of studies have examined the hydrothermal stability and reactions of amino acids. All amino acids have different chemical structures, and therefore react according to different pathways. However, all amino acids also have the same peptide backbone, and undergo similar decarboxylation and deamination reactions.

Klinger *et al.*<sup>133</sup> recently studied glycine and alanine, two of the simplest amino acids. They found the primary mechanisms of degradation of these amino acids to be decarboxylation and deamination. They found similar decomposition kinetics for these two compounds, with about 50% of their starting material degraded in 5–15 s in 350 °C water at 34 MPa. Both compounds had decomposition activation energies of about 160 kJ mol<sup>-1</sup>, which are similar to values reported earlier by Sato *et al.*<sup>134</sup> Klinger found no effect of pressure on the decomposition rate between 24 and 34 MPa at 300–350 °C.

Numerous other studies have studied many amino acids in hydrothermal systems. Li and Brill,<sup>135</sup> for example, report

decarboxylation kinetics for seven different amino acids at temperatures ranging from 310 to 330 °C.

#### 2.5. Formation of hydrocarbons and lipids from small organic materials

Recent work<sup>136,137</sup> has found that “Fischer–Tropsch-type” (FTT)† reactions can occur in hydrothermal systems, with water acting as the hydrogen source. In research focusing on the speculated origin of life at hydrothermal vents, McCollom *et al.*<sup>136</sup> were able to synthesize lipids of size C<sub>35</sub> or greater from formic acid or oxalic acid in hydrothermal systems. These reactions were studied on a longer time scale (2 to 3 days) than is industrially feasible for biomass conversion; they were able to produce *n*-alkanols, *n*-alkanoic acids, *n*-alkenes, *n*-alkanes and alkanones at temperatures of 175 °C in a stainless steel reactor. However, McCollom *et al.* did not report their pressure, and they likely had two phases present at these conditions in which the reaction could take place in either the liquid or the gas phase.

Meanwhile, Berndt *et al.*<sup>138</sup> and Holm and Charlou<sup>139</sup> saw the formation of smaller hydrocarbons, from methane to propane, in the presence of olivine without *any* organic feed. In their case, the only carbon source was CO<sub>2</sub>; the reducing power was supplied by the oxidation of Fe(II) to Fe(III). These experiments relied on olivine as a catalyst. However, subsequent research, involving radioactively labeled carbon, has cast doubt on the amount of hydrocarbons produced from CO<sub>2</sub> *versus* from reduced hydrocarbons already present in the olivine.<sup>200</sup>

### 3. Liquefaction in subcritical water

#### 3.1. “Bio-oil” and “bio-crude” production

Motivated by arguments about the biological origins of petroleum, researchers started proposing in the first half of the 20th century that renewable petroleum could be produced from biomass. In fact, Berl<sup>140</sup> suggested in 1944 that “cornstalks, corn cobs, sugar cane, bagasse, seaweed, algae, sawdust, Irish moss, molasses, sorghum, [and] grass” could be turned into a petroleum-like product, which he reported contained 60% of the starting material’s carbon and 75% of the starting material’s heating value. Berl used an alkaline solution of biomass in water at approximately 230 °C.<sup>141</sup>

Scattered research has continued since Berl’s time on the topic. The processes all produce a sort of viscous crude oil replacement, which has an important key difference from conventional crude oil: the oxygen content of the fuel is significantly higher, typically 10–20% in the “bio-crudes” *versus* < 1%<sup>142</sup> in conventional petroleum. The high oxygen content can impart a number of undesirable qualities to the oil product, such as lower energy content, poor thermal stability, lower volatility, higher corrosivity, and a tendency to polymerize.<sup>143,144</sup> This makes the bio-crudes generally unprocessable with current petroleum feedstocks—either they need to be burned directly as fuel oils, or

† FTT reactions derive their name from the Fischer–Tropsch reaction, which is the industrial catalytic synthesis of hydrocarbons from syngas (a mixture of CO and H<sub>2</sub>) that is traditionally used in gas- or coal-to-liquids processes.

they must be put through a deoxygenation process, as discussed in Section 3.1.1.

Elliott *et al.*<sup>145</sup> produced a review of hydrothermal liquefaction technologies developed in the 1983–1990 timeframe, and Demirbas<sup>146</sup> reviewed possible mechanisms of liquefaction. Additionally, a wealth of information on these processes exist in the books<sup>42–46</sup> produced as proceedings of the International Energy Agency's conferences on thermochemical biomass conversion.

A variety of liquefaction approaches exist in hydrothermal conditions. In general, hydrothermal liquefaction conditions range from 280 to 380 °C, 7 to 30 MPa with liquid water present, 10 to 60 min, often with catalysts present (which are generally alkaline), and sometimes with reducing gases such as CO and H<sub>2</sub>. The oil produced generally has a heating value of 30 to 36 MJ kg<sup>-1</sup> and an oxygen content of 10 to 20%. The biomass feedstocks used for liquefaction will typically have heating values of 10 to 20 MJ kg<sup>-1</sup> and oxygen contents of 30 to 50%, indicating that a significant amount of upgrading has resulted.

For comparison, bio-oils can also be made by “fast pyrolysis”, which occurs at atmospheric pressure under higher temperatures (~500 °C) with very short residence times (< 2 s). Oils from fast pyrolysis typically have much higher oxygen content and moisture, as compared to oils from hydrothermal liquefaction, and contain a large (75–80 wt%) proportion of polar organic compounds.<sup>147</sup> Table 3, modified from Elliott and Schiefelbein,<sup>148</sup> compares the elemental composition, moisture content, and heating values of sample oils from the two methods. Oils produced from hydrothermal liquefaction typically have more desirable quantities than fast pyrolysis oils and can be made with higher energetic efficiency (by avoiding evaporating water); however, fast pyrolysis oils have the advantage of short residence times and lower capital costs.

While hydrothermal liquefaction is able to create a lower-oxygen oil than fast pyrolysis, part of the oxygen, as well as part of the heating content of the feedstock, exists as small organic compounds that partition into the aqueous phase. (In fast pyrolysis, there generally is no aqueous phase; the water initially present as moisture as well as that formed by reactions either evaporates in the high-temperature process, or is miscible in the final oil product, which contains ~25 wt% moisture.) For example, Goudriaan *et al.*<sup>149</sup> report oxygen partitioning, as well as partitioning of mass and heating value (relative to that of the feedstock) amongst the oil, aqueous, and gaseous phases for the hydrothermal liquefaction of sugar beet pulp. This is

**Table 3** Comparison of sample bio-oils produced from hydrothermal liquefaction and from fast-pyrolysis. Adapted from Elliott and Schiefelbein.<sup>148</sup> The heating content provided is the higher heating value (HHV)

	Hydrothermal liquefaction	Fast pyrolysis
Moisture (wt%)	5	25
Elemental analysis (dry basis, wt%)		
C	77	58
H	8	6
O	12	36
Heating content (MJ kg <sup>-1</sup> )	35.7	22.6
Viscosity (cps)	15 000 @ 61 °C	59 @ 40 °C

**Table 4** Partitioning of heating content, oxygen, and mass amongst the products for the hydrothermal liquefaction of sugar beet pulp at 300–360 °C, 100–180 bar and 5–20 min. Adapted from Goudriaan.<sup>149</sup> All balances are defined as the mass (or heating value) in each product divided by the mass (or heating value) in the feedstock. Mass fraction is on a dry, ash-free basis

Product	Heating content balance	Oxygen balance	Mass balance
Bio-crude	79%	12–21%	41%
Aqueous organics	18%	9–20%	12%
H <sub>2</sub> O	—	31–40%	21%
CO <sub>2</sub>	—	35–40%	24%
Combustible gases	1.6%	—	1.5%

summarized in Table 4. In their experiments, about 79% of the feedstock's heating value is contained in the oil phase and 18% in the aqueous phase (with the remainder going to the gas phase and/or the enthalpy of reaction). Approximately 70% of the oxygen is removed as H<sub>2</sub>O and CO<sub>2</sub>, with about 15% remaining (organically bound) in both the oil phase and the aqueous phase.

The primary chemical goal of liquefaction is the removal of oxygen heteroatoms; as discussed in the introductory paragraphs of Section 2, this oxygen is preferentially removed as CO<sub>2</sub> or H<sub>2</sub>O, which themselves have no heating value, thus preserving as much of the feedstock's heating value as possible. Preferentially removing the oxygen as CO<sub>2</sub> may be desirable as this also has the advantage of increasing the H : C ratio, which can lead to a more desirable fuel product. However, as Dietersberger and Anderson<sup>150</sup> point out, supplementing biomass with an external hydrogen source (and removing oxygen as H<sub>2</sub>O) will yield a greater amount of biofuel per biomass input, with some of the fuel's energy content coming from the supplemental hydrogen stream.

Reducing gases (H<sub>2</sub> and CO) are often employed in liquefaction experiments, but their effect and necessity is unclear: early researchers thought it necessary to employ them, but Davis *et al.*<sup>151</sup> noted that in their system, “little or no reducing gas is consumed”. In their early experiments at the University of Illinois, He and coworkers determined that reducing gases were necessary, but in later experiments found similar results when reducing gases (CO or H<sub>2</sub>) or inert gases (CO<sub>2</sub>, N<sub>2</sub>) were used.<sup>152</sup>

Much of the pioneering liquefaction work was done by Appell and coworkers at the Pittsburgh Energy Research Center in the 1970s, which was later demonstrated at a pilot plant in Albany, Oregon. This process differed from most modern researchers' processes in that the high-pressure reaction took place in an oil-rich phase, rather than a water-rich phase. In their continuous process wood flour was heated to about 330 to 370 °C in the presence of ~5% Na<sub>2</sub>CO<sub>3</sub> catalyst, CO or H<sub>2</sub> reducing gas (3 to 6 mol kg<sup>-1</sup> wood), and water at a ratio of about 2.8 kg water per kg wood for residence times of 10 to 30 min (per pass). In order to have an oil-rich phase, a large amount of recycled oil product, at recycle ratios of ~19 : 1 was required for the process. Yields of 45 to 55% on a mass basis were achieved. (Note that, since feedstocks typically contain 40 to 45% oxygen and the oil may contain 10 to 15% oxygen, low mass yields are necessary.) Researchers at Lawrence Berkeley Laboratory pointed out that the high-pressure liquefaction could take place in a water-rich phase, rather than an oil-rich phase, which eliminated the need

for recycle but employed subsequent alkaline and acid treatments.<sup>151</sup> Both processes were demonstrated at the Albany, Oregon facility starting from the late 1970s, but research was halted by the US Department of Energy in the early 1980s as the price of petroleum began to drop and national interests shifted towards oxygenated fuel additives, such as ethanol. In all, Stevens reports that about 35 of barrels of bio-oil were produced at the Albany facility.<sup>151,153,154</sup>

In the 1980s, a liquefaction process known as “Hydrothermal Upgrading”, or the HTU process, was developed by Shell, but the oil company abandoned the process in 1988. The process development was resumed in 1997 by a Dutch consortium.<sup>149</sup> Biomass, generally lignocellulosic material (for example, onion peels), is heated to 330 to 350 °C under 10 to 18 MPa of pressure, for residence times of about 5 to 20 min. The resulting product is a water-insoluble heavy oil (“bio-crude”) with a heating value of 30 to 35 MJ kg<sup>-1</sup> and oxygen levels of around 10%. Fig. 15 shows a piece of wood being liquefied in water at 340 °C over 5 min in a sealed quartz capillary tube. Goudriaan *et al.*<sup>149</sup> report good preliminary results in subsequent conversion of the biocrude with hydrodeoxygenation and claim “scouting experiments have demonstrated that in this way a diesel fuel with excellent properties can be produced.”

At the University of Illinois, He and co-workers have worked to convert swine manure into oils *via* conversion at temperatures of 285 to 335 °C and pressures of 6.9 to 10.3 MPa.<sup>155</sup> The conversion was carried out at 20 wt% solids in a batch reactor with residence times of two hours. The produced oil was found to have heating values of approximately 35 MJ kg<sup>-1</sup> and to be made up of 71% carbon, 12% oxygen, 9% hydrogen, 4.1% nitrogen, 0.2% sulfur, and 3.4% ash.<sup>156</sup> They suggested that the high O : C and low H : C elemental ratios of the feedstock negatively affected the conversion, necessitating the use of a reducing gas, such as CO or H<sub>2</sub>. The oil yield, defined as the ratio of oil produced to volatile solids in the feed increased from 8% to 63% by the addition of a reducing gas, such as CO.<sup>155</sup> However, in a later paper,<sup>152</sup> the University of Illinois team found that a similarly high oil yield could be achieved with inert gases, such

as CO<sub>2</sub>, N<sub>2</sub>, or air; without clarifying the role of reducing gases in this liquefaction process.

Karagöz and co-workers at Okayama University (Japan) performed a number of studies exploring the effects of various parameters on the liquefaction of biomass. Their conditions were generally at 280 °C for 15 min. They performed carbon-number frequency tests on their oils, and found much of the oil had a carbon number of between 9 and 11.<sup>157</sup>

Researchers at the University of Arizona<sup>158</sup> employed a single-screw extruder as a means of generating high pressures and temperatures with biomass feedstocks with high solids contents. By using temperatures of 350 to 425 °C and pressures of up to 24 MPa, they generated pressure in the extruder and passed the reacting mixture through a high-pressure holding tube to increase the residence time; using CO as a reducing gas they produced oils with an oxygen content of less than 10% and an energy content of 36 MJ kg<sup>-1</sup>.

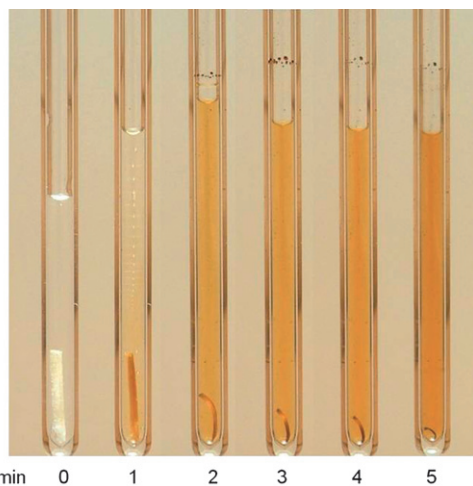
Minowa and colleagues<sup>159,160</sup> have explored liquefaction of a number of biomass feedstocks, from bagasse to coconut shells to model garbage, generally at conditions of 300 to 340 °C with Na<sub>2</sub>CO<sub>3</sub> catalyst and have reported yields of 27 to 60% (weight basis) of an oil with heating values of 33–37 MJ kg<sup>-1</sup> and ~12% oxygen.

Algae has long been proposed as an abundantly producible source of biomass. However, processing of algae into biofuels is not straightforward, and hydrothermal liquefaction may prove to be an efficient way of handling the algae, proposed as early as 1944 by Berl.<sup>140</sup> Dote *et al.*<sup>161</sup> liquefied a strain of micro-algae that contained 50% natural oils, and were able to produce a yield of 64% (mass basis) oil from this feedstock when processed at 300 °C with Na<sub>2</sub>CO<sub>3</sub> catalyst. Note that the yield is higher than the original oil content of the algae, suggesting that the hydrothermal process not only extracts the naturally occurring oils in the algae but also produces oils from the non-lipid components of the algal biomass.

### 3.2. Refinement of bio-oils into fuels

As noted earlier, the bio-oils produced by hydrothermal liquefaction processes are typically more viscous and higher in oxygen than conventional crude oil, although lower in oxygen than pyrolysis oils derived from flash pyrolysis.<sup>145</sup> Furimsky<sup>144</sup> and Elliott<sup>162</sup> have recently authored comprehensive reviews of technologies to upgrade biomass-derived oils; Elliott’s review focuses on hydrodeoxygenation technologies and processes, while Furimsky’s review focuses more on the underlying chemistry of hydrodeoxygenation. Processes utilized include hydro-treating and hydrocracking, often in the presence of a catalyst. Processes are typically similar for bio-oils derived from hydrothermal techniques as well as from atmospheric flash pyrolysis, although upgrading of oils produced in hydrothermal techniques may be more straightforward than for those produced by flash pyrolysis (as described in the previous section). Table 5 summarizes typical operating conditions, as summarized from the literature by Elliott, for hydrodeoxygenation of bio-oils.

These hydrodeoxygenation techniques are analogous to, but certainly not identical to, techniques for converting crude oil to fuels. Crude oil processing techniques typically focus on the removal of nitrogen and sulfur, as well as molecular-weight



**Fig. 15** Wood liquefying in water at 340 °C. Courtesy of Professor W. P. M. van Swaaij of the University of Twente; used with permission.



**Table 5** Typical operating conditions for hydrodeoxygenation tests with bio-oils. Liquid hourly space velocity and H<sub>2</sub> feed rate will vary with the amount of oxygen removed. Compiled from Elliott.<sup>162</sup>

Temperatures	250–400 °C
Pressures	10–18 MPa
Liquid hourly space velocity	0.1–0.8 (vol. bio-oil)/(vol. catalyst)/h
H <sub>2</sub> feed rate	100–700 (L H <sub>2</sub> )/(L bio-oil)
Catalyst active metals	CoO/MoO <sub>3</sub> , NiO/MoO <sub>3</sub> , NiO/WO <sub>2</sub> , Ni, Pt
Catalyst supports	Al <sub>2</sub> O <sub>3</sub> , γ-Al <sub>2</sub> O <sub>3</sub> , silica-alumina, Y-zeolite/Al <sub>2</sub> O <sub>3</sub>

reduction. In contrast, treatment of biomass-derived oils will typically be more focused on oxygen removal and molecular-weight reduction. A number of different catalyst materials are employed for hydrodeoxygenation, including nickel, cobalt, molybdenum, and platinum. Grange and Vanheuren<sup>163</sup> summarized many hydroprocessing catalysts in use for hydroprocessing in general, including hydrodesulfurization, hydrodenitrogenation, hydrodeoxygenation, and hydrodemetallisation. They also compared hydrodeoxygenation (HDO) of biomass (pyrolytic) oils to conventional petroleum hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and hydrocracking (HCK) techniques.

### 3.3. Hydrothermal liquefaction of food processing waste

A hydrothermal process that converts industrial wastes into fuels is being developed by Appel and coworkers at Changing World Technologies, Inc. (CWT). The first plant, located in Carthage, Missouri converts wastes (offal) from ConAgra's Butterball turkey production plant into diesel oil, fertilizer products and carbon.

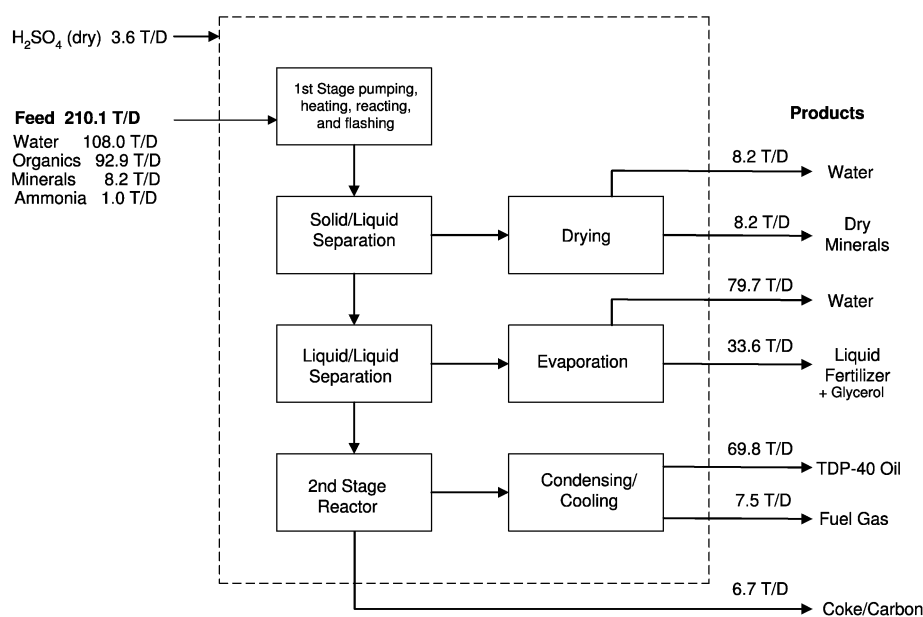
As seen in Table 1, the chemical structure of fatty acids is similar to the straight-chain hydrocarbons present in liquid transportation fuels, *e.g.*, gasoline and diesel oil. The main difference is the presence of the carboxyl group, as well as the

glycerol linkage of triacylglycerides. The fatty acids in many naturally occurring fats and oils, both vegetable and animal, often have chain lengths similar to those found in gasoline or diesel oil. Thus, if the carboxyl group could be eliminated a bio-based gasoline or diesel oil would result.<sup>164</sup>

The CWT process replaces the usual fat rendering practices that have been followed for decades to produce a range of by-products including animal feeds. Hydrothermal processing not only adds value to the wastes by producing fuel and fertilizer, it also eliminates the possibility of food chain accumulation of pathogens. It is also possible to incinerate this kind of organic waste, thereby recovering energy at the same time as eliminating the risk of spreading pathogens, but water content makes the offal a troublesome fuel.

The technology was first developed and tested in a pilot plant in Pennsylvania. A full-scale commercial plant has now been constructed to handle the turkey offal from a ConAgra Butterball turkey processing facility in Carthage, Missouri. The process is described by Roberts *et al.*<sup>164</sup> and Adams and Appel.<sup>165</sup> Interesting features of the process are that it handles a feed stream complex in composition and that there are no major waste streams from the process.

A process flow sheet, along with reported mass flow rates prepared by CWT is reproduced in Fig. 16. The process is divided into two main stages. In the first, hydrothermal stage the feed is macerated into slurry, then pressurized to about 4 MPa and heated to reaction temperature (200 to 300 °C). The solids are separated and the liquid is flashed to separate water. The non-aqueous phase is further processed by heat treatment in a second stage reactor (around 500 °C). Recovered from the first stage are a solid phase (minerals) and liquid phase (containing nitrogen), both possible to use for fertilizing purposes. From the second stage fuel gas, carbon and diesel oil are recovered. The fuel gas is used to meet internal process heat needs. The minerals, the liquid containing nitrogen, the carbon and the diesel oil are all marketable products. The oil is dominated by straight-chain



**Fig. 16** Process flow diagram with mass flow rates in tons per day, as reported by CWT. From Roberts *et al.*,<sup>164</sup> used with permission of CWT.

hydrocarbons with a chain length between 15 and 20, in the shorter range of conventional diesel oil.<sup>164</sup>

The environmental performance of the process, investigated using life-cycle assessment methodology based on CWT's released numbers, seems promising with low life-cycle emissions of greenhouse gases compared to those avoided by the use of the biofuel.<sup>166</sup> For these food processing wastes, it also seems promising compared to other thermochemical treatment possibilities.<sup>167</sup>

#### 4. Gasification in sub- and supercritical water

The pioneering work of Modell, first appearing in the 1970s, focused on using supercritical water (SCW) as a means to reform biomass into useful gaseous products.<sup>74,82,168–171</sup> His SCW proposal had the advantage of a rapid, direct route to gases including H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, and light hydrocarbons that was (mildly) exothermic and avoided char formation,<sup>82</sup> although these early experiments only produced low methane yields. Shortly after Modell's first set of supercritical water gasification (SCWG) publications appeared, several research groups began developing processes for biomass gasification in supercritical water. Over the last thirty years, research in hydrothermal gasification has fallen into three general categories based on target products: (1) hydrogen-rich gas *via* high temperature ( $T > 500$  °C) without catalysts or with non-metal catalysts (discussed in Section 4.1), (2) methane-rich gas *via* lower temperature (near-critical temperatures to  $\sim 500$  °C) with catalysts (discussed in Section 4.2), and (3) subcritical ( $T \ll T_c$ ) catalytic processing to a gaseous product (discussed in Section 4.2.3).

##### 4.1. High-temperature gasification to hydrogen

At temperatures in the vicinity of 600 °C in supercritical water, a H<sub>2</sub>-rich product gas can be formed from a variety of biomass

sources with near complete conversion of the biomass into gases. The carbon in the biomass primarily is converted into CO<sub>2</sub>. Most experimental studies have found that reaction temperatures (within the range of about 500 to 700 °C) will have a strong effect on yields and gas compositions, but pressure (at least for pressures above the critical pressure) has little effect on the extent of gasification or the composition. Studies have been conducted with and without catalysts; common catalysts include activated carbon and alkali salts.

A large proportion of the work in the field of high-temperature SCWG to hydrogen is attributed to five major research groups: Kruse, Dinjus, Boukis and others at Forschungszentrum Karlsruhe (FZK), Germany; van Swaaij and co-workers at the University of Twente, the Netherlands; Matsumura and co-workers at Hiroshima University, Japan; the State Key Laboratory of Multiphase Flow in Power Engineering of Xi'an Jiaotong University, China; and Antal and co-workers at the University of Hawaii. Table 6 lists the general operating conditions, feedstocks and reactor systems employed by these five groups. In the last five years, perhaps as a result of increased interest in biofuels, research in SCWG has seen significant growth. Results from these relatively new research groups are also included at the end of this section. For further discussions of high-temperature SCWG, the readers are referred to recent reviews by Matsumura *et al.*<sup>172</sup> and Calzavara *et al.*<sup>173</sup>

**University of Hawaii.** Professor Antal's group, which had previously studied steam gasification of biomass, added high-pressure pyrolysis and hydrolysis studies of biomass (and model compounds) starting around 1980.<sup>50,201–205</sup> While most of their earlier work with supercritical water focused on characterizing the complex chemical pathways encountered, Antal's research group began to examine supercritical gasification of glucose and wet biomass feedstocks in 1990.<sup>174</sup> These studies showed great

**Table 6** Selected high-temperature SCWG research groups

Research group	Feedstocks	$T/^\circ\text{C}$	$P/\text{MPa}$	Reactor system	Sample references
Antal, U. of Hawaii	<22 wt% wet biomass, sewage, corn starch, potato starch and wastes, wood sawdust, water hyacinth, cellulose, macadamia nut shell, sugar cane bagasse, glucose and other model compounds	$\sim 600$	22–34.5	Hastelloy & Inconel tubular reactors, capillary tube reactors, packed bed systems; catalysts: activated carbon and charcoal	174–180
Kruse, Dinjus and Boukis, FZK, Karlsruhe	1–5 wt% glucose, vanillin, glycine, sawdust, straw, cellulose, plants, meats, corn silage with ethanol and pyrolytic acid, pyrocatechol and phytomass, corn starch, clover grass, sewage sludge and lignin	400–700	25–50	Pilot plant, 2–4 min; batch, CSTR, tubular reactors; 60 s–1 h; alkali catalysts: KOH, K <sub>2</sub> CO <sub>3</sub> and KHCO <sub>3</sub>	181–187
van Swaaij, U. of Twente, Netherlands	Model compounds of 1–18 wt% formic acid, glucose, glycerol and pinewood	460–800	24–30	10–90 s, novel screening technique using fused-quartz capillary tubes (id = 1 mm); catalysts: alkali metal and Ru/TiO <sub>2</sub>	188–191
Matsumura, U. of Hiroshima, Japan	Sawdust, rice straw, cabbage; model compounds: cellulose, xylan, lignin reagents and glucose	<600	25	Pilot plant, hydrothermal pretreatment, partial oxidation (H <sub>2</sub> O <sub>2</sub> ), batch SS316 tubes, <20 min, fluidized bed reactors; catalysts: alkali metal, nickel and metal oxides	192–195
State Key Lab (Xi'an Jiaotong University, China)	Sawdust, rice straw, rice shell, wheat stalk, peanut shell, corn stalk, corn cob, sorghum stalk, CMC (carboxymethylcellulose), cellulose and glucose	600–800	25	Miniature plant and bench scale tubular reactors	196–199

promise by achieving >85% gasification of the carbon with virtually no char or tar formation. However, the yields of the gaseous products, (H<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub>, CO) were well shy of the equilibrium predictions, but interesting discoveries on the catalytic effect of the reactor walls triggered a more thorough investigation of catalytic reactions in the SCWG process.<sup>179</sup>

Starting in 1995, the Antal group showed that activated carbons and charcoal could completely gasify high concentrations (22 wt%) of glucose into a hydrogen-rich gas at 600 °C and 34.5 MPa. They examined a variety of activated carbons including spruce wood charcoal, macadamia shell charcoal, coal activated carbon and coconut shell activated carbon over a range of high temperatures (600–650 °C), supercritical pressures (22–34.5 MPa) and concentrated feeds (22 wt% and below). Although Antal and co-workers achieved complete gasification of their feeds to high hydrogen yields, they did experience deactivation of the carbon catalysts after several hours on stream. Gasification of the activated carbon itself was measured in one study, but the gas produced from the carbon catalysts was less than 3% of the gas produced from a concentrated glucose feed (1.2 M). These experiments were also plagued by plugging due to char from the biomass vapors and corrosion of nickel alloy reactors.<sup>175–178,206</sup>

**FZK.** Kruse and Dinjus at the Institut für Technische Chemie, Forschungszentrum Karlsruhe (FZK) in Germany formed a hydrothermal biomass research program centered on the fundamental aspects of reactions in supercritical water. Experimenting with real biomass waste and model compounds such as glucose and glycine, FZK researchers examined several parameters to investigate effects on yields of target gases like hydrogen and methane. They found that hydrogen yield was maximized at high temperatures and with the addition of alkali salts like KOH and K<sub>2</sub>CO<sub>3</sub>. Problems reported from their experiments include the observation of corrosion and low gas yields after conversion of protein-containing biomass.<sup>182,207–209</sup>

In the earliest reports of SCWG to come out of FZK, Schmieder *et al.*<sup>181</sup> and Kruse *et al.*<sup>210</sup> demonstrated complete gasification to primarily H<sub>2</sub> (and CO<sub>2</sub>) at 600 °C and 25 MPa from a range of feedstocks, employing batch and continuous tubular-flow reactors. The addition of potassium as KOH or K<sub>2</sub>CO<sub>3</sub> was found to drastically increase the yield of H<sub>2</sub>. Researchers at FZK have since reported experimental results from numerous batch, tubular and continuous stirred-tank reactor systems, including results for the gasification of zoomass (animal meat-containing biomass),<sup>182</sup> which was found to be more difficult to gasify than phytomass. The gasification difficulties were attributed to the presence of amino acids in the feedstock by experiments using model compounds, in which the presence of the amino acid alanine inhibited gasification.<sup>185</sup>

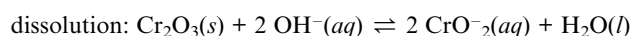
FZK has constructed a pilot-plant system, VERENA (a German acronym for the “Experimental facility for the exploitation of agricultural matter”).<sup>184</sup> VERENA, in operation since 2003, has a continuous flow capacity of 100 kg h<sup>-1</sup>, maximum temperature of 660 °C at 28 MPa and a maximum operating pressure of 35 MPa. VERENA has achieved gasification yields as high as 90–98% with feedstocks of 9–25 wt% ethanol, pyrolygineous acid and corn silage. While most results were very promising, the plant did experience some plugging of the preheaters after 3.5 h of operation. They suspected plugging was the result

of inorganic salts precipitating from the corn silage feed. Two significant improvements to VERENA have allowed successful operation for the planned 10 continuous hours. One improvement was limiting the pre-heating of the biomass-containing stream to temperatures below the critical point before entering the reactor, then heating to reaction temperatures (>500 °C) by mixing with a separate stream of supercritical water. The other improvement takes advantage of their down-flow reactor design which allows precipitating inorganic salts to accumulate at the bottom of the reactor, avoiding downstream plugging issues.<sup>211</sup>

Recently, D’Jesus *et al.*<sup>187,212</sup> examined the supercritical-water gasification of starch, clover grass, and corn silage. They used a continuous-flow reactor system in which the feed slurry was delivered through a pressurized piston, the opposite side of which was displaced by an HPLC pump that metered water. Similar to other experiments, pressure was found to have no major affect, but increasing temperature significantly increased the biomass conversion. The addition of potassium catalyst significantly improved the gasification of corn starch but had no significant effect on the gasification of clover grass and corn silage. The authors note that the latter two feedstocks contain naturally occurring potassium, which could be acting as a catalyst.

A significant portion of SCW research conducted at FZK includes the use of alkali salts to explore their catalytic effect. The observed catalytic effect of aqueous alkali salt solutions on the water-gas shift reaction has long been reported,<sup>213,214</sup> and researchers at FZK have made significant contributions to this body of knowledge.<sup>181,183,186,210</sup> While experimental evidence clearly shows a relationship between the addition of alkali salts and higher hydrogen yields, the mechanism is not well understood in SCW conditions.<sup>183</sup> The interaction of metal reactor walls with alkali salt solutions under SCW conditions further complicates our mechanistic understanding of the observed catalytic effect.

The evidence of corrosion products in several SCWG experiments with alkali salts (for example, Kruse *et al.*<sup>210</sup>) supports a theory that this alkali environment may be dissolving the protective metal oxide layer on the reactor walls. If the outer metal oxide layer dissolves, it exposes fresh, temporarily reduced metal to SCW. The metal can quickly oxidize in the SCW, producing hydrogen according to the following example reactions:<sup>215,216</sup>



Recent experiments conducted in sealed quartz capillary tubes explored the effects of KOH and NaOH without the complicating influence of metal alloy reactor walls. Kersten *et al.*<sup>191</sup> reported the results of a few experiments showing that NaOH increased the hydrogen yield from 9.9 vol.% to 17–21 vol.% following the gasification of 17 wt% glucose at 600 °C, 30 MPa, and 60 s. While these initial experiments are insightful, more detailed studies are warranted to improve our understanding of alkali salt catalysis in the presence and absence of metal reactors.

**University of Twente.** Investigators at the University of Twente in the Netherlands began a university-based SCWG research

program in the late 1990s. Among their greatest contributions is a novel high-throughput capillary technique. Potic *et al.*<sup>190</sup> describe the construction of small sealed quartz capillaries (id = 1 mm) that can withstand severe temperatures (900 °C) and pressures (60 MPa). A great advantage of these reactors is the absence of metal surfaces, which have been shown to have a catalytic effect on many reactions of interest; in this way, truly catalyst-free experiments can be conducted and the effect of added catalysts can be separated from the effects of metal reactor walls. Kersten *et al.*<sup>191</sup> conducted over 700 experiments in these reactors to investigate the SCWG of glucose, glycerol and pine-wood. They observed that in the absence of catalyst, complete gasification was only possible at very low concentrations, below 2 wt%; the addition of a Ru/TiO<sub>2</sub> catalyst allowed glucose solutions of up to 17 wt% to be gasified. Kersten and co-workers showed that pressure had little effect on yields. In some experiments, Inconel (a common material of construction for supercritical-water experiments) powder was added and found to have a dramatic effect, increasing the gasification of a 5 wt% glucose solution, emphasizing the catalytic effect that reactor walls may have in supercritical water experiments.

**Hiroshima University.** Following his work in Antal's group at the University of Hawaii, Matsumura began an aggressive biomass gasification research program in Japan which now resides at the University of Hiroshima. Matsumura leads a growing effort in Japan focused on uniting various researchers in Japan and internationally to enable faster progress in biomass conversion processing in supercritical water. Much of Matsumura's work has focused on lower temperature catalytic gasification and is addressed in the next section. He has been the lead author on two major biomass gasification reviews,<sup>41,172</sup> and his group has developed a novel hydrothermal pretreatment step to improve the ability to feed more concentrated biomass streams. Kato and Matsumura successfully fed cabbage through 1 mm tubing using pretreatment at 147–197 °C.<sup>192</sup> Subsequently, they incorporated this pretreatment step into an SCWG pilot plant which is now operating near the Hiroshima campus.

**State Key Lab, China.** Researchers at the State Key Laboratory of Multiphase Flow in Power Engineering (Xi'an Jiaotong University, China) have worked on SCWG since 1997 and published results of that work started to appear in international journals in 2002. State Key Lab employs several different reactor systems including a miniature plant with a movable-piston feed pump system to handle slurry feeds.<sup>198</sup> Their feedstocks consist of model compounds including glucose, carboxymethylcellulose, cellulose, lignin and xylan and raw materials like sawdust, rice straw, rice shell, wheat stalk, peanut shell, corn stalk, corn cob, and sorghum stalk, with typical operating conditions of 25 MPa pressure, 650 °C temperature, and 10 wt% feed. The authors found encouraging gasification efficiency, often >80% conversion of carbon, and high hydrogen yields for almost every feed except lignin, which appears to be the most challenging reactant to gasify.

**Additional investigations—high temperature SCWG.** Growing interest in SCWG has encouraged the formation of new research

groups who have made recent, significant contributions. The results from several of these groups are presented here.

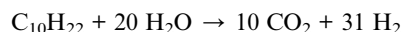
As a novel means to overcome some of the feeding issues in supercritical-water gasification, Penninger and co-workers<sup>217,218</sup> flash pyrolyze (see Section 3) their feed, which consists of beechwood sawdust. In this way, the minerals are concentrated in the char produced and not fed to their reactor. They use the condensate of this reaction, which is now a liquid and easier to pump, to feed their supercritical-water reactor, made of Incoloy tubing operated at 600–650 °C and 28 MPa. They achieved gasification efficiencies in the range of about 60 to 80%, with H<sub>2</sub>, CH<sub>4</sub>, CO, and CO<sub>2</sub> as their major products. Under certain conditions, the carbon monoxide fraction of the gas was as high as 34.5%. Problems were encountered in their runs associated with tar build-up in their preheater exit.

Williams and Onwudili of the University of Leeds used lower temperature (300–380 °C, with pressures of 9.5–22.5 MPa) batch reactor experiments to compare the gasification of glucose, starch, and cellulose. (Starch and cellulose are polymers of glucose monomers with different linkages between the glucose residues.) They found all of these compounds produced H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub> and lesser amounts of C<sub>2</sub>–C<sub>4</sub> hydrocarbons along with oils and char. Glucose was found to produce the highest amount of H<sub>2</sub>, while cellulose was found to produce the greatest amount of chars, carbon monoxide, and light hydrocarbons. They additionally gasified Cassava waste, and found it produced similar levels of char to the cellulose. In their experiments, they used hydrogen peroxide to partially oxidize the feed; the H<sub>2</sub>O<sub>2</sub> level was at about 36% of that needed to completely oxidize the feed.<sup>219</sup>

Hong and Spritzer,<sup>220,221</sup> of General Atomics, have developed a continuously operated reactor with a thermal sleeve (a corrosion-resistant sleeve inside of a pressure vessel) to study the supercritical-water partial oxidation (SWPO) of several feedstocks at 23.5 MPa, including corn starch, wood, coal, and municipal solid waste compost. By using partial oxidation, they avoid having to provide external heating to their process. In their first-phase experiments, they reported needing to supplement their feedstock with ethanol as a reductant in order to enhance this heating, caused by the problems of char/tar formation and their limited ability to pump wood slurries. They reported yields, in their “directly-heated” system, comparable to Antal's yields in their “indirectly-heated” system, after compensating for the heating differences. General Atomics completed a pilot-scale testing campaign, and projected that by using negative-cost waste streams that they would be able to produce H<sub>2</sub> at \$3 per GJ or less. No further testing took place after the 2005 report, as the U.S. Department of Energy shifted the focus of its hydrogen energy program.

Taylor *et al.*,<sup>222</sup> at Sandia National Laboratories, conducted several reforming experiments with primarily methanol, but also ethanol, ethylene glycol, acetone and diesel fuel, in supercritical water from 550 to 700 °C and 27.6 MPa in an Inconel 625 tubular flow reactor. With methanol feed concentrations of 15 to 45 wt% and 3 to 6 s residence time, a gas stream was produced containing 70 vol.% H<sub>2</sub>, 20 vol.% CO<sub>2</sub> and small amounts of CH<sub>4</sub> and CO. Feeds of ethanol and ethylene glycol produced less hydrogen (45% and 60% H<sub>2</sub> by composition, respectively) and more methane while feeds of acetone and diesel fuel resulted in reactor plugging and black deposits.

In related research on hydrocarbon reforming in SCW, Pinkwart *et al.*<sup>223</sup> recently reported the results of hydrocarbon reforming in SCW in the presence of 4 different commercial steam reforming catalysts (1–45 wt% NiO, various Mg, K, Ca, Si binders on Al<sub>2</sub>O<sub>3</sub> supports). Their experiments included two different feedstocks, which were 10 vol.% of *n*-decane and 2.5–20 vol.% of diesel fuel, in a tubular flow reactor at 550 °C and 25 MPa. After 10 s residence time over a 32.4 wt% NiO catalyst, 80% of the *n*-decane feed was converted into a hydrogen-rich gas, yielding almost 4 moles of H<sub>2</sub> gas per mole of *n*-decane compared with 0.05 H<sub>2</sub> molar yield without catalyst. Although hydrogen yield was clearly higher with catalyst in almost all cases, the highest yield of 4 moles H<sub>2</sub>/mole of *n*-decane, or 13% yield, is well short of the stoichiometric goal of 31 moles of H<sub>2</sub> gas for complete reforming to CO<sub>2</sub> as given by the following reaction:



Reforming of diesel fuel required longer residence times to achieve the highest yields; for example, after 40 s, a hydrogen yield of 2 moles H<sub>2</sub> per mole diesel fuel was obtained with no evidence of coke formation. Unfortunately, Pinkwart and co-workers did not report any analysis of commercial catalyst stability and activity during their experiments.

#### 4.2. Moderate-temperature gasification to methane-rich gas

At the lower temperatures (~400 °C) that favor the production of methane in gasification reactions, catalysts are generally needed to achieve high gasification rates. Catalysts are used not only to increase the rate of a desired chemical reaction (activity), but also to steer the product distribution toward the desired one (selectivity). Since the catalyst will not influence the chemical equilibrium composition, increasing the rate of a gasification reaction with a catalyst is only useful if thermodynamics are favorable. However, a catalyst may still be useful in the case of unfavorable thermodynamics if it is not the goal to reach chemical equilibrium. Guo *et al.*<sup>198</sup> have calculated the equilibrium gas composition for the system of 5 wt% biomass (for wood sawdust, with formula CH<sub>1.35</sub>H<sub>0.617</sub>) and 95 wt% water, calculated for a pressure of 25 MPa; see Fig. 17.

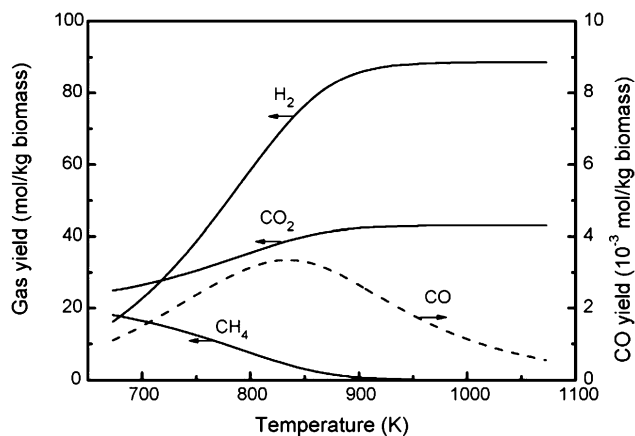


Fig. 17 Predicted equilibrium gas yields for gasification of 5 wt% wood sawdust at 25 MPa. From Guo *et al.*<sup>198</sup> Used with permission.

Although Fig. 17 predicts the equilibrium for a range of temperatures, in practice it is not possible to obtain a gas composition close to the thermodynamic equilibrium for temperatures below 600 °C without using catalysts. The reasons are as follows:

1. Decomposition of glucose yields reactive intermediates such as 5-HMF which can form polymeric materials of very low reactivity; see Section 2.

2. Methane may be formed by decarboxylation of acetic acid or by decarbonylation of acetaldehyde (“primary methane”), or by the hydrogenation of CO and/or CO<sub>2</sub> (“secondary methane”). Since in particular the hydrogenation reactions are very slow in the absence of a catalyst, the methane concentration will usually remain well below the equilibrium value.

3. Some organic intermediates will form solid coke (char), which, although not being a thermodynamically stable product, has a very low reactivity at these temperatures.

Also, performing a truly non-catalytic experiment in supercritical water media is complicated by a number of factors:

1. Reactor walls may act as heterogeneous catalysts.

2. Alkali salts present in real biomass may act as homogeneous catalysts.

3. Corrosion products from the reactor (transition metal ions such as Ni, Fe, Cr) may act as catalysts.

Catalytic gasification at moderate temperatures (below ~500 °C) has been studied by several researchers with a primary objective to produce either a gas with a medium calorific value (*i.e.*, methane-rich) or to produce hydrogen. At temperatures below 500 °C catalytic effects of reactor walls generally become less important, and the product distribution is affected mainly by the added catalyst. However, baseline experiments without added catalyst should always be conducted to check the validity of this assumption. For methanol reforming to hydrogen in supercritical water at 600 °C, 25 MPa, and 1.1 min residence time, Boukis *et al.*<sup>224</sup> saw their conversion increase from ~86% for a new Inconel 625 reactor to ~99.9% for the same reactor that had been conditioned with H<sub>2</sub>O<sub>2</sub>, which produced measurable changes to the elemental distribution and the roughness of the inner surface of the reactor. For a slurry of 10 wt% wood sawdust (spruce), Waldner<sup>225</sup> reported a baseline conversion to gases§ of about 21% at 409 °C in the absence of a catalyst. For cellulose, Minowa and coworkers<sup>226</sup> found only about 10% carbon conversion to gases at 350 °C and 60 min residence time. 67% of the feed carbon was recovered as char, 5% as oil and 13% dissolved in the aqueous phase.

The general agreement on how catalysts achieve complete conversion of the biomass feed is centered on the catalyst’s ability to gasify reactive intermediates that are rapidly formed from the feed molecules by hydrolysis and dehydration. The gasification step must also be fast enough to avoid the formation of polymeric materials and eventually char. Some researchers call these reactive intermediates collectively “water soluble products”.<sup>227–229</sup> These water-soluble products can react *via* two competing pathways, the first one leading to gaseous products (CO, CO<sub>2</sub>, H<sub>2</sub>), and the second one to oils and finally char.<sup>228</sup> Reactive

§ Carbon in all gaseous products (CO<sub>2</sub>, CH<sub>4</sub>, CO) to total carbon in the feed.

intermediates that are water-soluble have been identified to be mainly phenols and furfurals.<sup>182,209,225,230–233</sup>

A good catalyst will achieve fast C–C bond rupture, especially for opening aromatic rings (phenols), and at the same time will dissociate H<sub>2</sub>O to yield reactive O and OH radicals on the catalyst surface. These radicals will then combine with the adsorbed C<sub>x</sub>H<sub>y</sub>O<sub>z</sub> fragments, and finally release CO and CO<sub>2</sub>. The adsorbed hydrogen atoms from water splitting and from the cleaved C<sub>x</sub>H<sub>y</sub>O<sub>z</sub> fragments will combine to form H<sub>2</sub>. These are the “minimum” mechanistic features that a good gasification catalyst must exhibit. “Optional” features are a fast equilibration of the water–gas shift reaction, and the hydrogenation of CO and CO<sub>2</sub> to CH<sub>4</sub> and H<sub>2</sub>O. Depending on the selected catalysts, a hydrothermal gasification process will thus yield either a hydrogen-rich or a methane-rich gas.

A more detailed discussion of catalysis in a hydrothermal environment for the production of methane from biomass can be found in Vogel,<sup>234</sup> see also recent reviews by Matsumura *et al.*,<sup>172</sup> Osada *et al.*,<sup>235</sup> and Elliott.<sup>288</sup> Table 7 summarizes research performed with biomass and model compounds in a hydrothermal environment using heterogeneous catalysts up to 500 °C. In the three subsections that follow, we summarize research in the United States, Japan, and Europe.

**United States.** Modell, Reid and Amin<sup>82,170</sup> were the first to report, in 1978, that wood could be gasified in supercritical water without the formation of tars and char, but the conversion to gaseous products was low. The MIT group also studied the effect of adding different catalysts (five different Ni/Al<sub>2</sub>O<sub>3</sub> catalysts, one Co/Mo catalyst, and one Pt/Al<sub>2</sub>O<sub>3</sub> catalyst) on the gasification of glucose, cellulose, hexanoic acid, and polyethylene. According to Modell,<sup>82</sup> the key for avoiding the formation of tars and char was the rapid introduction of the reactants into the hot pressurized water.

Pioneering work in the field of catalytic hydrothermal biomass gasification has been carried out by Elliott and co-workers starting in the 1980s at the Pacific Northwest National Laboratory and resulted in the TEES process (Thermochemical Environmental Energy System).<sup>236–244,272–275</sup> Typical TEES conditions are in the subcritical region (350 °C, 20 MPa), although the early publications list results at supercritical conditions as well. Several catalysts were examined and tested for long-term activity. Ruthenium, rhodium, and nickel proved to be active metal catalysts. Stable supports for these metals included ZrO<sub>2</sub> (monoclinic),  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> (rutile), and carbon. For most feedstocks, the product gas consisted of >50 vol.% CH<sub>4</sub>, 40–50 vol.% CO<sub>2</sub>, <10 vol.% H<sub>2</sub> and traces of higher hydrocarbons. For wood as feedstock, Sealock *et al.*<sup>273</sup> reported a maximum methane yield of 0.22 (g of CH<sub>4</sub>)/(g of wood) with 33 vol.% CH<sub>4</sub> in the product gas using a stirred batch autoclave with a stainless steel liner operated at 450 °C and 34 MPa for 150 min with Harshaw Ni as the catalyst. The TEES process has been tested with a number of actual biomass feedstocks including distillers’ dried grains and solubles (DDG&S), dairy manure, nylon wastewater, olive wash water, delactosed cheese whey, brewer’s spent grain and spent grain liquor. Nickel sintered rapidly but could be stabilized by doping with another metal.<sup>276,244</sup> Catalyst deactivation was observed when inorganic salts precipitated on the catalyst’s surface or when N- or S-compounds remained associated with the metal.<sup>243</sup>

**Japan.** Yoshida and co-workers<sup>195</sup> gasified lignin, cellulose, xylan, rice straw, and wood of unspecified origin in an unstirred stainless steel batch reactor at supercritical conditions (400 °C, 25 MPa, residence time 25 min) using 60%Ni/SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> as catalyst. They attained a methane yield of 0.112 (g of CH<sub>4</sub>)/(g of wood), with a methane volume fraction of 0.28 in the product gas. They also studied mixtures of cellulose and lignin at the same conditions. In another study performed at 400 °C, 26–29 MPa, and using the same Nickel catalyst, they showed that mixtures of lignin with cellulose or xylan resulted in lower gas and hydrogen yields than without lignin.<sup>111</sup> Yoshida and Oshima<sup>262</sup> proposed a sequential reaction system, consisting of a pyrolysis reactor, a partial oxidation reactor and a catalytic reactor (63%Ni/SiO<sub>2</sub>–MgO). When the residence times were optimized for each reactor, up to 96% of carbon gasification was attained at 400 °C and 25.7 MPa with glucose-lignin mixtures.

Arai’s group at Tohoku University conducted detailed studies with supported noble metal catalysts. Osada *et al.*<sup>116</sup> gasified organosolv lignin and cellulose at 400 °C using Ru/TiO<sub>2</sub> and Ni/Al<sub>2</sub>O<sub>3</sub> as catalysts. After 15 min with the Ru/TiO<sub>2</sub> catalyst only 31% of the carbon in the lignin was gasified, whereas for cellulose this value was 74%. Furthermore, with Ru/TiO<sub>2</sub> no char was formed. The nickel catalyst was much less active. In a follow-up study, they investigated several supported noble metal catalysts for the gasification of lignin and propyl phenols.<sup>113,115,245–247,277</sup> Their findings suggest a decomposition of the lignin to lower molecular weight products, such as alkylated phenols, and a catalytic gasification of these phenolics over the noble metal catalyst. Interestingly, only the first decomposition step was apparently affected by the water density. Higher water densities enhanced the decomposition of the lignin but did not influence the gasification of 4-propyl phenol. Turnover numbers (*i.e.*, moles converted per mole of surface sites) were determined from the moles of gasified carbon after 15 min of reaction time at 400 °C for all the catalysts tested. The highest value was obtained for the 2%Ru/TiO<sub>2</sub> catalyst, the lowest was for 17%Ni/Al<sub>2</sub>O<sub>3</sub>. Repeated experiments with the same used catalysts revealed that only Ru/TiO<sub>2</sub> was stable. Ru/C and Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> lost activity upon repeated use which was accompanied by a loss of specific surface area. The deactivating effect of different sulfur compounds (elemental sulfur, sulfuric acid, thiophene, 4-hydroxythiophenol, 4-methylthiophenol, 2-methyl-1-propanethiol) was investigated at 400 °C for different supported noble metal catalysts. Turnover frequencies (*i.e.*, moles converted per mole of surface site per time) based on carbon gasification rates were reduced to about 7–16% of the ones obtained without added sulfur compounds. Surprisingly, the rate of deactivation did not depend strongly on the type of the sulfur compound. A mechanistic study indicated that sulfur most likely blocks the sites necessary for C–C bond scission and for methanation but not for the water–gas shift reaction nor for the decomposition of C<sub>1</sub> compounds such as formaldehyde. Regeneration of a sulfur-poisoned Ru/TiO<sub>2</sub> catalyst by washing with sub- or supercritical water for several hours was successfully demonstrated.

Sato and co-workers tested 10% and 20%Ni/MgO catalysts for the gasification of organosolv lignin at 400 °C.<sup>114,245</sup> Upon reuse the catalyst proved not to be stable, documented by a decrease in methane concentration and total gas yield. The MgO was found to react to Mg(OH)<sub>2</sub> under these conditions.<sup>248</sup>

**Table 7** Summary of (heterogeneous) catalytic conversion of biomass and model compounds studied at hydrothermal conditions ( $T \leq 500$  °C). DAC: Diamond Anvil Cell; N.R.: not reported; MIBK: methyl isobutyl ketone; DDG&S: distillers' dried grains and solubles

Feedstock	Catalyst	$T/^\circ\text{C}$	$P/\text{MPa}$	Water density/ $\text{kg m}^{-3}$	Reactor	Reference
Glucose, cellulose, hexanoic acid and polyethylene	11–28%Ni/Al <sub>2</sub> O <sub>3</sub> , CoMo/Al <sub>2</sub> O <sub>3</sub> , 0.6%Pt/Al <sub>2</sub> O <sub>3</sub>	374	22.1	N.R.	Autoclave, stirred	82,170
Kelp, sunflowers, corn stover, water hyacinth, digestion effluent, napier grass, sorghum, potato waste, spent grain, grape pomace, anaerobic digestion sludge, black liquor, cellulose wood flour (Douglas fir) and peat	68%Ni/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	350–450	13.8–37.3	N.R.	Autoclave, stirred	236–238
<i>p</i> -Cresol	Various unsupported base metals ( <i>e.g.</i> , Cu, Co, Zn, Cr, W); various unsupported and supported nickel catalysts including powders, mesh, wires, skeletal; nickel nitrate; various commercial supported Ni catalysts; various supported commercial noble metal catalysts (Ru, Rh, Pt, Pd)	350	20	N.R.	Autoclave, stirred	239
Benzene, biphenyl, anthracene, polystyrene, hexane, pentadecane, eicosane, polyethylene, <i>p</i> -, <i>m</i> -, <i>o</i> -cresol, propylene glycol, ethanol, vinegar, CCl <sub>4</sub> , CHCl <sub>3</sub> , nylon wastewater, polyol wastewater and olive processing water	48%Ni/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	350	20	N.R.	Autoclave, stirred	240
<i>p</i> -Cresol, phenol, MIBK, CCl <sub>4</sub> , trichloroethylene, methanol, nylon wastewater, olive wash water, cheese whey, delactosed, brewer's spent grain, sucrose and propylene glycol	5%Ru/Al <sub>2</sub> O <sub>3</sub> , 5%Ru/ZrO <sub>2</sub> , 48%Ni/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> , BASF G1-80, 62% Ni/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> , Raney Ni	350–360	20–21	N.R.	Continuous fixed-bed, Carberry	241,242
Dairy manure and DDG&S	Ru/C	320–360	21	N.R.	Continuous fixed-bed	243
Phenol	BASF G1-80 (stabilized), 3%Ru/TiO <sub>2</sub> , 8%Ru/C	350	21	N.R.	Continuous fixed-bed	244
2-Isopropylphenol, 4-isopropylphenol, 2-propylphenol, 4-propylphenol, lignin (organosolv) and cellulose	2%Ru/TiO <sub>2</sub> , 5%Ru/C, 5%Ru/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> , 5%Rh/C, 5%Pt/C, 2%Pt/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> , 5%Pd/C, 5%Pd/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> , 17%Ni/Al <sub>2</sub> O <sub>3</sub>	400	N.R.	0.33	Batch, unstirred	115,116,245–247
Lignin (Organosolv)	10%Ni/MgO, 10%Co/MgO, 20%Ni, MgO	400	30–37	0.3	Batch, unstirred	112,114,248
Cellulose	Ni/Kieselguhr	400, 350	13, 18	N.R.	Autoclave, stirred	249–251
Cellulose	50%Ni/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> , Ni on different supports	200–350	4–22	N.R.	Autoclave, stirred	226–229

Table 7 (Contd.)

Feedstock	Catalyst	TPC	P/MPa	Water density/kg m <sup>-3</sup>	Reactor	Reference
Cellulose	65%Ni/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> , 5%Pd/Al <sub>2</sub> O <sub>3</sub> , 5%Pd/C, 5%Pd/CaCO <sub>3</sub> , 5%Pd/BaCO <sub>3</sub> , 5%Pd/ZrO <sub>2</sub> , 1%Pd/Al <sub>2</sub> O <sub>3</sub> , 5%Pt/Al <sub>2</sub> O <sub>3</sub> , 1%Pt/C, 10%Pt/C	350	16–20	N.R.	Autoclave, stirred	252
Coal leachate and phenol	47%Ni/C	200–350	20	N.R.	Continuous fixed-bed	253–256
Microalgae ( <i>Chlorella vulgaris</i> )	50%Ni/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	350	18	N.R.	Autoclave, stirred	257
Cellulose and glucose	Ni powder, 50%Ni/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	350	16.5	N.R.	DAC, Autoclave	258,259
Cellulose, polymers, naphthalene, dibenzofuran, carbazole and phenyl ether	RuO <sub>2</sub>	450	44	0.28	Autoclave, stirred	260
Cellulose, pulp, lignin, coal, waste paper and paper sludge	RuO <sub>2</sub> , Ni	450	44	N.R.	Batch, unstirred	261
Sawdust, lignin, cellulose, rice straw and xylan	60%Ni/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	400	25	0.17	Batch, unstirred	111,195
Glucose and lignin sulfonate	63%Ni/SiO <sub>2</sub> -MgO	400	25.7	N.R.	Continuous pyrolysis/partial oxidation/fixed-bed	262
Sawdust (spruce)	Skeletal Ni	300–410	12–34	N.R.	Batch, unstirred	225
Phenol, anisole, acetic acid, formic acid and ethanol	Skeletal Ni, skeletal Ni/Ru, 2%Ru/C	350–500	30	N.R.	Continuous fixed-bed	263,264
Sawdust (spruce) and ethanol	1%Ru/TiO <sub>2</sub> , 2%Ru/C (granular), 7%Ru/C (granular), 7%Ru/C (graphite), 5%Ru/C (powder), 3%Ru/C (extrudates), skeletal Co	400	30	N.R.	Batch, unstirred; continuous fixed-bed	234,264,265
Acetic acid, formaldehyde, 2-propanol and glucose	ZrO <sub>2</sub> , CeO <sub>2</sub> , MoO <sub>3</sub> , TiO <sub>2</sub>	400	25–40	0.17–0.52	Batch, unstirred	266–268
Cellulose and glucose	ZrO <sub>2</sub>	400, 440	N.R.	0.2, 0.35	Batch, unstirred	269
Lignin (Organosolv) and <i>n</i> -hexadecane	ZrO <sub>2</sub>	400	30, 40	0.35, 0.52	Batch, unstirred	270
Stearic acid	CeO <sub>2</sub> , Y <sub>2</sub> O <sub>3</sub> , ZrO <sub>2</sub>	400	25	0.17	Batch, unstirred	58
Glucose	Nano ZnO, ZnAl <sub>2</sub> O <sub>4</sub>	300	N.R.	N.R.	Batch	271
Glucose	Raney Ni	500	30	N.R.	Autoclave, tumbling	232
Cellulose and sawdust	Ru/C, Pd/C, nano (CeZr) <sub>x</sub> O <sub>2</sub> , nano CeO <sub>2</sub> , CeO <sub>2</sub> powder	500	27	N.R.	Autoclave, unstirred	196

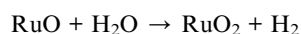
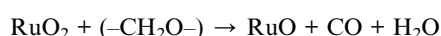


Minowa and co-workers<sup>252</sup> conducted extensive studies on cellulose gasification at 200–400 °C using nickel catalysts, later also using supported noble metals in a stirred autoclave. Sodium carbonate was found to increase the yield of gases in the presence of catalysts. The gas yield was also a strong function of the amount of Ni catalyst added. A simplified mechanism involving water-soluble intermediates that can either polymerize to oil and further to char or react to gases was consistent with the measured product distribution.<sup>226–229,249–251</sup> More recent work focused on the visualization of cellulose and glucose dissolution and gasification using a diamond anvil cell (DAC).<sup>258,259</sup>

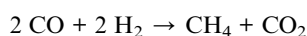
Minowa and Sawayama<sup>257</sup> have proposed a cyclic biomass gasification process based on cultivating microalgae that are further gasified hydrothermally. The effluent from the gasification containing the nutrients could be recycled to the algae. This concept was taken one step further in the self-sustaining biofuel vision SunCHem.<sup>278</sup> In this process, the nutrients are separated as a concentrated brine and recycled to the algae, together with the CO<sub>2</sub> separated from the product gas. Before gasifying the algae, valuable chemicals may be extracted.

Miura's group at Kyoto University prepared a catalyst with a high nickel content on a pyrolytic carbon support by impregnating an ion exchange resin with a nickel salt and treating the dried solid in a nitrogen atmosphere at 500 °C. This catalyst was used at 350 °C and 20 MPa for gasifying organics leached from coal as well as for gasifying model compounds.<sup>253</sup> No sintering was observed after 100 h on stream for the catalyst prepared at 500 °C, but sintering occurred before 100 h for carbonization temperatures in the range of 600 to 800 °C.<sup>254–256</sup>

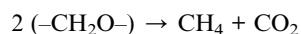
Park and Tomiyasu<sup>260</sup> have used unsupported RuO<sub>2</sub> as catalyst at 450 °C and 44 MPa. They were able to gasify cellulose, several polymers and model compounds. Experiments carried out with D<sub>2</sub>O enabled them to devise a reaction mechanism involving a redox cycle between Ru(IV) and Ru(II). With (–CH<sub>2</sub>O–) as proxy for biomass, their mechanism for the gasification step can be written as follows:



They postulated that CO and H<sub>2</sub> would then further react to form methane and CO<sub>2</sub> according to:



The net reaction would result in:



Later, the same group reported using RuO<sub>2</sub> to gasify pulp, lignin, coal, waste paper, and paper sludge.<sup>261</sup>

Watanabe and co-workers at Tohoku University<sup>266,269,267,268,58</sup> studied the effect of metal oxides such as zirconia, ceria, titania, and molybdenum oxide on the decomposition of acetic acid, formaldehyde, glucose, cellulose, and lignin at 400–440 °C in a batch reactor. In some experiments KOH or NaOH was added. Besides CO<sub>2</sub>, acetone was found to be formed from acetic acid in the presence of zirconia. Methane was not formed when zirconia was present.<sup>266</sup> Zirconia also doubled the gasification efficiency

for glucose and cellulose.<sup>269</sup> In the decomposition of formaldehyde, CeO<sub>2</sub> and ZrO<sub>2</sub> produced more methanol than TiO<sub>2</sub> and MoO<sub>3</sub>, which could be correlated to the basicity of the metal oxide.<sup>267,268</sup> The partial oxidative gasification of *n*-hexadecane and lignin was studied at 400 °C using zirconia as catalyst.<sup>270</sup> The decarboxylation of stearic acid (C<sub>17</sub>H<sub>35</sub>COOH) was enhanced by ZrO<sub>2</sub> in supercritical water at 400 °C and 25 MPa.<sup>58</sup> The same group also studied ZnO and ZnAl<sub>2</sub>O<sub>4</sub> nanoparticles as gasification catalysts for glucose at 300 °C with limited success.<sup>271</sup>

Hao *et al.*<sup>196</sup> studied the gasification of cellulose and sawdust in supercritical water at 500 °C and 27 MPa using Ru and Pd supported on carbon as well as cerium oxides prepared by different methods. The Ru/C catalyst exhibited a superior activity compared to Pd/C and ceria.

**Europe.** Sinag *et al.* at FZK (Forschungszentrum Karlsruhe, Germany)<sup>232</sup> investigated the influence of Raney Nickel on the degradation chemistry of glucose in supercritical water at 500 °C and 30 MPa in a tumbling autoclave. The yield of both intermediates, phenols and furfurals, was decreased, and the gas yield increased by the presence of the catalyst.

In work at the Paul Scherrer Institut in Switzerland, Vogel and co-workers have demonstrated that complete conversion of spruce sawdust can be achieved without forming tars or char if a sufficiently active catalyst is used. Waldner and Vogel<sup>225</sup> gasified spruce sawdust slurries with feed concentrations up to 30 wt% around 400 °C in a batch reactor, reaching a methane yield corresponding to the chemical equilibrium. Using fused quartz capillaries, Vogel *et al.*<sup>263</sup> visualized the onset of gas formation from a spruce slurry using Raney nickel as catalyst. The temperature at which gasification starts was determined by Waldner<sup>265</sup> to be around 250 °C independent of the heating rate, using a pressure differential approach from two batch experiments, one being a blank run. Several catalysts were screened for their activity and selectivity in batch experiments with spruce sawdust. From the most promising ones, Raney nickel, 1%Ru/TiO<sub>2</sub>, and 2%Ru/C were further tested for their long-term stability in a continuous catalyst test rig. A mixture of five organic compounds, representing hydrolyzed wood, was used as feed solution. Raney nickel sintered after a short time, even as a Ru-doped variant, whereas 1%Ru/TiO<sub>2</sub> was not active enough. 2%Ru/C was hydrothermally stable for more than 200 h on stream at 400 °C and 30 MPa with space velocities of 1.6 up to 33 g<sub>organics</sub>/g<sub>cat</sub>/h. The addition of small amounts of sodium sulfate (corresponding to 8 ppm of sulfate at the entrance to the reactor) were found to deactivate the catalyst gradually. This deactivation could be explained by an irreversible bonding of the sulfate anion to surface ruthenium, probably Ru(II) or Ru(III), considering the mechanism proposed by Park and Tomiyasu.<sup>260</sup> However, sulfate might not be the actual poison under reaction conditions as it may be reduced to sulfide at these conditions.<sup>234,264</sup>

**4.2.1. Scalability of batch reactor experiments to continuous process designs.** As documented by Table 7, most experimental investigations for the catalytic SCWG of biomass and model compounds have been performed in stirred or unstirred batch reactors. These reactors enjoy a relatively simple handling and a versatility regarding the feed, especially for solids-containing feedstocks that are very difficult to pump at high pressures and low flow rates. For full-scale applications, a continuous process

design is required, as batch processes cannot provide viable economics for this type of process. There are several issues that must be carefully evaluated when using results from batch experiments to design a continuous process. One important issue concerning tar and coke formation is discussed in some detail in the following.

For batch reactor experiments with the catalyst premixed with the feedstock, Waldner<sup>265</sup> has shown that the catalyst must be active as low as about 250 °C to avoid secondary reactions of the organic intermediates to form tars and coke. In batch experiments starting with the feed mixture including the catalyst, tar and coke formation is only observed for catalysts of insufficient activity. In a continuous process design with a preheater and a catalytic gasification reactor connected in series, tar and coke formation may be observed even if a very active gasification catalyst is used because, once formed in the preheater, the tars and char exhibit very low reactivities at temperatures <500 °C. For such a continuous process design, the reaction severity (a function of temperature and residence time) in the absence of a gasification catalyst must thus be minimized in order to avoid tar and coke formation. For this reason, batch experiments with the catalyst premixed with the feedstock are only of limited use for assessing the coke formation potential of a certain feedstock. One possibility for overcoming this experimental limitation is to heat up the feed mixture without the catalyst, preferably applying the same temperature-time trajectory as in the preheater of the continuous process, and rapidly introducing the catalyst into the batch reactor after the heat up time. Vogel *et al.*<sup>263</sup> have shown, using a variant of this procedure, that spruce sawdust can also be gasified completely in a sequential non-catalytic batch heat up and catalytic gasification experiment. In this sense, detailed knowledge of the liquefaction chemistry, as reviewed in Sections 2 and 3, is critical for properly designing a continuous catalytic gasification process that avoids tar and char formation.

#### 4.2.2. Summary of moderate-temperature gasification.

- Solid lignocellulosic biomass (*e.g.*, wood sawdust) can be completely gasified to a methane-rich gas around 400 °C and 30 MPa in a hydrothermal environment if a suitable catalyst is used. This temperature is much lower than conventional atmospheric gasifiers which are operated at 800 to 900 °C.

- Active heterogeneous catalysts include supported noble metals such as Ru, Rh, Pt (but low loadings are needed to keep costs affordable), skeletal Ni, supported Ni (high loadings > ~45 wt% are needed), and unsupported noble metal oxides (*e.g.*, RuO<sub>2</sub>). The choice of the support is crucial as only few materials are stable at hydrothermal conditions.

- Unpromoted Ni will sinter rapidly and deactivate. An exception seems to be the 47% Ni on pyrolytic carbon used by Miura's group. Useful—meaning active, selective, and stable—catalysts that have been tested for several days at  $T \leq 500$  °C with clean (salt-free) feedstocks include 2% and 8% Ru/C, promoted BASF G1-80 (supported Ni), 3% Ru/TiO<sub>2</sub> (rutile), and 47% Ni/C.

- Some inorganic salts, present in the biomass or formed from organically bound N, S, and P during hydrolysis, will form scale in heat exchangers and reactors and lead to corrosion, as well as poison catalysts. Studies on catalyst stability using model compounds should therefore also include runs with solutions of model compounds and inorganic salts.

- Sulfur poisoning is a major concern in SCWG. In contrast to gas-phase steam reforming conditions, the exact sulfur species and deactivation mechanism under hydrothermal conditions has not yet been elucidated.

- For the gasification of low molecular-weight organic compounds, as produced during hydrolysis, a surface redox mechanism involving two oxidations states of the metal has been suggested and is consistent with experimental findings.

**4.2.3. Lower-temperature gasification via catalysis of glucose and reduced organics.** Researchers at the University of Wisconsin have produced hydrogen from small organic molecules, such as glucose and sorbitol, in liquid water at 225 to 265 °C and 2.9 to 5.6 MPa using a platinum-based catalyst.<sup>279</sup> They were able to produce H<sub>2</sub> from glucose with up to 84% conversion (based on carbon; 84% of the carbon in the feedstock ended up in the product gases) and a 36% selectivity to H<sub>2</sub> at 265 °C and 5.6 MPa, and were able to produce H<sub>2</sub> from more reduced compounds, such as methanol and ethylene glycol, with greater than 90% conversion and selectivity towards hydrogen.

In subsequent work, Huber *et al.*<sup>280</sup> was able to achieve similar gasification with only a Raney nickel/tin catalyst, which is much less expensive than platinum-based catalysts. However, Huber and co-workers were only successful in gasifying relatively reduced simple organic compounds, such as ethylene glycol, glycerol, and sorbitol, and did not report being able to gasify glucose.

This work provided a significant breakthrough in hydrothermally producing hydrogen at much lower temperatures than in previous studies. However, the researchers only report successful studies with pure species (not mixed biomass streams), had greater success with more reduced compounds such as methanol than with glucose, and had greater success at dilute feed concentrations (~1 wt%) than at more concentrated (~10 wt%) conditions.<sup>281</sup>

## 5. Recovery of inorganic components

Biomass consists of a mixture of organic and inorganic species: elementally, biomass is composed of carbon, hydrogen, oxygen, nitrogen, phosphorus, sulfur, potassium, sodium and a number of other elements, most of which exist as either heteroatoms with the carbon or as ions. Only the carbon and hydrogen are of use as fuels. However, many of the other elements (particularly nitrogen, phosphorus and potassium) have a high commercial and environmental value if they can be recovered in biologically available forms for use as fertilizer.

The major components of fertilizer are chemical compounds of nitrogen, phosphorus, and potassium (the so-called N-P-K fertilizers). Nitrogen is biologically available in the form of ammonia (NH<sub>4</sub><sup>+</sup>) and to a lesser extent nitrate (NO<sub>3</sub><sup>-</sup>). Phosphorus is biologically available in the form of phosphate (PO<sub>4</sub><sup>3-</sup>). Potassium is biologically available in its ionic form, K<sup>+</sup> (associated with an anion such as chloride, sulfate, or nitrate).<sup>282</sup>

The fertilizer industry is very energy and natural resource intensive. Phosphorus itself is mined, and is a finite resource. Although most nitrogen-based fertilizers are manufactured from nitrogen gas in the air, the overall industry is extremely natural gas intensive. Most nitrogen fertilizer is derived from, or applied

**Table 8** Ionic constituents of Swiss swine manure solids as measured with ion chromatography after Soxhlet extraction. Concentrations are given in mg kg<sup>-1</sup> on a dry basis. ND = not detected. From Peterson *et al.*<sup>283</sup>

Cation	mg kg <sup>-1</sup>	Anion	mg kg <sup>-1</sup>
NH <sub>4</sub> <sup>+</sup>	47 000	PO <sub>4</sub> <sup>3-</sup>	67 000
K <sup>+</sup>	9100	NO <sub>3</sub> <sup>-</sup>	21 000
Na <sup>+</sup>	6700	SO <sub>4</sub> <sup>2-</sup>	11 000
Mg <sup>2+</sup>	3800	Cl <sup>-</sup>	5500
Ca <sup>2+</sup>	2700	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	1600
		(COO) <sub>2</sub> <sup>2-</sup>	1200
		F <sup>-</sup>	38
		C <sub>2</sub> H <sub>5</sub> COO <sup>-</sup>	30
		CH <sub>3</sub> COO <sup>-</sup>	ND

directly as, anhydrous ammonia (NH<sub>3</sub>) which is made by the well-known Haber–Bosch process. This process reacts atmospheric N<sub>2</sub> with H<sub>2</sub> to form NH<sub>3</sub>; the H<sub>2</sub> in turn is typically produced from natural gas (CH<sub>4</sub>) *via* steam reforming and the water–gas shift reaction. When running at stoichiometric efficiency, 3/8 of a mole of CH<sub>4</sub> is consumed to produce each mole of ammonia, and the overall methane-to-ammonia reaction is endothermic ( $\Delta H_{\text{rxn}} = 16 \text{ kJ mol}^{-1} \text{ NH}_3$  at standard conditions, not counting the heat of vaporization of water), which generally requires the consumption of more fossil fuels for heating needs. A recent study<sup>1</sup> found that on average, in the US, 51 MJ of energy is required per kilogram of NH<sub>3</sub> produced.

Many biomass feedstocks contain large amounts of potential fertilizers. For example, Table 8 shows the inorganic species present in a manure considered for gasification at the Paul Scherrer Institut. Other ions can be formed from hydrothermal reactions of heteroatomic species in the biomass. If the inorganic species of biomass can be recovered as fertilizers, potential environmental and economic gains can be realized from these processes. Many of these species occur as ions (NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, K<sup>+</sup>, PO<sub>4</sub><sup>3-</sup>, *etc.*), which can lose their solubility in supercritical water as discussed in Section 1.2. If these ions can be precipitated out and recovered in hydrothermal processes,<sup>283</sup> then fertilizers can be recovered in addition to the biofuels.

## 6. Critical issues and research needs

While hydrothermal technologies have many potential benefits over conventional methods of processing biomass to useful fuels, the fact remains that these technologies are not being widely commercialized today. Part of this is due to the high pressures needed for processing which requires special reactor and separator designs and the capital investments needed for full-scale plants. There are still a number of other critical issues hindering commercialization that need to be resolved so that the technologies can be piloted and ultimately scaled up. These include:

### 1. Solids loading

The “rule of thumb” employed by most knowledgeable workers acknowledges the need for solids loading in excess of 15–20 wt% in order to achieve practical economies. At lower concentrations, the associated capital costs of the heat exchangers, the heat losses, and the pumping expenses for moving all of that water

through the plant can create economic barriers. Sometimes, spectacular findings can be announced involving high conversions at low feed concentrations; if these results are not scaleable to higher concentrations, they are of little commercial value.

### 2. The feedstock and impurities

Many hydrothermal processes work well on “clean” lignocellulosic feedstocks, and are proven for substances such as ground wood, which is a significant advantage over conventional biofuels processes. However, the truly low-cost feedstocks are mixed waste streams, which can include manures, sewage sludges, and other feedstocks which will often contain high levels of impurities, including inorganics. Under these conditions, the handling of the impurities becomes crucial: the ionic species can create massive problems by precipitating out, clogging reactors and plugging catalyst pores.<sup>34,35</sup> However, the inorganics provide the opportunity to produce a valuable fertilizer by-product of the process if managed properly.

### 3. Heat transfer and recovery

Hydrothermal technologies operate at high temperatures, and have severe heating requirements to reach these temperatures, although these are lower than the heating requirements if the system were unpressurized (which would result in water vaporization). This emphasizes the importance of heat integration; that is, recovering the heat from the hot effluent stream to heat the incoming cold stream. Although Elliott *et al.*,<sup>241</sup> Boukis *et al.*,<sup>284</sup> and Nakamura *et al.*<sup>285</sup> have independently demonstrated and measured high heat exchanger efficiencies in their pilot plants, it will be important to continue to emphasize this factor in the large-scale design in order to achieve high efficiencies at commercial scales, particularly if fouling becomes pronounced.

### 4. The feeder

Feeding a mixture of 15 wt% wood sawdust, food wastes, sewage sludge or algae into a reactor operating above 22 MPa is challenging. These problems are particularly vexing at the laboratory scale, as it is difficult to find small pumps capable of high pressures (which will have small orifices) that can effectively pump high solids concentrations. Groups have solved this problem by a number of means, including using starch gels with cement pumps, pre-hydrolyzed feeds, solids-free feeds, or by pumping water against a piston containing the biomass slurry. Feeding pressurized slurries becomes less of a problem at full scale, however, as high-pressure slurry pumps start to become available for flow rate capacities of around 100 kg h<sup>-1</sup>.

### 5. Coking and deactivation of heterogeneous catalysts

Heterogeneous catalysts, those that are solids that remain in the reactor as the reacting solution flows past them, are prone to fouling and subsequent inactivation. Many researchers have demonstrated high yields of their desired products in batch or short-time continuous reactions. However, continuous or semi-continuous studies with long periods online often show significant declines in catalyst effectiveness. Coking is a serious issue with biomass streams, as is precipitation of inorganics, and fixing

of sulfate onto certain catalysts. Additionally, some catalyst supports will degrade or oxidize under hydrothermal conditions. Researchers are addressing these three issues, but they must be overcome to ensure continuous, long-term operation of a full-scale plant.

## 6. Recovery of homogeneous catalysts

Homogeneous catalysts, meaning those that are dissolved and fed into the reactor with the reactants such as KOH or H<sub>2</sub>SO<sub>4</sub>, offer the advantage of not suffering from coking and inactivation problems, as heterogeneous catalysts are prone to do. However, these catalysts must be recovered and reused at the end of the process in order to achieve an economic process.

## 7. Wall effects

Much research is conducted within Inconel and Hastelloy vessels, which are constructed of alloys with a high content of nickel. This nickel on the wall surface can act as an important catalyst on its own, and it is difficult to separate the wall effects of catalysis from the effects of the intended catalyst. This may ultimately lead to scale-up issues if not properly understood. This was shown to be an issue in supercritical-water oxidation (SCWO),<sup>286</sup> and has been reported by Boukis and co-workers<sup>224</sup> to occur in supercritical-water gasification (SCWG). Van Swaaij's group,<sup>191</sup> by using fused quartz capillaries, has reported that the water-gas shift reaction appears to be drastically enhanced in the presence of nickel-containing metal surfaces.

## Acknowledgements

We would like to thank Bill Peters, Greg Stephanopoulos, Bill Green, Curt Fischer, Daniel Klein-Marcusamer, Rory Monaghan and members of the Tester group from MIT; Larry Walker from Cornell; Robert Shaw from the Army Research Office; Brian Appel and Terry Adams from Changing World Technologies; Glenn Hong of General Atomics; Doug Elliott and Don Stevens from the Pacific Northwest National Laboratory; Phil Marrone from Science Applications International Corporation; Jeff Resch of General Mills; Peter Girguis of Harvard University; and Samuel Stucki from the Paul Scherrer Institut for discussions and insights into hydrothermal processing, fuels, and the chemistry and biology in the vicinity of oceanic hydrothermal vents. We acknowledge and appreciate partial funding support from the Society for Energy and Environmental Research (through the U.S. Department of Energy award DE-FG36-04GO14268; support by the DOE does not constitute endorsement by the DOE of the views expressed in this article), Shell Oil Company, the Paul Scherrer Institut, the Martin Foundation, the Knut and Alice Wallenberg Foundation, and the Coral Industries Endowment of the University of Hawaii.

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