

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

4,800

Open access books available

122,000

International authors and editors

135M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.

For more information visit www.intechopen.com



Gasification Kinetics in Continuous Supercritical Water Reactors

Brian Pinkard, John Kramlich, Per Reinhall and Igor Novosselov

Abstract

Supercritical water gasification (SCWG) is an emerging technology with synergistic applications in renewable energy and waste processing. Supercritical water (SCW) functions as a green reaction medium during the gasification process, serving to dissolve and decompose complex organic molecules via ionic, radical, hydrolysis, and pyrolysis reaction mechanisms. Researchers investigate the decomposition of model compounds in order to predict product yields and conversion efficiencies during the gasification of heterogeneous biomass waste, food waste, sewage sludge, and other available feedstocks. Continuous, laboratory-scale reactors are often employed to study reaction kinetics, pathways, and mechanisms. This chapter synthesizes previous work investigating model compound gasification in continuous supercritical water reactors (SCWRs). A summary of continuous reactor design strategies is presented for practical benefit, followed by a discussion on reaction chemistry in the supercritical water environment. Reaction pathways and mechanisms have been investigated for several model compounds, lending insight toward the conditions needed for the complete conversion of real-world feedstocks. Several studies assume first-order reaction kinetics and propose Arrhenius parameters for the decomposition reaction. The first-order rate assumption must be carefully evaluated, and the applicable temperature range must be specified. Opportunities for further research are discussed.

Keywords: supercritical water, gasification, chemical kinetics, reaction mechanisms, reaction modeling, model compounds

1. Introduction

Supercritical water (SCW) exhibits unique physiochemical properties beneficial for oxidation or gasification of organic (carbon-containing) compounds ranging from simple molecules to complex heterogeneous waste. Near the critical point (374°C, 22.1 MPa), water exists in a high-temperature, dense fluid phase with high concentrations of H^+ and OH^- ions. These conditions serve to facilitate enhanced ionic chemistry and acid-catalyzed reactions [1]. At temperatures above the critical point, the density, viscosity, and ion product of water drop significantly. In this high-temperature, low-density phase water exhibits superb mass transfer properties, and organic compounds become fully miscible and/or soluble [2]. However,

ionic reactions are no longer favored. Instead, pyrolysis, hydrolysis, and free radical reaction mechanisms dominate in this higher-temperature region. These two overlapping reaction regimes explain why SCW is of interest as a reaction medium for applications related to the thermochemical conversion of organic waste into heat and/or gaseous fuel.

An understanding of chemical reaction rates, pathways, and mechanisms involved in decomposing model compounds in SCW sheds important insight into the reaction chemistry of complex organic molecules in SCW. Interest in supercritical water gasification (SCWG) for industrial-scale applications is growing due to increased interest in generating low-cost “green” H₂ from renewable feedstocks. However, there are a number of technical barriers in developing large-scale plants; these include (i) controlling char formation, (ii) limiting salt precipitation which rapidly corrodes reactor components, (iii) identifying the optimal process parameters for high conversion efficiency (CE), (iv) identifying suitable gasification catalysts, and (v) designing an effective heat exchanger for waste heat recovery. Studies of model compounds can aid in addressing some of these challenges.

This chapter summarizes previous studies investigating reaction chemistry in continuous supercritical water reactors (SCWRs). Common reactor designs used to investigate reaction chemistry are discussed, enabling the researchers to replicate or to extend the knowledge of the previous studies. A synthesis of these studies yields important insights into common reaction mechanisms, pathways, and decomposition rates of certain compound classes. Opportunities for further investigations are described, and the practical value of these studies is highlighted.

2. Continuous supercritical water reactors for investigating reaction chemistry at the laboratory-scale

Achieving high temperatures and pressures, mitigating corrosion of reactor components, rapid heating and quenching of the reagent, acquiring accurate experimental data, and strategies for achieving a well-mixed, uniform flow must all be considered in the design of a supercritical water reactor for studies of reaction chemistry. Solutions for mitigating some of these challenges have been reported in the literature, but open questions remain regarding the best methods to mitigate char formation and salt precipitation in reactors designed to process complex feedstocks [3].

2.1 Batch vs. continuous reactors

Studies of reaction chemistry in SCW have been conducted using both batch and continuous reactors at the lab-scale. Batch reactors offer a unique opportunity to study reaction kinetics, mechanisms, and pathways of model compounds in the absence of a catalytic surface. The reactor can be constructed using a number of materials, including quartz capillaries and stainless steel tubing, which are filled with reactants and heated to reaction temperatures in a fluidized bath or electric furnace. Reactions occur at fixed conditions for the desired residence time, after which the reaction is quenched, and products are recovered for ex situ analysis. One limitation of batch reactors is that mass transfer (and, therefore, molecular interaction) is limited by molecular diffusion rates.

Continuous reactors are more complicated and expensive to fabricate. For industrial applications of chemical processes, a continuous setup is preferred over a batch setup. Process throughput is much higher, energy efficiency is significantly

improved, heat recovery can be utilized, and opportunities exist for in situ process monitoring and control.

Continuous SCWRs are nearly always manufactured from nickel-base alloys (e.g., Inconel 625, Hastelloy C-276), which offer excellent corrosion resistance and good material strength at high temperatures. However, it is important to mention that nickel-base alloys also provide a catalytic surface for gasification reactions. For this reason, reaction rate parameters determined using batch SCWRs are not applicable for continuous SCWRs. DiLeo and Savage demonstrated this by gasifying methanol with and without a nickel wire in a batch quartz capillary reactor. The nickel wire increased methanol conversion from 20% after 2 h to 90% after 5 min (both at 550°C) [4]. Continuous reactors can enhance the catalytic effect even further, especially in turbulent flow regimes.

It should be noted that the catalytic effects within continuous reactors are dependent on reactor geometry and “aging” of the reactor components. Smaller diameter reactors with high surface-to-volume ratios (S/V) show increased catalytic effects due to increased molecular interaction between the reagents and the reactor wall. Also, reactor aging leads to the decreased catalytic activity over time, due to the formation of carbon layers on the reactor wall, leaching of metals, sintering, catalytic deactivation, and other effects.

For these reasons, this section will primarily focus on common designs of continuous reactors at the lab-scale. A representative schematic of a continuous SCWR is provided in **Figure 1**.

2.2 Heating and pressurization

The most reliable way to achieve independent pressure and mass flow control in a continuous SCWR is to operate a constant flow rate pump(s) in series with a back pressure regulator (BPR). Spring-loaded or dome-loaded BPRs are simple to use and reliable [3, 5]. High-performance liquid chromatography (HPLC) pumps are often used for pumping liquid reagents to high pressures with precise flow rate control in

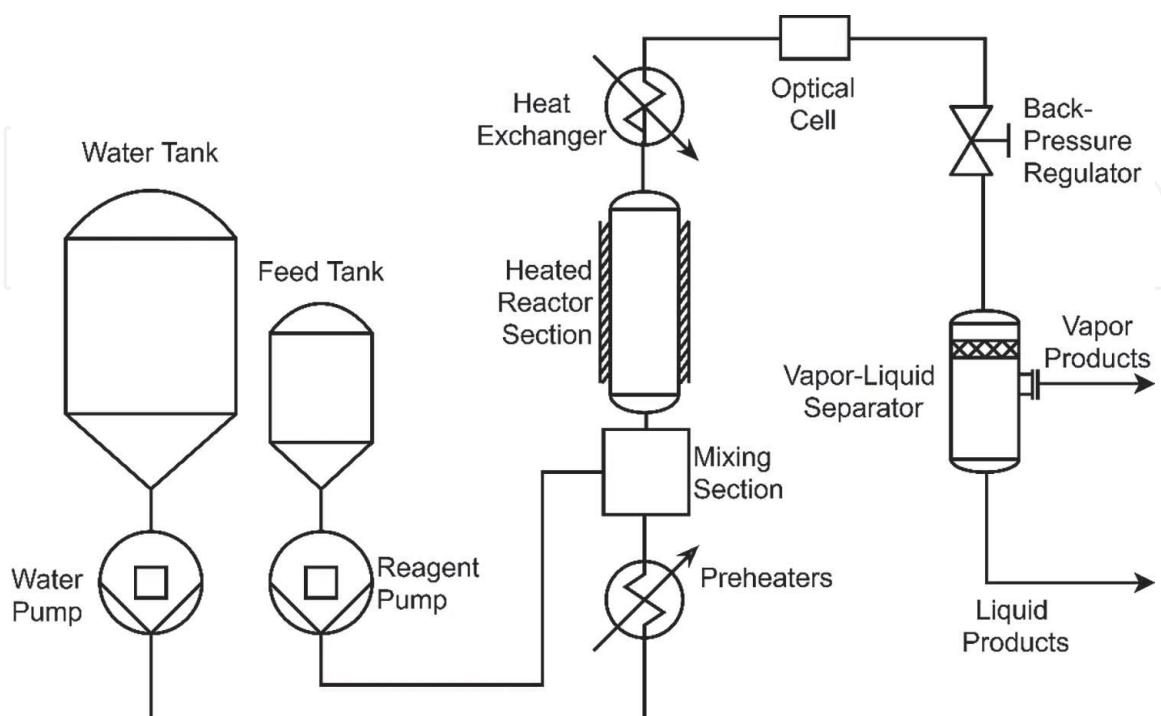


Figure 1. Representative schematic of a continuous supercritical water gasification reactor with post-critical reagent injection and in situ monitoring.

the range of 0.01–30 mL/min [6–9]. Diaphragm, syringe, and piston pumps can be employed when higher flow rates are needed or when pumping a slurry [7, 10].

Reagent heating is important to consider as water can exhibit complex heat transfer characteristics near the critical point. Enhanced or deteriorated heat transfer can occur due to a combination of rapidly changing thermophysical properties and factors such as reactor geometry and the ratio of mass flux to heat flux. Generally, deteriorated heat transfer can be avoided by installing a downward-oriented heating section, which takes advantage of buoyancy effects for more efficient heating. A coiled heating section with a small diameter for high S/V is also desirable for improved heat transfer near the critical point [11, 12].

Resistive heaters, electric furnaces, and immersive fluidized baths have been used to reach the desired reaction temperatures [5, 7, 10, 13–15]. Resistive cartridge heaters are attractive options for preheating, as the tubing can be tightly wound around the cartridge to minimize heat loss. Electric furnaces offer precise control, are well-insulated, and are easy to install. A fluidized bath is a great option for maintaining isothermal conditions in the reactor section but can be expensive and bulky. Some combination of these heating methods is generally sufficient to achieve (a) rapid and efficient heating past the critical point and (b) isothermal reactor conditions.

2.3 Corrosion mitigation

Corollary to its ability to rapidly decompose organic compounds, supercritical water is extremely corrosive to most metals and metal alloys, especially if alkali metals or halogens are present. Thus, corrosion mitigation strategies need to be considered during SCWR design. Many studies have focused on corrosion control methods in SCWRs and SCW heat exchangers [16–18]. Generally, four corrosion mitigation strategies have been proposed and are thoroughly discussed in a review by Marrone et al. [16]. These are (i) preventing corrosive species from interacting with the reactor surface, (ii) forming a corrosion-resistant barrier, (iii) manufacturing the reactor from materials resistant to corrosion, and (iv) tuning operating conditions to minimize severe corrosion conditions. For reactors used to study reaction chemistry of organic compounds that do not contain heteroatoms, it is generally sufficient to rely on the corrosion resistance of the reactor material.

2.4 Mitigating char formation

Char has been reported as a common recalcitrated product formed during the gasification of aromatic compounds or homogeneous biomass components, such as lignin and cellulose [19–23]. Char can rapidly clog reactors, and it should be avoided or suppressed if possible. Broadly, char yields are known to decrease in the presence of certain metal catalysts (such as nickel and ruthenium), which are thought to effectively cleave C–C bonds in the aromatic rings of polycyclic aromatic hydrocarbons (PAHs). Many open questions remain surrounding the exact mechanisms responsible for char formation in SCW. Multiple studies have confirmed that char formation rates are highly dependent on temperature and the initial feedstock concentration. The literature suggests that ionic mechanisms near the critical point are responsible for charring and coking from compounds such as glucose, fructose, and cellulose [20], while free radical mechanisms form char during SCWG of aromatic compounds at higher temperatures, such as phenol, benzene, and lignin [21, 22]. While the industrial implementation of SCWG would require a method for suppressing char formation at high feedstock loadings, researchers can circumvent this issue by performing experiments with low feedstock concentrations [19]. There

is a need to study the effect of feedstock type and concentration on char formation rates and char morphology.

2.5 Reagent mixing strategies

For studying reaction chemistry in a lab-scale SCWR, the mixing strategy used to introduce the reagent into the SCW environment should be carefully considered. Mixing can be achieved by (i) premixing water and reagent before heating to supercritical conditions or (ii) injecting reagent directly into supercritical water. If chemical kinetic rates are sought, post-critical injection is a preferred mixing strategy, as it rapidly heats the reagent to reaction temperatures and establishes a definite reaction start time [24].

Premixing is required if the feedstock is solid or viscous and must be pumped as an emulsion or when high reagent loading is considered. Premixed reagents should be rapidly heated, as char and tar formation can be significant when reagents are heated slowly [6, 16].

2.6 Reactor monitoring and data acquisition

The vast majority of SCWG studies rely on *ex situ* product analysis to quantify yields and determine reaction pathways. Several *ex situ* techniques exist for analyzing gaseous, liquid, and solid products; for properly characterizing full reaction networks and kinetic rates, all reaction products must be identified and quantified for each experimental condition. Gaseous products (H_2 , CO, CO_2 , CH_4) are often identified and quantified using gas chromatography (GC) with a thermal conductivity detector (TCD) and flame ionization detector (FID). Liquid products may be identified using HPLC, nuclear magnetic resonance (NMR) spectroscopy, Fourier transform infrared (FTIR) spectroscopy, or Raman spectroscopy. However, some researchers prefer to report the total organic carbon (TOC) concentration in the liquid phase by using a TOC analyzer, which is sufficient for calculating carbon CE. Occasionally solid products are analyzed *ex situ*, using scanning electron microscopy (SEM), proton-induced X-ray emission (PIXE), Raman spectroscopy, or FTIR spectroscopy [3].

In-line effluent analysis methods are available, such as GC and TOC analysis. These methods may lack the sensitivity and specificity required for the determination of chemical rates, but they can provide real-time input for process control. Alternatively, *in situ* product analysis greatly speeds the collection of the experimental data. *In situ* Raman spectroscopy is one of the most promising *in situ* analysis methods, as it is particularly well-suited for analyzing aqueous mixtures [25]. Water has a strong fluorescence and infrared signal, but a weak Raman signal, allowing product species to be identified and quantified [5]. For example, immersion *in situ* Raman spectroscopy was used to analyze formic acid decomposition [5], the conversion of ethanol to fuel gas [26], and the oxidation of methanol and isopropyl alcohol in SCW [27, 28]. Note that any spectroscopic methods are susceptible to fouling of the optical access point in the system.

2.7 Performance metrics

From a system-level perspective, effective SCWG is best described as a complete conversion of the mass and energy content of the original feedstock into gaseous products. Three performance metrics are commonly used to quantify this conversion: (i) gasification efficiency (GE), (ii) carbon CE, and (iii) hydrogen efficiency

(HE). GE is defined as the ratio of the total mass of the gaseous product to the initial mass of the feedstock, expressed mathematically as:

$$GE(\%) = \frac{x_{H_2} + x_{CO} + x_{CO_2} + x_{CH_4} + x_{Gas,other}}{x_{feedstock}} * 100 \quad (1)$$

CE is another metric used to quantify completeness of gasification; it is especially relevant if solid or liquid carbonaceous compounds are formed as refractory gasification products. It is defined as the ratio of moles of carbon in the product gas to moles of carbon in the feedstock:

$$CE(\%) = \frac{n_{CO} + n_{CO_2} + n_{CH_4} + xn_{C_xH_y}}{n_{C,feedstock}} * 100 \quad (2)$$

A less frequently used metric is HE, defined as the ratio of moles of hydrogen in the gaseous product to moles of hydrogen in the feedstock:

$$HE(\%) = \frac{2x_{H_2} + 4n_{CH_4} + yn_{C_xH_y}}{n_{H,feedstock}} * 100 \quad (3)$$

HE and GE values from SCWG can be well above 100%, due to a prominent role of the water-gas shift (WGS) reaction during gasification, which can produce H₂ gas via reaction of CO with water.

For determining rates of molecular decomposition in SCW, first-order reaction behavior is commonly assumed. This assumption is typically valid for pyrolysis or hydrolysis reactions or monomolecular decomposition reactions. However, this assumption is not valid for free radical reactions where radical induction and radical pooling behavior are present; more complex reaction modeling is required. The first-order decomposition rate (k) is determined by fitting an exponential decay curve to the reactant concentration varying with residence time, at a given experimental temperature.

Once a range of first-order decomposition rates (k) is determined at various temperatures, Arrhenius parameters can be determined by fitting the $\ln(k)$ vs. $1/T$ curve with the following expression:

$$\ln(k) = \ln(A) - \frac{E_A}{RT} \quad (4)$$

This linear curve fit yields the activation energy (E_A) and pre-exponential factor (A) for the first-order decomposition reaction.

3. Gasification kinetics of model compounds in continuous supercritical water reactors

Model compounds serve as useful surrogates for studying the reaction chemistry of biomass constituents in supercritical water. Current interest in converting wet biomass waste into useful fuel has prompted studies of aromatic compounds as model compounds for lignin [22, 29, 30]; glucose and fructose, as cellulose surrogates [7, 14, 31–38]; alcohols, as model compounds for common liquid gasification intermediates and by-products [26, 39–44]; and amino acids—as model compounds for protein [15, 45–50]. Overall, these studies serve as the basis for approximating

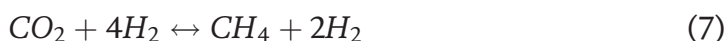
the operating conditions required to upgrade heterogeneous biomass into high-value fuels, such as “green” hydrogen.

For most studies, reaction mechanisms, pathways, kinetics, and yields are determined by varying the temperature, feedstock concentration, and residence time. Few studies investigate the effect of pressure on reaction chemistry; however, no significant pressure-related trends have been observed. The only time pressure that significantly impacts reaction chemistry is near the critical point, where pressure change can affect the thermophysical properties of SCW, such as density and ion product. For all studies reviewed here, the pressure is taken at 25 MPa unless specified otherwise.

Prevailing reaction mechanisms that deserve mention are the WGS reaction and the methanation reactions. The WGS increases H₂ yields by converting CO to CO₂, expressed as:



Methanation serves to reduce H₂ yields by converting it to methane, via the following two pathways:



Overall, both the WGS and methanation reactions are highly important to the final gaseous product composition.

3.1 Aromatic compounds

One of the most recalcitrant biomass constituents is lignin, a heterogeneous organic polymer with numerous aromatic rings. In order to gain insight into lignin decomposition in SCW, phenol, benzene, and guaiacol have been proposed as lignin surrogates.

Huelsman and Savage [22] gasified phenol in an SCW batch reactor at 500–700° C; the authors identified major reaction products as H₂, CO, CO₂, CH₄, benzene, phenol, PAHs, and char. The presence of benzene and phenol as products indicates two competing reaction mechanisms are at play: aromatic ring growth and ring cleaving. The relative importance of the two mechanisms is highly dependent on the reaction temperature and the concentration of aromatics.

Yong and Matsumura [29] gasified phenol and benzene (separately) in a continuous SCWR at 370–450°C in the residence time range of 0.5–100 s. Observed products from each reagent include benzene, phenol, catechol, naphthalene, char, TOC in the liquid phase, and gaseous products. Catechol and naphthalene are indicative of the aromatic ring growth pathways leading to char formation. Increasing temperature and residence time led to increased yields of gas, TOC, and char. Generally, free radical mechanisms have been thought to be responsible both for decomposition to gaseous products and for ring growth to char. First-order decomposition was assumed, and Arrhenius parameters for general disappearance of phenol and benzene were proposed, as shown in **Table 1**. Yong and Matsumura [30] also gasified guaiacol, another aromatic model compound for lignin, at 300–450°C and residence times of 0.5–40 s. Again, yields of benzene, phenol, catechol, gas, TOC, and char were reported. Char formation was so significant that the initial guaiacol concentration had to be limited to 0.1 wt% to prevent reactor plugging. The higher temperatures and residence times increased yields of gas, TOC, and char. In this temperature range, hydrolysis, pyrolysis, ionic, and free radical

Compound	Temperature range (°C)	Pre-exponential factor "A" (s ⁻¹)	Activation energy "E _A " (kJ/mol)	Source
Phenol	370–450	7.72×10^1	53.06	[29]
Benzene	370–450	2.78×10^4	91.16	[29]
Guaiacol	300–450	6.52×10^1	32.40	[30]
Glucose	300–460	6.9×10^7	95.54	[34]
Glucose	750–800	1.2×10^3	70	[36]
Methanol	450–650	Not reported	191	[40]
Glycerol	445–600	Not reported	145	[44]
Glycerol	450–650	Not reported	196	[40]
Glycine	200–340	3.51×10^{13}	166	[48]
Glycine	250–450	3.6×10^{11}	160	[15]
Alanine	200–340	2.65×10^{12}	154	[50]
Alanine	250–450	1.4×10^{12}	156	[15]
Serine	200–340	9.85×10^{12}	149	[50]
Aspartic acid	200–340	5.40×10^{13}	148	[50]
Formic acid	320–420	1.58×10^6	85.8	[52]
Formic acid (subcritical)	300–374	4.0×10^1	39.7	[5]
Formic acid (supercritical)	374–430	3.6×10^{12}	175	[5]

Table 1.

First-order Arrhenius parameters of model compound gasification.

reaction mechanisms were all thought to be active. First-order Arrhenius parameters for guaiacol decomposition into intermediate products can be found in **Table 1**.

3.2 Glucose and fructose

Glucose has received considerable attention as a model compound due to its natural prevalence in biomass. Early studies of SCWG by Modell [32] investigated the decomposition of glucose, and early results showed that glucose could be completely converted to gaseous products without significant char formation after 20 s at 600°C [31].

Kabyemela et al. [33] investigated SCWG of glucose at 300–400°C and residence times of 0.02–2 s. Short residence times and low temperatures allowed for the identification of significant intermediate products, such as fructose, saccharinic acids, erythrose, glyceraldehyde, dihydroxyacetone, 1,6-anhydroglucose, pyruvaldehyde, and 5-hydroxymethylfurfural (5-HMF). The presence of numerous molecules containing furan rings, such as 5-HMF, illustrates the potential to form char via ionic mechanisms near the critical point. In a similar study, Aida et al. [14] gasified glucose at 350–400°C and residence times of 0.2–1.7 s with the explicit goal of optimizing furfural and 5-HMF yields. At these relatively low temperatures and short residence times, products were identified as fructose, erythrose, glycolaldehyde, glyceraldehyde, hydroxyacetone, 5-HMF, and furfural. Promdej and Matsumura [34] gasified glucose in the 300–460°C range, proposing Arrhenius parameters for the decomposition reaction (**Table 1**). Reported products include 5-HMF, furfural, and char, with subcritical temperatures favoring char formation.

These studies show good agreement in reported product yields in the region of enhanced ionic chemistry around the critical point.

SCWG of glucose has also been studied at higher temperatures. Goodwin and Rorrer [35] used a microchannel reactor to gasify glucose at 650–750°C; complete conversion was achieved after 2 s at 750°C. Intermediate products were identified as acetic and propanoic acids, 5-HMF, 2,5-hexanedione, phenol, lactic acid, formic acid, and furfural. Small inner reactor diameters were credited with improving heat transfer to the reaction environment and enhancing gasification, likely due to an increased catalytic wall effect. Hendry et al. [36] gasified 10–15 wt% glucose for residence times of 4.0–6.5 s and 750–800°C. Higher temperatures and lower initial concentrations improved conversion rates, which were used to calculate the Arrhenius parameters. There is significant discrepancy between the Arrhenius parameters proposed by Promdej and Matsumura [34] vs. Hendry et al. [36], which is likely due to the different temperature ranges tested. Near the critical point ionic chemistry is dominant, while free radical mechanisms are favored at temperatures well above the critical point.

Both Castello et al. [8] and Weiss-Hortala et al. [51] gasified glucose/phenol mixtures to study the effect of phenol on the gasification of glucose. Broadly, it was found that the presence of phenol inhibited H₂ production while promoting CH₄ production, with an overall decrease in gas yield.

Fructose has also been studied as a model compound for waste fruits and vegetables. Kabyemela et al. [37] subjected fructose to SCW at 300–400°C for 0.02–2 s, to determine decomposition pathways and kinetic rates. Major liquid products were identified as dihydroxyacetone, glyceraldehyde, erythrose, pyruvaldehyde, acetic acid, formic acid, and 5-HMF. The yields and kinetic rates were very similar to those obtained during glucose gasification at the same conditions [36]. Aida et al. [38] also studied SCWG of fructose, at temperatures up to 400°C and residence times from 0.14 to 0.78 s. In agreement with Kabyemela et al. [37], liquid yields of glyceraldehyde, dihydroxyacetone, pyruvaldehyde, lactic acid, and 5-HMF were reported.

Nanda et al. [7] gasified fructose at higher temperatures from 550 to 700°C, residence times of 30–75 s, and initial concentrations of 4–10 wt%. Broadly, higher temperatures and lower concentrations increased gasification efficiency. Higher concentrations of phenolic compounds were observed at 700°C, possibly indicating that char-forming pathways are enhanced at higher temperatures. Finally, residence times past 60 s increased CH₄ yields due to the consumption of H₂ via methanation reactions.

3.3 Alcohols

Several studies have investigated methanol decomposition in SCW, due to its chemical simplicity and prevalence as a refractory intermediate gasification product. Boukis et al. [39] reformed methanol in a continuous SCWR at T = 400–600°C, for residence times of 3–100 s, and initial methanol concentrations from 5 to 64 wt%. Gaseous yields of H₂, CO, CO₂, and trace CH₄ were detected, with higher temperatures and residence times increasing conversion rates. Bennekom et al. [40] also gasified methanol in a continuous reactor at T = 450–650°C and residence times of 6–173 s. H₂, CO, and CO₂ were reported as main products, with trace yields of methane, formaldehyde, and formic acid. The results show that methanol reforms to H₂ and CO in SCW, with CO converted to CO₂ by the WGS reaction.

Limited investigations are available related to the conversion of ethanol to gaseous products in SCW. Schanzenbacher et al. [41] subjected ethanol to SCW in a continuous reactor at temperatures from 433 to 494°C, for residence times from 2

to 12 s. Maximum conversion of 16.5% was observed, with acetaldehyde identified as the only reaction by-product. Pinkard et al. [26] gasified ethanol in a continuous SCWR at 560°C for residence times of 3–8 s, identifying reaction products as H₂, CO, CO₂, ethylene, ethane, and acetaldehyde.

Glycerol has been extensively studied due to its abundance as a by-product of biodiesel production. Reforming of this low-cost and widely available feedstock could be a source of inexpensive renewable H₂. Buhler et al. [42] reported intermediate products from glycerol gasification to include methanol, acetaldehyde, allyl alcohol, propionaldehyde, acrolein, ethanol, formaldehyde, and standard gaseous products. Non-Arrhenius decomposition behavior was observed, which was attributed to competing ionic and free radical reaction pathways. May et al. [43] reported acetaldehyde, hydroxyacetone, and acetic acid as major products from glycerol gasification in a continuous SCWR. Guo et al. [44] gasified glycerol at T = 445–600°C, reporting high conversion rates after 9 s at 600°C. The activation energy for decomposition was determined and is presented in **Table 1**. Bennekom et al. reported the activation energy for glycerol decomposition, for temperatures of 450–650°C, residence times of 6–173 s, and initial concentrations from 5 to 20 wt%.

3.4 Amino acids

Hydrothermal decomposition of amino acids has been studied in the context of valorizing protein-rich wastes from agriculture and seafood processing. Glycine, alanine, and leucine have all been identified as intermediate products from fish waste decomposition in subcritical water [45]. Islam et al. [46] also identified glycine and alanine as intermediate compounds from the decomposition of more complex amino acids, making them ideal model compounds for protein-rich waste.

Samanmulya and Matsumura [47] gasified glycine from 500 to 650°C with 1.0, 3.0, and 5.0 wt% initial concentrations. Higher temperatures and lower initial concentrations increased gasification efficiency; higher yields of char and tar were thought to decrease carbon conversion at higher concentrations.

Sato et al. [48] measured the decomposition of glycine at subcritical temperatures of 200–340°C. Gaseous yields were low, but liquid products were identified as ammonia, methylamine, glycolic acid, and formic acid. At subcritical conditions, ionic mechanisms likely facilitated the decomposition reactions. Klinger et al. [15] gasified glycine at subcritical and supercritical temperatures from 250 to 450°C. Strong temperature dependence was observed, with key liquid products identified as methylamine, diketopiperazine, glycolic acid, and formaldehyde. The decomposition rates for both studies are presented in **Table 1**. The slight discrepancy in observed products and reported reaction parameters is likely due to the different experimental temperature ranges; at supercritical temperatures, ionic mechanisms are suppressed, while free radical mechanisms are enhanced.

Samanmulya et al. [49] gasified alanine from 500 to 650°C with 1.0, 2.0, and 3.0 wt% initial concentrations. Results showed no change in gasification efficiency for varied initial concentrations, a positive indication of first-order reaction kinetics. Carbon conversion rates were found to be similar to those determined for glycine gasification, indicating that both amino acids likely react via similar free radical reaction mechanisms in high-temperature SCW. However, the gaseous yield from glycine was found to be rich in H₂ and CO₂, while the gaseous yield from alanine contained much more CO and CH₄. This can be attributed to the methyl (CH₃) group present in the alanine molecule, which likely reacts to form CH₄.

Sato et al. [50] investigated the decomposition of alanine at subcritical temperatures from 200 to 340°C major reaction products were identified as ammonia, ethylamine, carbonic acid, lactic acid, and pyruvic acid, which is in good agreement

with the work of Klinger et al. [15], which identified major reaction products as lactic acid, ethylamine, acetaldehyde, and CO₂ from alanine decomposition at 250–450°C. Arrhenius rate parameters from both studies are presented in **Table 1** and show good agreement, likely due to the similar reactor configuration and temperature range used in the two studies.

Several studies also investigated the gasification kinetics of more complex amino acids, such as valine, leucine, proline, serine, and aspartic acid to determine the effect of the amino acid functional group on conversion rates and final product yields. Arrhenius parameters for the decomposition of serine and aspartic acid are presented in **Table 1**. The activation energies determined for all amino acids are within a similar range, showing that functional group has only a minor effect on the overall conversion rates of amino acids in SCW.

3.5 Other relevant model compounds

Some intermediate SCWG products are common across a range of feedstocks, notably aldehydes and organic acids. Formic acid has been identified as an intermediate product from SCWG of glucose [35], fructose [37], and glycine [48].

Yu and Savage [52] studied formic acid gasification in a continuous SCWR to understand the decomposition pathways and rates. Temperatures were varied between 320 and 500°C, pressures between 18 and 30.7 MPa, and residence times between 1.4 and 80 s. Major products were consistently identified as H₂ and CO₂, with minor yields of CO. Overall, this suggests the dominance of a decarboxylation pathway with a minor dehydration pathway. Arrhenius parameters for formic acid decomposition are presented in **Table 1**. Zhang et al. [53] also gasified formic acid in a continuous SCWR at temperatures between 550 and 650°C for residence times between 16 and 46 s. Again, H₂ and CO₂ were present as dominant reaction products, with minor CO yields. Trace yields of formaldehyde and methanol were also reported at the highest tested temperatures.

Pinkard et al. [5] gasified formic acid in a continuous SCWR at T = 300–430°C and residence times in the range of 4–65 s. In situ Raman spectroscopy was used to calculate kinetic rates and Arrhenius parameters. It was found that the transition across the critical point increased the reaction rate, favoring the production of H₂ and CO₂ via the decarboxylation reaction pathway. The notable change in reaction rate across the critical point indicates the importance of both ionic and free radical reactions to the overall decomposition of formic acid in SCW. Arrhenius parameters for formic acid decomposition in subcritical and supercritical water are presented in **Table 1**.

3.6 Gasification catalysts

It is beyond the scope of this chapter to review the body of work investigating various catalysts for SCWG. We direct the reader to the comprehensive reviews on the subject [2, 3]. However, it is worth mentioning some broad findings from this extensive area of research.

Numerous alkali metal compounds (some naturally present in biomass) have been investigated as suitable gasification catalysts. Broadly, these tend to enhance decomposition and increase gaseous product yields. A major disadvantage to adding salts is the persistent corrosion issue, as salts are insoluble in SCW, leading to precipitation of a molten or solid salt layer on the reactor walls. This scaling rapidly corrodes reactor components, increasing the frequency of component replacement.

Noble metals are effective gasification catalysts, with nickel and ruthenium generally accepted as the most promising and effective across a wide range of

compounds and reaction regimes. Typically, metal catalysts are impregnated in a support compound (e.g., activated carbon, $\gamma\text{-Al}_2\text{O}_3$), after which they are crushed and loaded into a packed bed reactor. Both nickel and ruthenium are effective at cleaving C-C bonds, reducing char formation. However, issues exist with catalyst stability, longevity, and process economics. Nickel suffers from sintering and deactivation as carbon layers tend to accumulate on the catalytic surface, while ruthenium catalysts are expensive and can be poisoned by the presence of sulfur. More research is needed toward an economically viable catalyst for SCWG.

4. Discussion and opportunities for further exploration

In general, conversion rates for gasification of organic compounds in SCW can be improved by increasing the temperature and the residence time and by decreasing the initial feedstock concentration. Amino acids, carbohydrates, and simple organic acids are the compound classes with the fastest decomposition rates, with aromatic compounds and alcohols being the most recalcitrant compounds. Arrhenius plots with all mentioned compounds are presented in **Figures 2** and **3** for comparison between compound classes.

Additional studies are needed to understand chemical reactions in supercritical water. It is likely that key functional groups will behave similarly under SCW conditions and further experimentation and interpretation are needed to describe the reactions routes and rates. In situ product identification has the potential to provide accurate data for characterization of decomposition pathways. Special attention should be given to char-forming compounds, in order to understand the mechanisms leading to char formation and the conditions required to promote gasification. Additionally, the role of both homogeneous and heterogeneous catalysts in affecting reaction rates, pathways, and mechanisms should be explored and quantified.

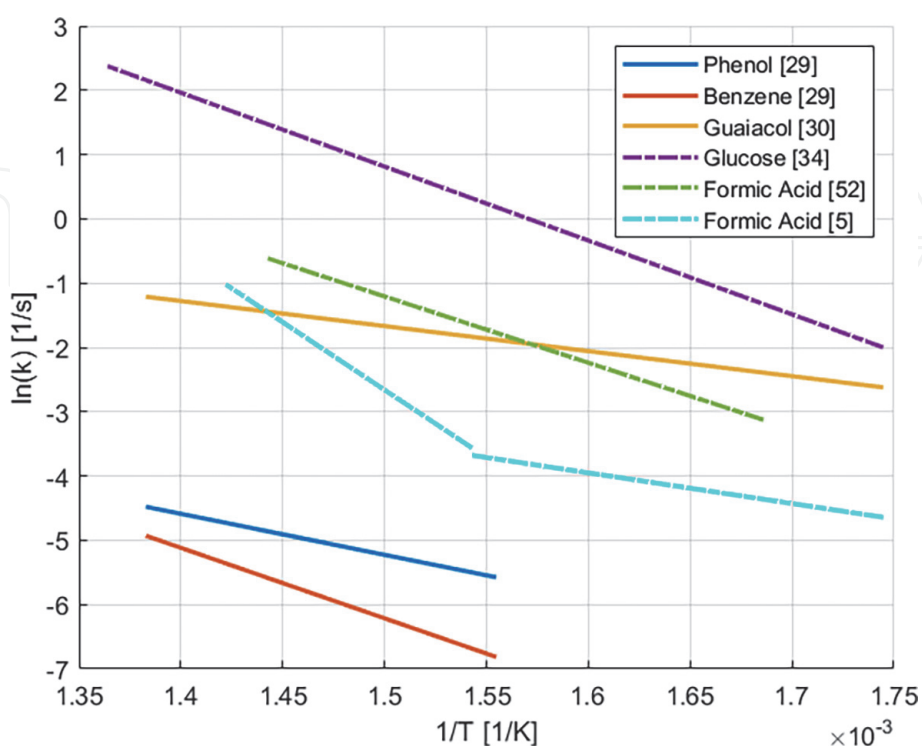


Figure 2.
Decomposition rates of model compounds in sub- and supercritical water.

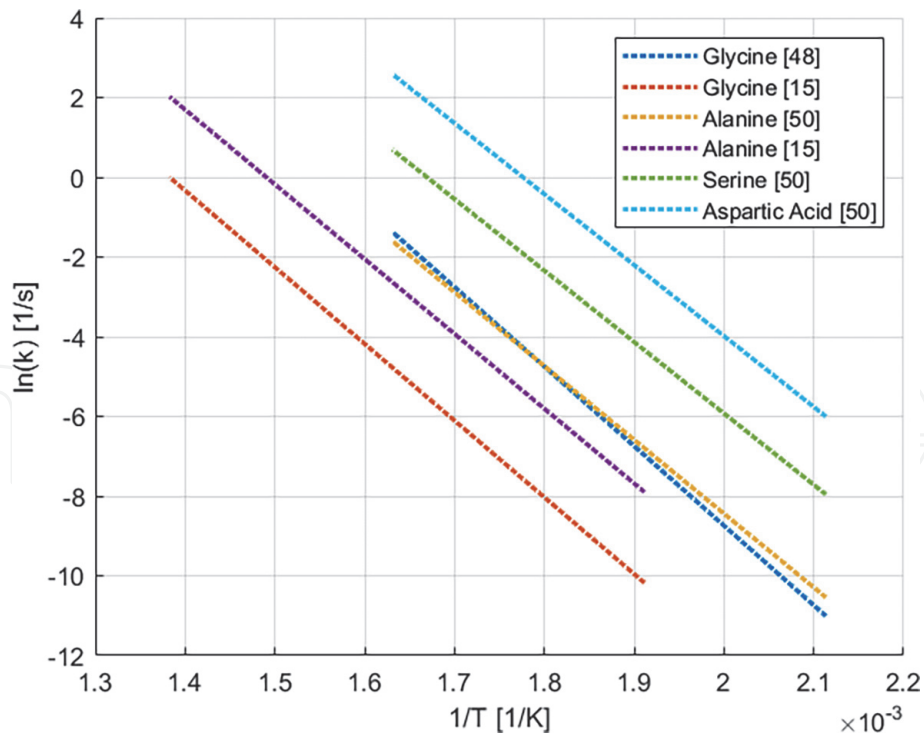


Figure 3.
Decomposition rates of model amino acids in sub- and supercritical water.

5. Conclusions

Supercritical water gasification promises to revolutionize the processing of waste streams to value-adding gaseous fuels. Technical barriers remain between the current state-of-the-art and widespread industrial adoption of the technology, several of which can be addressed through studying the chemistry of model compounds in supercritical water. The knowledge gained in these studies can be applied toward developing reaction pathways and mechanisms, lending insight toward reaction behavior of more complex feedstocks.

Acknowledgements

The authors would like to recognize funding provided by the DOD Defense Threat Reduction Agency (DTRA), Grant HDTRA1-17-1-0001. Special thanks to the University of Washington for providing resources toward the completion of this work.

Additional thanks to David Gorman, Kartik Tiwari, Elizabeth Rasmussen, Vedant Maheshwari, Anmol Purohit, Stuart Moore, Eric Molnar, Justin Davis, and other members of the Novoselov Research Group at the University of Washington who contributed to advancing knowledge of chemical reactions in supercritical water.

IntechOpen


IntechOpen

Author details

Brian Pinkard, John Kramlich, Per Reinhall and Igor Novosselov*
University of Washington, Seattle, WA, USA

*Address all correspondence to: ivn@uw.edu

IntechOpen

© 2019 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/3.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. 

References

- [1] Savage PE. Organic chemical reactions in supercritical water. *Chemical Reviews*. 1999;**99**:603-621. DOI: 10.1021/cr9700989
- [2] Guo Y, Wang SZ, Xu DH, Gong YM, Ma HH, Tang XY. Review of catalytic supercritical water gasification for hydrogen production from biomass. *Renewable and Sustainable Energy Reviews*. 2010;**14**:334-343. DOI: 10.1016/j.rser.2009.08.012
- [3] Pinkard BR, Gorman DJ, Tiwari K, Rasmussen EG, Kramlich JC, Reinhall PG, et al. Supercritical water gasification: Practical design strategies and operational challenges for lab-scale continuous flow reactors. *Heliyon*. 2019; **5**:e01269. DOI: 10.1016/j.heliyon.2019.e01269
- [4] DiLeo GJ, Savage PE. Catalysis during methanol gasification in supercritical water. *The Journal of Supercritical Fluids*. 2006;**39**:228-232. DOI: 10.1016/j.supflu.2006.01.004
- [5] Pinkard BR, Gorman DJ, Rasmussen EG, Kramlich JC, Reinhall PG, Novosselov IV. Kinetics of formic acid decomposition in subcritical and supercritical water—A Raman spectroscopic study. *International Journal of Hydrogen Energy*. 2019;**44**: 31745-31756. DOI: 10.1016/j.ijhydene.2019.10.070
- [6] Caputo G, Rubio P, Scargiali F, Marotta G, Brucato A. Experimental and fluid dynamic study of continuous supercritical water gasification of glucose. *The Journal of Supercritical Fluids*. 2016;**107**:450-461. DOI: 10.1016/j.supflu.2015.09.022
- [7] Nanda S, Reddy SN, Hunter HN, Dalai AK, Kozinski JA. Supercritical water gasification of fructose as a model compound for waste fruits and vegetables. *The Journal of Supercritical Fluids*. 2015;**104**:112-121. DOI: 10.1016/j.supflu.2015.05.009
- [8] Castello D, Kruse A, Fiori L. Low temperature supercritical water gasification of biomass constituents: Glucose/phenol mixtures. *Biomass & Bioenergy*. 2015;**73**:84-94. DOI: 10.1016/j.biombioe.2014.12.010
- [9] Lee IG, Kim MS, Ihm SK. Gasification of glucose in supercritical water. *Industrial & Engineering Chemistry Research*. 2002;**41**:1182-1188. DOI: 10.1021/ie010066i
- [10] Molino A, Migliori M, Macri D, Valerio V, Villone A, Nanna F, et al. Glucose gasification in super-critical water conditions for both syngas production and green chemicals with a continuous process. *Renewable Energy*. 2016;**91**:451-455. DOI: 10.1016/j.renene.2016.01.065
- [11] Shen Z, Yang D, Wang S, Wang W, Li Y. Experimental and numerical analysis of heat transfer to water at supercritical pressures. *International Journal of Heat and Mass Transfer*. 2017; **108**:1676-1688. DOI: 10.1016/j.ijheatmasstransfer.2016.12.081
- [12] Pioro IL, Duffey RB. Heat-transfer enhancement at supercritical pressures. In: Pioro IL, Duffey RB, editors. *Heat Transfer & Hydraulic Resistance at Supercritical Pressures in Power Engineering Applications*. New York: ASME Press; 2007. DOI: 10.1115/1.802523.ch9
- [13] Hanush RG, Rice SF, Hunter TB, Aiken JD. Operation and Performance of the Supercritical Fluids Reactor (SFR). No. SAND-96-8203. Albuquerque, NM: Sandia National Labs; 1995
- [14] Aida TM, Sato Y, Watanabe M, Tajima K, Nonaka T, Hattori H, et al.

- Dehydration of d-glucose in high temperature water at pressures up to 80 MPa. *The Journal of Supercritical Fluids*. 2007;**40**:381-388. DOI: 10.1016/j.supflu.2006.07.027
- [15] Klinger D, Berg J, Vogel H. Hydrothermal reactions of alanine and glycine in sub- and supercritical water. *The Journal of Supercritical Fluids*. 2007;**43**:112-119. DOI: 10.1016/j.supflu.2007.04.008
- [16] Marrone PA, Hong GT. Corrosion control methods in supercritical water oxidation and gasification processes. *The Journal of Supercritical Fluids*. 2009;**51**:83-103. DOI: 10.1016/j.supflu.2009.08.001
- [17] Boyd W, Pray H. Corrosion of stainless steels in supercritical water. *Corrosion*. 1957;**13**:33-42. DOI: 10.5006/0010-9312-22.10.280
- [18] Kritzer P. Corrosion in high-temperature and supercritical water and aqueous solutions: A review. *The Journal of Supercritical Fluids*. 2004;**29**: 1-29. DOI: 10.1016/S0896-8446(03)00031-7
- [19] Pinkard BR, Gorman DJ, Tiwari K, Kramlich JC, Reinhall PG, Novosselov IV. Review of gasification of organic compounds in continuous-flow, supercritical water reactors. *Industrial & Engineering Chemistry Research*. 2018;**57**:3471-3481. DOI: 10.1021/acs.iecr.8b00068
- [20] Chuntanapum A, Matsumura Y. Char formation mechanism in supercritical water gasification of model compounds. *Industrial & Engineering Chemistry Research*. 2010;**49**: 4055-4062. DOI: 10.1021/ie901346h
- [21] Matsumura Y, Goto S, Takase Y, Inoue S, Inoue T, Kawai Y, et al. Suppression of radical char production in supercritical water gasification by addition of organic acid radical scavenger. *Energy & Fuels*. 2018;**32**: 9568-9571. DOI: 10.1021/acs.energyfuels.8b02063
- [22] Huelsman CM, Savage PE. Reaction pathways and kinetic modeling for phenol gasification in supercritical water. *The Journal of Supercritical Fluids*. 2013;**81**:200-209. DOI: 10.1016/j.supflu.2013.05.012
- [23] Peterson AA, Vogel F, Lachance RP, Froling M, Antal MJ Jr, Tester JW. Thermochemical biofuel production in hydrothermal media: A review of sub- and supercritical water technologies. *Energy & Environmental Science*. 2008; **1**:32-65. DOI: 10.1039/B810100K
- [24] Tiwari K, Pinkard BR, Gorman DJ, Davis J, Kramlich JC, Reinhall PG, et al. Computational modeling of mixing and gasification in continuous-flow supercritical water reactor. In: *Proceedings of the 12th International Symposium on Supercritical Fluids (ISSF '18)*; 22-25 April. Antibes: Valence: ISASF; 2018. p. 2018
- [25] McCreery RL. *Raman Spectroscopy for Chemical Analysis*. Vol. 225. Hoboken: John Wiley & Sons; 2005. 437 p. DOI: 10.1002/0471721646
- [26] Pinkard BR, Rasmussen EG, Kramlich JC, Reinhall PG, Novosselov IV. Supercritical water gasification of ethanol for fuel gas production. In: *Proceedings of the ASME 2019 13th International Conference on Energy Sustainability (ASME ES '19)*; 15-17 July. Bellevue. New York: ASME; 2019. p. 2019
- [27] Rice SF, Hunter TB, Ryden AC, Hanush RG. Raman spectroscopic measurement of oxidation in supercritical water. 1. Conversion of methanol to formaldehyde. *Industrial & Engineering Chemistry Research*. 1996; **35**:2161-2171. DOI: 10.1021/ie950510f

- [28] Hunter TB, Rice SF, Hanush RG. Raman spectroscopic measurement of oxidation in supercritical water. 2. Conversion of isopropyl alcohol to acetone. *Industrial & Engineering Chemistry Research*. 1996;**35**: 3984-3990. DOI: 10.1021/ie9505118
- [29] Yong TLK, Matsumura Y. Kinetics analysis of phenol and benzene decomposition in supercritical water. *The Journal of Supercritical Fluids*. 2014;**87**:73-82. DOI: 10.1016/j.supflu.2013.12.018
- [30] Yong TLK, Matsumura Y. Kinetic analysis of Guaiacol conversion in sub- and supercritical water. *Industrial & Engineering Chemistry Research*. 2013; **52**:9048-9059. DOI: 10.1021/ie4009748
- [31] Yu D, Aihara M, Antal MJ Jr. Hydrogen production by steam reforming glucose in supercritical water. *Energy & Fuels*. 1993;**7**:574-577. DOI: 10.1021/ef00041a002
- [32] Amin S, Reid RC, Modell M. Reforming and decomposition of glucose in an aqueous phase. In: *Proceedings of the Intersociety Conference on Environmental Systems*. San Francisco; 1975. ASME Paper 75-ENAS-21
- [33] Kabyemela BM, Adschiri T, Malaluan RM, Arai K. Kinetics of glucose epimerization and decomposition in subcritical and supercritical water. *Industrial & Engineering Chemistry Research*. 1997; **36**:1552-1558. DOI: 10.1021/ie960250h
- [34] Promdej C, Matsumura Y. Temperature effect on hydrothermal decomposition of glucose in sub- and supercritical water. *Industrial & Engineering Chemistry Research*. 2011; **50**:8492-8497. DOI: 10.1021/ie200298c
- [35] Goodwin AK, Rorrer GL. Conversion of glucose to hydrogen-rich gas by supercritical water in a microchannel reactor. *Industrial & Engineering Chemistry Research*. 2008; **47**:4106-4114. DOI: 10.1021/ie701725p
- [36] Hendry D, Venkitasamy C, Wilkinson N, Jacoby W. Exploration of the effect of process variables on the production of high-value fuel gas from glucose via supercritical water gasification. *Bioresource Technology*. 2011;**102**:3480-3487. DOI: 10.1016/j.biortech.2010.11.003
- [37] Kabyemela BM, Adschiri T, Malaluan RM, Arai K. Glucose and fructose decomposition in subcritical and supercritical water: Detailed reaction pathway, mechanisms, and kinetics. *Industrial & Engineering Chemistry Research*. 1999;**38**:2888-2895. DOI: 10.1021/ie9806390
- [38] Aida TM, Tajima K, Watanabe M, Saito Y, Kuroda K, Nonaka T, et al. Reactions of D-fructose in water at temperatures up to 400°C and pressures up to 100 MPa. *The Journal of Supercritical Fluids*. 2007;**42**:110-119. DOI: 10.1016/j.supflu.2006.12.017
- [39] Boukis N, Diem V, Habicht W, Dinjus E. Methanol reforming in supercritical water. *Industrial & Engineering Chemistry Research*. 2003; **42**:728-735. DOI: 10.1021/ie020557i
- [40] Bennekom JGV, Venderbosch RH, Assink D, Heeres HJ. Reforming of methanol and glycerol in supercritical water. *The Journal of Supercritical Fluids*. 2011;**58**:99-113. DOI: 10.1016/j.supflu.2011.05.005
- [41] Schanzenbacher J, Taylor JD, Tester JW. Ethanol oxidation and hydrolysis rates in supercritical water. *The Journal of Supercritical Fluids*. 2002;**22**:139-147. DOI: 10.1016/S0896-8446(01)00119-X
- [42] Buhler W, Dinjus E, Ederer HJ, Kruse A, Mas C. Ionic reactions and

- pyrolysis of glycerol as competing reaction pathways in near- and supercritical water. *The Journal of Supercritical Fluids*. 2002;**22**:37-53. DOI: 10.1016/S0896-8446(01)00105-X
- [43] May A, Salvado J, Torras C, Montane D. Catalytic gasification of glycerol in supercritical water. *Chemical Engineering Journal*. 2010;**160**:751-759. DOI: 10.1016/j.cej.2010.04.005
- [44] Guo S, Guo L, Cao C, Yin J, Lu Y, Zhang X. Hydrogen production from glycerol by supercritical water gasification in a continuous flow tubular reactor. *International Journal of Hydrogen Energy*. 2012;**37**:5559-5568. DOI: 10.1016/j.ijhydene.2011.12.135
- [45] Kang K, Quitain AT, Daimon H, Noda R, Goto N, Hu HY, et al. Optimization of amino acids production from waste fish entrails by hydrolysis in sub and supercritical water. *The Canadian Journal of Chemical Engineering*. 2009;**79**:65-70. DOI: 10.1002/cjce.5450790110
- [46] Islam MN, Kaneko T, Kobayashi K. Reaction of amino acids in supercritical water-flow reactor simulating submarine hydrothermal systems. *Bulletin of the Chemical Society of Japan*. 2003;**76**:1171-1178. DOI: 10.1246/bcsj.76.1171
- [47] Samanmulya T, Matsumura Y. Effect of activated carbon catalytic on supercritical water gasification of glycine as a model compound of protein. *Journal of the Japan Institute of Energy*. 2013;**92**:894-899. DOI: 10.3775/jie.92.894
- [48] Sato N, Daimon H, Fujie K. Decomposition of glycine in high temperature and high pressure water. *Kagaku Kogaku Ronbunshu*. 2002;**28**: 113-117. DOI: 10.1252/kakoronbunshu.28.113
- [49] Samanmulya T, Inoue S, Inoue T, Kawai Y, Kubota H, Munetsuna H, et al. Gasification characteristics of alanine in supercritical water. *Journal of the Japan Petroleum Institute*. 2014;**57**:225-229
- [50] Sato N, Quitain AT, Kang K, Daimon H, Fujie K. Reaction kinetics of amino acid decomposition in high-temperature and high-pressure water. *Industrial & Engineering Chemistry Research*. 2004;**43**:3217-3222. DOI: 10.1021/ie020733n
- [51] Weiss-Hortala E, Kruse A, Ceccarelli C, Barna R. Influence of phenol on glucose degradation during supercritical water gasification. *The Journal of Supercritical Fluids*. 2010;**53**: 42-47. DOI: 10.1016/j.supflu.2010.01.004
- [52] Yu J, Savage PE. Decomposition of formic acid under hydrothermal conditions. *Industrial & Engineering Chemistry Research*. 1998;**37**:2-10. DOI: 10.1021/ie970182e
- [53] Zhang Y, Zhang J, Zhao L, Sheng C. Decomposition of formic acid in supercritical water. *Energy & Fuels*. 2010;**24**:95-99. DOI: 10.1021/ef9005093