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Gasification of Biomass in Supercritical Water, Challenges for the Process Design—Lessons Learned from the Operation Experience of the First Dedicated Pilot Plant

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Abstract: Gasification of organic matter under the conditions of supercritical water ($T > 374$ °C, $p > 221$ bar) is an allothermal, continuous flow process suitable to convert materials with high moisture content (<20 wt.% dry matter) into a combustible gas. The gasification of organic matter with water as a solvent offers several benefits, particularly the omission of an energy-intensive drying process. The reactions are fast, and mean residence times inside the reactor are consequently low (less than 5 min). However, there are still various challenges to be met. The combination of high temperature and pressure and the low concentration of organic matter require a robust process design. Additionally, the low value of the feed and the product predestinate the process for decentralized applications, which is a challenge for the economics of an application. The present contribution summarizes the experience gained during more than 10 years of operation of the first dedicated pilot plant for supercritical water gasification of biomass. The emphasis lies on highlighting the challenges in process design. In addition to some fundamental results gained from comparable laboratory plants, selected experimental results of the pilot plant "VERENA" (acronym for the German expression "experimental facility for the energetic exploitation of agricultural matter") are presented.

Keywords: supercritical water; biomass; gasification; process design

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1. Introduction

There are several motivating forces for the treatment of wet waste biomass. Most important is the need to treat a waste stream that, if not treated, would pollute the environment. Bad odors, harmful bacteria, dangerous proteins (prions), harmful DNA, residual pharmaceuticals, and last, but not least, uncontrolled emission of methane should be prevented. Other aims are the need to recover phosphorous as a nutrient [1–3] and the need to recover or save energy and thus reduce CO_2 emissions by converting biomass to a combustible gas and substitute fossil fuels [4,5].

To gain energy, wet waste biomass can be converted in general in three different ways: combustion or conventional gasification (optionally with a pyrolysis step as pre-treatment) [4,6–9], fermentation (biogas production) [4,10], and hydrothermal conversion processes such as liquefaction [11–13] or gasification under the conditions of supercritical water [14–16]. The first possibility has the advantage of extensive experience in technical applications but the drawback of a high energy demand for drying. The second option, a biotechnological process, requires large reactors due to a very low space–time yield and, especially, the conversion of lignocellulosic materials is generally difficult and rate-limiting [17,18]. Nevertheless, this technology is well known and has been applied worldwide for a long time. The latter variant, gasification in supercritical water (SCWG), has none of the drawbacks of the two other technologies, but also none of their benefits (existing technical applications). Therefore, research and development (R&D) demand is still high, and several aspects of the technology need to be improved to reach successful technical applications.

In hydrothermal conversion processes, biomass can be converted without prior drying, using water at high temperatures and increased pressure as reaction medium. The SCWG process exploits the special features of supercritical water, which comprise a low viscosity and density as well as a non-polar behavior, promoting mixing and reaction with organic compounds [19,20]. This requires an operating pressure >221 bar (usually 250–300 bar) as well as temperatures well above 400 °C (up to 700 °C). The SCWG product gas is a mixture consisting mainly of H_2, CH_4, and CO_2. [14].

In terms of the use of catalysts, there are two different process variants described in literature. One possibility is the application of noble metal catalysts [21–23], which enables a lower reaction temperature (<500 °C) and results in a higher methane content in the product gas. In the second option, earth alkali salts (carbonates) are employed as additives [24–27]. This requires higher reaction temperatures and leads to an increased hydrogen content in the product gas.

In general, the SCWG reaction conditions are very demanding for the construction material of the reaction system. Additionally, trace elements contained in the biomass such as sulfur, chlorine, phosphorous, and salts of alkali metals can cause corrosion [28] or, in combination with tar or char formation, can lead to a reactor blockage [29,30].

In the last few years, the interest in realizing technical application of the gasification in supercritical water has increased. New research directions such as production of methane (SNG) [24] and treatment of sewage sludge combined with recovery of phosphorous [31], as well as the production of clean hydrogen [32], are replacing the previous focus on electricity generation. Projects to build dedicated plants are in progress [33]. However, production of electricity is by far the simplest application.

Since the early 2000s, the Karlsruhe Institute of Technology (KIT; former Research Center Karlsruhe) has been operating a dedicated pilot plant for SCWG, known as "VERENA" (acronym for the German expression "experimental facility for the energetic exploitation of agricultural matter") [24,34–36]. The research activities with the pilot plant have provided a comprehensive knowledge regarding the potential and challenges of a technical implementation of the SCWG process. In the present work, these challenges for process design are described and discussed. For a better understanding of the SCWG process, selected experimental data of typical gasification experiments is additionally provided.

2. Materials, Methods, and Influencing Process Parameters

2.1. Description of the SCWG Process as Realized in the VERENA Pilot Plant

The KIT pilot plant VERENA has a maximum throughput of 100 kg/h (maximum 20 wt.% dry biomass), usual throughput is 50 kg/h. The maximum operating pressure and temperature are 350 bar and 700 °C, respectively. Standard reaction conditions are typically 660 °C and 280 bar. The plant consists of three main sections: the feed system, the reaction system, and the separation system. A simplified process scheme is depicted in Figure 1.

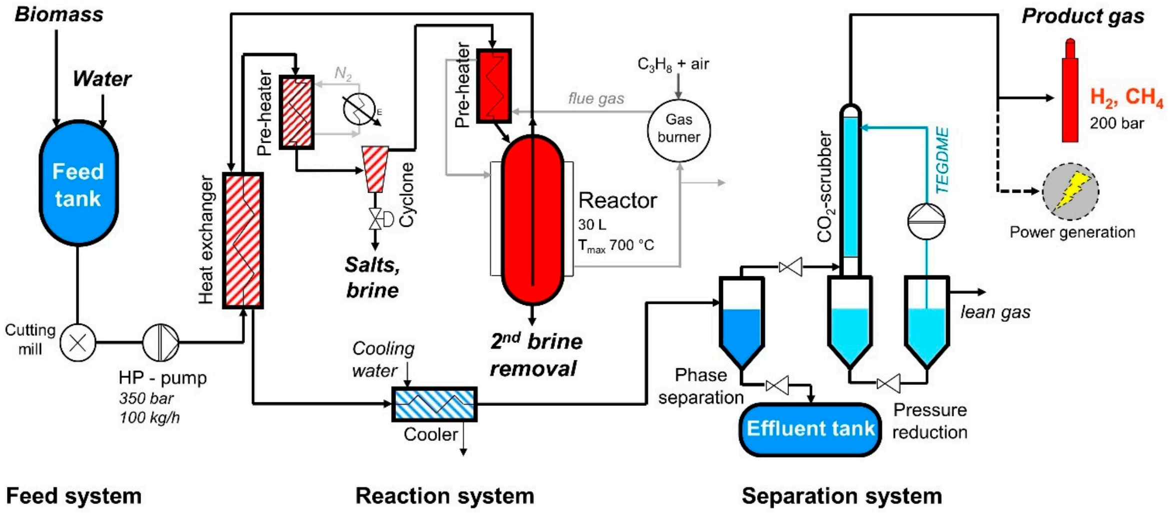

Figure 1. Simplified scheme of the VERENA (acronym for the German expression "experimental facility for the energetic exploitation of agricultural matter") pilot plant (one-stream process configuration). Adapted from [37].

The feed system consists of several tanks, a macerator, a colloid mill, and several high-pressure pumps. Liquid organic wastes such as crude glycerol can be pumped directly to the reaction system. Biomass or waste materials containing larger particles have to be pretreated (see Section 2.2). The water content of the feed is adjusted to gain a homogeneous feed suitable for pumping. The obtained slurry is dosed into the reaction system by a mass flow controlled high-pressure metering pump [36].

The feed slurry then enters the first component of the reaction system, a double-pipe heat exchanger with an exchange surface of 1.8 m^2, and is heated in counter-current flow by the hot effluent of the reactor ($T \approx 550$ °C). During operation with concentrated biomass slurries, some fouling occurs, and the heat transfer coefficient (h) is reduced.

In another process layout, an second heat exchanger/preheater (less than 20 kW, indirect electrical heating) is installed after the first heat exchanger and adjusts the temperature of the fluid from about 400 °C up to 480 °C. This enables an efficient separation of inorganic salts, as their solubility is drastically reduced at supercritical conditions. Separation therefore occurs by gravity and flow inversion (sharp change from downflow to upflow) or by a high-temperature, high-pressure cyclone. The cyclone has a narrow inner diameter (i.d.) of 35 mm. This device separates salts, which have formed solids suspended in the supercritical water or dense brines, before precipitation on the tubing wall. The linear velocity of the feed stream at a temperature of 400 °C is in the range of 2 m/s and reaches approximately 4 m/s at 450 °C. This is due to the lower density of the supercritical water at higher temperatures. The resulting man-made gravity is 10 to 30 times higher than usual and enables a fast separation. The solids from the cyclone are removed in a discontinuous mode by very short pressure releases from 280 bar to ambient pressure with a high throughput. The mean output of the separated brine stream is about 1 kg/h. The salt separation at this position is not obligatory. In case of feed materials with a low fraction of inorganic components or in process configurations with a different preheater design, it is possible to omit the salt separation at this stage of the process.

The next component of the reaction system is the main preheater, which is externally heated by the flue gas of a burner with 60 kW (maximum) power. It is operated at an external wall temperature (high-pressure tube, 9/16″ outer diameter (o.d.), 60 m length) of 700 °C.

The preheated feed slurry is then led into the downflow reactor, a slim vessel with a volume of approximately 30 L (10 cm i.d.) to guarantee the required residence time. There is not enough surface available to heat the reactor externally, but the hot flue gas exiting the preheater is recirculated to prevent temperature losses. A feature, first time realized in the VERENA pilot plant, is the separation of brines and solids from the main product stream in the lower part of the reactor. The main product is directed to the upwards via a thin tube and subsequently led to the heat exchanger. Brines or solids, if not already removed in the cyclone, accumulate in the lower part of the reactor and are drained in a manner similar to the cyclone (see Figure 1). This is beneficial in order to avoid clogging and to reduce fouling of the heat exchanger. These process layouts were invented at the time of construction of the VERENA pilot plant (see Section 6).

Another layout provides a moderate heating of the biomass below the critical temperature (374 °C), using only a small part of the heat exchanger. Thus, precipitation of inorganic salts at this stage is avoided. The largest part of the heat exchanger and the preheater is employed for a second stream of pure water, which reaches high temperatures. Both streams are mixed at the top of the reactor (see Figure 2), which enables heating of the biomass up to reaction temperature. The salts are transported downwards by gravitation and accumulate at the lowest part of the reactor, where they are drained by the brine removal system. Due to the dilution of the feed stream inside the reactor, this process layout is suitable for concentrated feeds. A cyclone is not necessary.

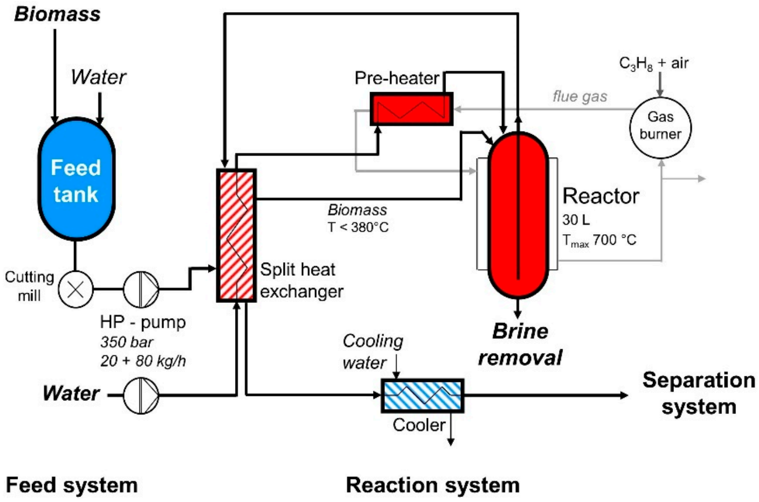

Figure 2. Two-stream process configuration: simplified scheme of the feed and reaction system. Adapted from [38].

In the third section of the pilot plant, the product gas is separated and stored in high-pressure gas bottles. At supercritical conditions, the gaseous reaction products are soluble in water and thus leave the reactor as part of a homogeneous phase, passing the heat exchanger and a cooler. By cooling down the reaction mixture, gases separate from the water phase. Via a level control, the liquid phase is passed on to a separator operated at ambient pressure to remove lean gas. Finally, the effluent is collected in a tank, analyzed, and discharged to a treatment plant.

The pressure of the gas phase can be reduced in one or two steps, respectively. One phase separator is additionally equipped with an integrated scrubber to remove CO_2, gaining a mixture of only combustible gases. The scrubbing column for CO_2 separation is filled with Pall rings. By dissolving CO_2 in cold water or tetraethylene glycol dimethyl ether (TEGDME), its content in the product gas is reduced. The remaining product gas can then be filled into high-pressure gas bottles. Excess gas is expanded to a pressure required for further treatment.

2.2. *Typical Pretreatment of the Feed Material*

Depending on the composition and, especially, the size and texture of the feed material, a mechanical pretreatment is obligatory for successful operation. Another typical aspect of feed preparation for VERENA experiments is the addition of alkali salts as catalyst. Here, $KHCO_3$ or K_2CO_3 are preferred, sodium salts are also suitable. Recommended concentration of $KHCO_3$ is between 50 ppm and 3000 ppm, depending on the feed material. The effect of the catalyst is described in more detail in Section 2.3.

With model compounds such as methanol, the feed becomes a homogeneous aqueous solution, which requires no pretreatment. Therefore, solely the definition of the concentration (compound-based or based on total organic carbon (TOC)) and the addition of catalyst is necessary. Thus, in case of model compounds, the feed system consists of only one tank and two pumps with different pressure levels.

For fresh biomass (plant parts, grasses), the pretreatment starts with a coarse size reduction, followed by additional pretreatment steps. At first, a cutting mill is typically used to obtain biomass particles of few mm. With a second milling step using a colloid mill, the size of the particles can be further reduced. For example, with corn silage, 84 wt.% of the biomass particles were smaller than 0.5 mm after the second pretreatment step [39]. Another option is the utilization of a macerator or a meat grinder. Table 1 shows the distribution of particle sizes after different steps of mechanical pretreatment of green waste (grassy material).

Table 1. Analysis of biomass particle size (green waste) after different pretreatment steps.

Particle Size (mm)	Total Mass Fraction (%)		
	After 1. Treatment (Meat Grinder)	After 2. Treatment (Meat Grinder)	After 3. Treatment (Macerator)
>3.35	1.7	-	0
>2.0	5.4	2.5	0.9
>1.0	13.5	11.8	3.3
>0.5	12.0	15.2	8.9
<0.5	67.4	70.5	86.9

For biomass and organic waste materials that already comprise only smaller particles (e.g., industrial sludge, sewage sludge, or brewer's spent grain), the use a colloid mill is sufficient. Generally, a particle size of less than 1 mm is recommended for the feed slurry that is led to the reactor. In all cases, sedimentation of solids should be avoided by steering or by thickening the feed by thixotropic substances. The latter is frequently applied in the KIT lab-scale apparatuses (see Section 2.3).

2.3. Main Influence Parameters of the Gasification Process

Several years ago, systematic parametric studies were performed in the laboratories of KIT with corn silage as feed material [40,41]. Based on these results, the main influence parameters of the SCWG process are described in this section.

Parallel to the pilot plant, KIT also operates a lab-scale facility named "LENA" (German acronym: "laboratory plant for the energetic exploitation of agricultural matter"). The configuration is quite similar to the pilot plant. A detailed description can be found in [42]. The lab-scale plant is equipped with a piston-like feeding system capable of handling even viscous feed slurries or larger solid particles (maximum 8 mm). Xanthene is added to the slurry to increase viscosity and prevent sedimentation of solid particles in the cylinder. Throughput capacity is up to 1000 g wet feed per hour. Temperatures up to 700 °C and an operation pressure up to 300 bar can be realized. The benefits of a small plant are obvious, investment, maintenance, and personal costs are almost an order of magnitude lower than for the pilot plant. This enables regular operation and testing of several modifications of the process design.

The gasification yield and the composition of the product gas depend on the biomass and the dry matter (DM) content of the feed slurry. Other main influence parameters are the reaction temperature and the mean residence time in the reaction zone. In Figure 3, it is shown that gasification can be performed even with a high DM concentration of 20 wt.%. However, the gasification yield is reduced to 80%. The residual 20% of carbon forms unwanted side products (tar or even char). Consequently, the carbon content (TC) in the reactor effluent rises. Furthermore, the concentration of methane (and other light hydrocarbons (C_2–C_3)) in the product gas increases, with a simultaneous decrease in hydrogen. For technical purposes, an application at lower concentrations of biomass between 8 and 12 wt.% DM results in a positive energy balance and a higher yield of product gas. If economically feasible, an even lower biomass concentration of only 5 wt.% DM should be favored.

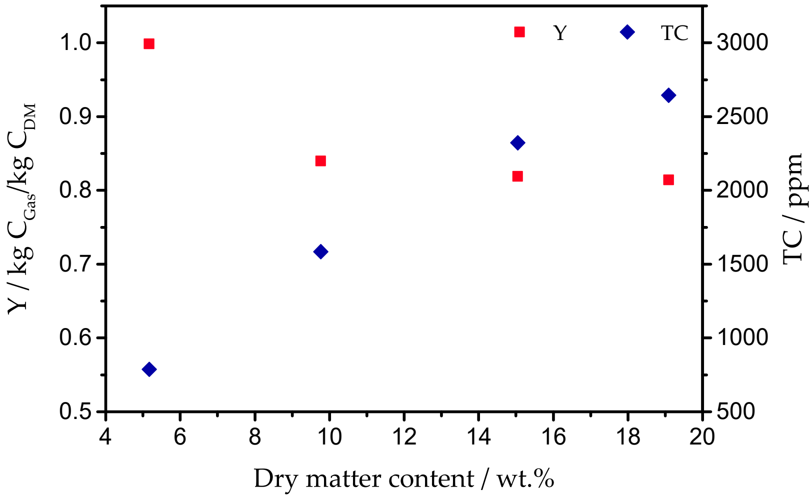

Figure 3. Carbon gasification yield (Y) and total carbon (TC) in the reactor effluent as a function of the dry matter content of the feed slurry (corn silage). Reaction temperature 700 °C, pressure 250 bar. Original data available in [43].

The relation of reaction temperature and mean residence time is illustrated in Figure 4. At a low concentration of biomass (corn silage) of only 5 wt.%, complete gasification is achieved at 700 °C and a mean residence time of 1.5 min. At lower temperatures, complete gasification cannot be reached even at much longer mean residence times. A reaction temperature of 650 °C is a reasonable compromise for technical applications. Gasification yield is usually higher than 90% and the reaction is completed in a few minutes. Additionally, a reaction temperature of 650 °C can be realized even with allothermal heating concepts, available reactor materials, and common reactor design.

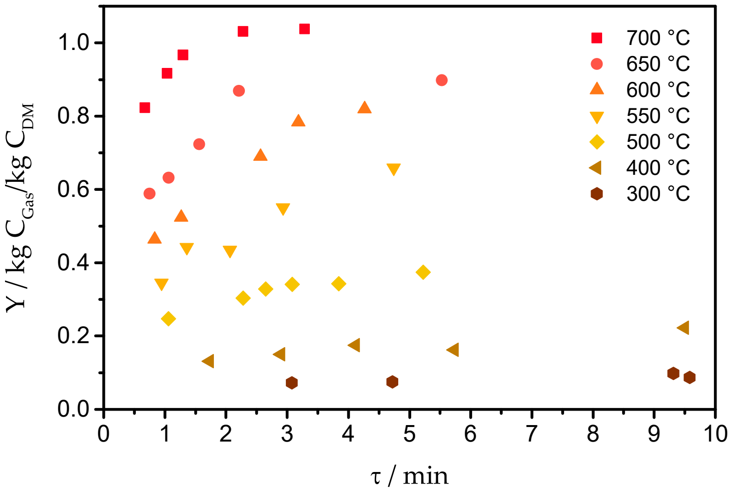

Figure 4. Carbon gasification yield (Y) as a function of the mean residence time (τ) in the hot reaction section of the reactor at different temperatures. Corn silage, 5 wt.% dry matter (DM). Original data available in [43].

The results obtained at lab-scale [40,41,43] are in accordance with the those of pilot plant experiments [39] at similar conditions (reaction temperature, pressure, mean residence time, and concentration of DM).

The use of catalysts also has a decisive influence. At KIT, alkali salts are generally used as homogeneous catalyst. Only a few experiments were conducted with metal catalysts (see Table 2).

Alkali salts are known to increase the gasification yield [25–27,44–46] and reduce coke formation [27,44]. Taking K_2CO_3 as an example, the catalytic effect is explained via the formation of potassium formate, the decay of which eventually produces H_2 and CO_2 [47,48]. In summary, alkali salts promote the conversion of CO via the water–gas shift reaction, generating higher H_2 yields (and additionally CO_2) [49].

To achieve higher conversion rates at low temperatures, heterogeneous catalysts are widely used, especially in case of methane as target product [29]. Several authors report improved gasification efficiency by using ruthenium, nickel, or activated carbon [21,22,50–54]. It was shown that Ni-catalysts promote reactions such as steam reforming and methanation [21,50,52,55]. A more detailed overview on catalyzed SCWG can be found in [56] and [57].

3. Selected Gasification Results of the VERENA Pilot Plant

Throughout the past two decades, various feed materials have been tested in the VERENA pilot plant. Next to model compounds such as methanol or glycerol, different biomass and waste materials have been converted to a combustible product gas. Table 2 gives an overview on treated materials, experimental conditions, and the product gas composition.

The experiments performed with the pilot plant have been reported in individual publications [24,34,36–39,58–62]. A comparison of results obtained with the different process layouts described in Section 2.1 can be found in [36]. Here, the conditions of reaction differ. The reaction temperature in the second (two-stream) layout is only 510 °C, the concentration of carbon in the feed slurry is approximately 2 wt.%. With the first process layout (one stream), the corresponding values are 620 °C and 5 wt.%. The hydrogen-to-methane ratio was 1.82 and 0.77, respectively. Most importantly, with the two-stream process layout, there was no interruption due to blocking.

While operation with model compounds in general was largely without disruption, various difficulties aroused when biomass or waste material were used. Solid particles enhanced erosion, high concentration of inorganic salts in combination with tars and chars led to blockages, and trace elements contained in the biomass boosted corrosion effects. These, as well as other, challenges are discussed in the following section.

Table 2. Product gas composition and experimental conditions of the VERENA pilot plant with different feed materials (model compounds and biomass/waste materials).

	Experimental Conditions					Product Gas Composition (vol.%)				
Feed Material & Reference	**T (°C)**	**p (bar)**	**Feed Conc.* (wt.%)**	**Flow Rate (kg/h)**	**Catalyst**	**H_2**	**CH_4**	**CO_2**	**C_{2+}**	**CO**
Methanol [37]	550	250	5	100	n.a.	80.4	4.8	15.5	-	1.3
Ethanol [59]	545	280	52.2	$20^{\dagger} + 80\ H_2O$	285 ppm K^+	60.8	23.7	10.9	3.4	1.3
Ethanol [39]	625	280	14.4	100	100 ppm K^+	46.2	24.8	20.2	6.1	0.8
Glycerol [38]	594	280	60	$9.8^{\dagger} + 40\ H_2O$	285 ppm K^+	56.6	13.5	26.4	4.0	1.2
Crude glycerol [38]	584	280	50	$16.2^{\dagger} + 64\ H_2O$	11,020 ppm K^+	34.3	13.4	30.1	6.1	12.4
Pyroligneous acid [37]	620	270	TOC:3.73	50	111 ppm K^+	36.4	31.0	27.4	3.2	0.5

Table 2. *Cont.*

	Experimental Conditions					Product Gas Composition (vol.%)				
Feed Material & Reference	**T (°C)**	**p (bar)**	**Feed Conc.* (wt.%)**	**Flow Rate (kg/h)**	**Catalyst**	**H_2**	**CH_4**	**CO_2**	**C_{2+}**	**CO**
Corn silage [39]	610	280	9.2	50	n.a.	31.6	28.0	27.8	9.9	0.5
Green waste *[unpublished data]*	620	280	9.6	50	n.a.	18.7	20.1	52.5	7.5	1.1
Brewer's spent grain *[unpublished data]*	608	250	17.8	25 † + 51 H_2O	2500 ppm K^+	35.0	23.0	26.8	14.5	0.7
Sewage sludge [63]	654	280	11.8	45.3	2500 ppm K^+	18.8	39.7	23.9	14.6	2.1
Sewage sludge [63]	640	270	8.5	50	2500 ppm K^+	29.6	33.6	18.3	16.6	1.9
Digestated sludge [24]	423	280	6.7	25	ZnO Ru/C	16	60	21	-	0.1

* based on dry matter content for biomass and waste materials. † Two-stream process concept: feed material + water mixed at the reactor entrance. n.a. = not appicable.

4. Challenges for Process Design

4.1. Reactor Materials

4.1.1. Mechanical Strength

The selection of suitable resilient reactor materials is crucial for the implementation of the process. Especially in case of an allothermal process design (heating by external heat), only a few materials can fulfill the requirements created by the combination of high reaction temperature and high operating pressure. To keep the wall thickness in acceptable dimensions, an offset yield point ($R_{p0,2}$) of 100 N/mm^2 at 700 °C is necessary. Only a few nickel-based alloys meet this criterion. One of them is alloy 625, which is well available in different dimensions. Furthermore, the requirements of the approval authorities (in Germany, usually the TÜV) must also be met. Authority approval should be obtained for each single component. Alloy 625 becomes brittle at temperatures above 600 °C [64]; however, at the same time, the material becomes about eight times stronger, which helps to overcome the problem. Other additional materials, e.g., alloy 617 or alloy 602, are also approved for operation up to very high temperatures and have a very good mechanical strength.

Another hurdle is that these materials are usually only available in the form of sheets or rods. Especially alloy 602 is extremely difficult to form. However, high-pressure tubing is needed to connect the components and to construct the heat exchanger and the preheater. Consequently, most applications use tubing made of alloy 625. The reactor of the VERENA pilot plant is made of alloy 617. The lab-scale reactors are made of alloy 625 or alloy 602.

4.1.2. Corrosion Resistance

The next challenge is the corrosion resistance of the reactor material. Temperatures up to 700 °C, high pressure, and many chemical elements present in the waste biomass create a significant corrosion load [65,66]. At KIT (and the former Nuclear Research Center Karlsruhe, respectively), the investigation on the corrosion resistance of reactor materials under SCW conditions started in 1992 and has continued, with interruptions, until now. With regard to these corrosion studies, a dedicated laboratory plant and corresponding analytics are in operation. Corrosion experiments involve long time exposures up to 1000 h. Constant process conditions and a simple composition of the solution environment are necessary to assign corrosion phenomena to chemical species. Therefore, experiments were performed with simple solutions containing alcohols or salts. A selection of the experimental results, most of them published in conference proceedings, is given here.

Water-based solutions containing only carbon species will not affect nickel-based alloys. Alloy 625, the most available and widely used Ni-based alloy, shows severe ductility loss after service at 600–800 °C. This is due to the composition of the alloy itself and must be taken into account in the design of the apparatuses. In general, chemical load, especially hydrogen, can enhance ductility loss. In [65], no additional hydrogen embrittlement of alloy 625 was measured under SCWG conditions.

Under the reaction conditions (temperature up to 700 °C and pressure of 250–300 bar) only water, gases, and organic matter form a homogeneous phase. Salts form solids or brines. Both have high concentration and can affect the reactor material. The solubility of potassium carbonate in supercritical water (at 700 °C) is very low. In [67], the effluent contained only 48 and 115 ppm K^+, less than 10% of the potassium amount of the feed solution. An accumulation of potassium in the reactor occurs. Presumably, a concentrated corrosive brine solution is formed in the part of the reactor with a temperature higher than 600 °C. This is the zone of the reactor where corrosion becomes visible. Morphology of the corrosion of alloy 625 is general material deterioration up to 1 mm/147 h, as shown in [67]. Diluted salt solutions containing only 50 ppm K^+ do not cause corrosion on alloy 625 up to an exposure time of 250 h [68].

In another study [69], corrosion of alloy 625 in a solution containing 3000 ppm $KHCO_3$ starts at 500 °C. At 700 °C, general deterioration reaches 1 mm in 423 h. At 550 °C, corrosion is slower up to 0.7 mm/628 h. Again, general corrosion with dealloying of molybdenum and partly nickel is observed. There is an indication that corrosion starts with intergranular attack. In [70], corrosion of alloys 602, 625, 617, C-263, and stainless steel 316 were compared in an aqueous environment with 860 ppm K^+. Exposure was at 700 °C and 300 bar, exposure time was 211 h. Alloy 602 showed a mass loss of 30 mg/cm^2, SS316 even 50 mg/cm^2. The other alloys almost disintegrated. Corrosion of alloy 602 accelerated after 414 h of exposure at 660 °C. Still, alloy 602 is much more resilient concerning corrosion than the other alloys. In [68], alloy 602 and alloy 33 showed corrosion rates of 1 and 1.8 mm/a (600 °C, 300 bar, K^+ = 1170 ppm). Alloy 617 exhibits lower corrosion rates than 625, most probably because it is stabilized by cobalt contained in this material. Nevertheless, corrosion rates are high with 3 mm/a, similar to stainless steel 316. Corrosion experiments in an environment containing alkali chlorides (Cl^- = 1430–1820 ppm) [71] generated similar results than the ones with $KHCO_3$ solutions. There was no evidence of stress corrosion cracking. Again, alloy 625 showed general corrosion up to 1 mm in 1090 h. Alloy 602 showed only a few µm of corrosion-related deterioration after an exposure of 608 h.

Thus, one solution for the mitigation of corrosion is separation of the salts at an early point of the SCWG process. Of utmost importance is the application of high-strength reactor materials, which do not contain molybdenum (e.g., alloy 602 or alloy 214). It is essential to avoid accumulation of alkali salts in the part of the reaction system with temperatures higher than 500 °C.

4.1.3. Erosion

High fluid velocities are achieved during the reduction of process pressure. If solids are present, especially abrasive ones, erosion can become significant. No problems are apparent during operation without salts. Severe erosion occurs during the treatment of sewage sludge, which also contains sand and several salts, up to half of the dry matter is of inorganic nature. Erosion is more pronounced in the parts of the plant where salt separation occurs. Careful consideration of the design and construction materials used at process sections exhibiting high flow velocities or sharp curves can minimize erosion.

4.1.4. Mechanical Connections: Welding vs. Adaptors, Dimensions of Tubes

The SCWG system consists mainly of high-pressure tubes. In total, their length can reach several hundred meters. The pilot plant VERENA is constructed using 9/16″ o.d. and 8 mm i.d. tubes made of alloy 625. The dimension of the tube should enable sufficient flow velocities to avoid precipitation of solids and enhance heat exchange efficiency (narrow i.d.).

In addition, a moderate pressure drop (less than 10 bar) is favorable. In general, an overall mechanical strength has to be ensured for a robust commercial application.

The tube segments (usually 6 m) can be welded or connected with high-pressure adapters. Welding is cheaper and more reliable, but the connection should be inspected by X-rays, a costly and difficult procedure. Adapters are expensive and require mechanical work at the ends of each tube, but can be reopened for inspection. Adapters are prone to leaks, especially in the high-temperature section of the plant during heat-up or cooling down. In the VERENA pilot plant, high-pressure adaptors are used, and welding is minimized to very few positions. Experienced technical personnel is required to tighten the adaptor, especially for the high-temperature part of the plant.

4.2. Design of High-Pressure Components

4.2.1. Heat Exchanger and Preheater Design

The heat exchanger in an SCWG system influences the energetic efficiency of the plant and the process in general. Up to 80% of the sensible heat in the system is recycled through the heat exchanger. However, to achieve efficient heat exchange, flow velocities should be relatively high, resulting in small cross-sections. These in turn are prone to blockage. A considerate design and careful pretreatment of the feed material will mitigate these issues.

The preheater in the VERENA pilot plant is also a heat exchanger. It transfers heat of an external source, e.g., hot gas or even direct heating, to the feed stream. Thus, the challenges are quite similar to the previously-mentioned heat exchanger. Clogging due to precipitated salts or unwanted byproducts such as coke are common. Salt separation before the preheater or an improved design can help to overcome this challenge.

Both sections are affected by fouling. This phenomenon reduces the effectiveness and should be considered during dimensioning of the components. A corresponding fouling factor should thus be taken into account during the design of the heat exchanger. The exchange surface has to be sufficiently large. Fouling strongly depends on the feed material. In pilot-scale experiments with brewer's spent grain, the calculated heat transfer coefficient of the VERENA heat exchanger dropped from 579 W/m^2K (pure water during heating phase) to 319 W/m^2K after operation with biomass. This was traced to the influence of the product gas, the solids in the feed, and corresponding fouling (deposits, mainly Mg and Ca salts). The effect is even more pronounced in operation with sewage sludge. Fouling in the high-pressure system can be reduced by higher flow velocity, a better smooth inner surface, and geometry of the apparatus. If fouling is apparent, a chemical cleaning is necessary. This is best realized by lowering the temperature to values below 350 °C while maintaining a high pressure and pumping a special cleaning agent into the system. Due to the high temperature, the cleaning period is presumably very short. In order to prevent fouling, this operation can be performed periodically.

In the limited experimental time of the VERENA pilot plant, no severe plugging occurred in the sections with temperatures lower than 400 °C. For the VERENA, this is the highest temperature that can be reached at the exit of the main heat exchanger. At temperatures higher than 450 °C, clogging with a mixture of inorganic salts and organic matter is a common issue. This is one of the most important challenges in the design of the reaction system.

4.2.2. Reactor Design and Volume

The main function of the reactor is to provide sufficient time for the feed material to react with the supercritical water. The mean residence time in the reactor should be in the range from a few seconds (model compounds react very fast) up to about 5 min (e.g., corn silage, see Figure 4). The density of water under reaction conditions defines the required volume. At 660 °C and 280 bar, the density is approximately 72 kg/m^3. The active volume (hot zone) of the reactor used in the VERENA pilot plant is 30 L. The overall reaction is neither endothermic nor exothermic. Thus, it is not necessary to heat the reactor, but a very good isolation should be installed.

The reactor of the VERENA pilot plant has an internal flow inversion and at the lowest part, the flow velocity reaches zero. The temperature in this section is about 350 °C. This allows reliable separation of solids from the product stream, which is crucial in terms of a successful operation (see also Section 4.3.1).

4.2.3. Phase Separation and Pressure Regulation

In a small lab-scale plant, pressure reduction occurs in one step and phase separation occurs at ambient conditions. In a larger plant, phase separation should be performed at high pressure to benefit from a compressed product gas, which enables efficient gas treatment and storage. In principal, phase separation is simple. After cooling down the reaction mixture to ambient temperature, a reduction of flow velocity using a sufficiently large autoclave is sufficient. In the VERENA pilot plant, the gas phase is expanded to lower pressure (e.g., from 280 to 200 bar) and another valve regulates the level of the wastewater phase. The detection of the phase boundary is not trivial, as foaming can occur. Nevertheless, there are several ways to realize the detection of the phase boundary. Within the VERENA, it is realized by multiple ultrasonic measurements.

The pressure control for the gas phase is provided by back-pressure regulators using robust, commercially available components. The pressure valves for the wastewater phase should be equipped with filters to ensure reliability.

4.3. Challenges Related to the Reaction Conditions and Economic Aspects

4.3.1. Separation of Solids

In the heat exchanger, the density of water starts reducing to values lower than 1 g/mL (1000 kg/m^3) and reaches approximately 0.2 g/mL at reaction conditions. At the same time, the dielectric constant declines as well, and solubility of inorganic salts becomes low. Various salts become practically insoluble. In addition, some of them form sticky brines. The best way to avoid deposits, and consequently plugging and corrosion, is to separate the salts at an early stage of the process. This can be realized in a semicontinuous mode with devices such as a cyclone or using special filters. However, the latter requires maintenance.

If salt separation occurs at an early stage of the process, as described above, the salt concentrate (approximately 1–10 wt.% of the feed stream) will also contain organic compounds, in concentrations comparable to the feed. In the VERENA pilot plant, salts are collected in a high-pressure, high-temperature cyclone installed in front of the preheater and additionally removed at the bottom part of the reactor (see also Section 2). Table 3 illustrates the efficiency of this separation method; inorganic components are mainly detected in the brine concentrates.

Table 3. Example of salt separation efficiency in the VERENA pilot plant: concentration of inorganic elements in different output streams. Feed material: green waste.

Element	**Concentration in Different Output Streams (ppm)**		
	Separation 1: Cyclone	**Separation 2: Reactor Bottom**	**Reactor Effluent**
Sodium	41.6	4.3	4.6
Potassium	6860	377	n.a.
Magnesium	82.3	0.5	0.05
Calcium	1385	14.5	0.75
Silicium	266	31.8	10.5
Iron	5.2	<0.05	<0.05
Phosphorus	132	0.9	<0.5

n.a. = not appicable.

To enable the salt separation, the two components must be drained every few minutes. For this purpose, high-pressure valves are automatically opened for a short time (some ms). The resulting high-pressure gradients are necessary to transport the solids through the narrow tubing. However, erosion of these valves can be severe, due to the very high flow velocity in combination with solids.

During salt separation, organic matter or product gas will also be lost. In the VERENA pilot plant, unconverted organic material is especially drained at the cyclone. In experiments with sewage sludge, the concentration of total organic carbon (TOC) in the cyclone salt concentrate was approximately 14,000 ppm. At the second discharge point at the bottom of the reactor, TOC concentration is naturally much lower (1500 ppm) [63]. Nevertheless, this removal of organic material reduces the efficiency of the process. Additionally, organic matter in the salt concentrate increases further treatment costs. However, it is one of the main benefits of the SCWG process that salts, especially those containing phosphorous, can be recovered as a concentrate.

Generally, salt separation in the initial process stages is beneficial to avoid undesired accumulation of salts and thus a blockage of the system. In addition, corrosion of the reactor material is reduced if inorganic components are separated prior to reaching the reaction zone.

4.3.2. Formation of Tars and Wastewater Quality

As mentioned in Section 2, the gasification rate of organic matter especially depends on the reaction temperature, the concentration of organic matter, and the mean residence time. A high gasification rate not only increases the efficiency of the gasification, but is also important for other reasons. The part of the biomass which is not gasified will form tars, coke, or reduce the quality of the wastewater. Coke and tars can cause technical problems during the process; therefore, their formation should be suppressed. In addition, the disposal is costly. Due to the size of the VERENA pilot plant and the various components, achieving a complete carbon balance is not trivial. In comparable studies at lab-scale with brewer's spent grain, usually more than 90% of carbon could be traced at the end of the experiment. It can thus be concluded that a maximum of roughly 10% of carbon deposits is in the plant as tar or coke. With model compounds, almost no tar or char formation is detected.

Pollution of the wastewater is also an economical issue. The amount of wastewater is relatively high (same order of magnitude as the total amount of feed slurry (90%)) and the costs for the wastewater treatment mainly depend on the load of organic compounds. TOC concentration in the reactor effluent of the VERENA pilot plant is usually in the range of 1000–3000 ppm. A possible option to reduce treatment cost is the recycling of wastewater (see Section 4.3.4).

As mentioned, reaction temperatures close to 700 °C are beneficial for complete gasification and thus, avoidance of tar formation. Furthermore, a lower biomass concentration is advantageous (at best in the single-digit wt.% range).

4.3.3. Recycling of Wastewater

Typically, the DM content of biomass materials is too high to perform gasification in supercritical water. A dilution is required, which can also be done by recycling the wastewater of the process [72]. This reduces the amount of wastewater and consequently the treatment cost. The organic components contained in the wastewater can be gasified. By this way, the expenses for the wastewater treatment are further reduced.

Usually, the SCWG wastewater contains only very low amounts of inorganic salts. Thus, no additional technical challenges are to be expected from recycling the reactor effluent.

4.3.4. Product Gas Upgrading

The reaction temperature affects the product gas composition [32,73–75] and it is theoretically possible to influence the H_2 to CH_4 yield by the lowering the reaction temperature. For practical reasons, this is not feasible because of the low gasification rate at lower temperatures. Application of metal catalysts will considerably increase the concentration of methane; however, the concentration of hydrogen will still be relatively high, due to thermodynamic equilibria. Additional downstream gas upgrading (e.g., methanation reactor) is necessary to produce pure SNG. If pure hydrogen is the desired product, a comparable gas treatment (reforming of hydrocarbons) is necessary. Both reactions require heterogeneous catalysts, which are sensible against impurities in the SCWG product gas (tar, sulfur). Their removal prior to gas upgrading is essential.

In the VERENA pilot plant, the gaseous phase is only treated in a washing column at 200 bar. Either water or TEGDME (both circulated by a high-pressure pump) are used. This step removes CO_2 and other sour components from the product gas. With this gas scrubber, the CO_2 content in the raw product gas could be reduced from 32 to 1 vol.%. Losses of H_2 were lower than 10% [39]. So far, a further upgrading is not implemented. After this energy-effective treatment at high pressure, the CO_2-free combustible gas is filled into high-pressure gas bottles for further utilization.

5. Conclusions

Gasification under the conditions of supercritical water is a promising process for the conversion of wet waste biomass and wastes. It is suitable for decentralized (medium size) applications and has been demonstrated with various feed materials. However, several technical issues still have to be overcome. In this work, the experiences gained during the operation of the SCWG pilot plant VERENA at KIT were described, focusing on the challenges arising during supercritical water gasification of biomass wastes. This summary is intended as an aid to anyone interested in realizing the SCWG process on a larger scale.

Due to the very wide spectrum of biomass composition and the different environments in case of decentralized applications, individual adaption of the process is necessary. This requires R&D work with the specific feed material and a suitable process design, respectively. Economic efficiency is important, as the feed used is usually of low value, as well as the primary products of the process (combustible gas and salt concentrate). Investment costs are high, due to extreme process conditions. With an automatized operation, at least the operating costs can be reduced. Depending on the intended use of the product gas, a corresponding upgrading step has to be implemented.

There are environmental benefits due to the decentralized character of the application (no need to transport waste biomass, no uncontrolled emissions) and thus, public acceptance should be good. If solutions to the existing process challenges are developed, SCWG represents a promising option for the disposal or utilization of organic waste materials.

6. Patents

At the time of the construction of the VERENA pilot plant, only little information—compared to the current situation—was available in literature. Various details of the plant were new developments. Hence, several patent applications resulted from the work related to the pilot plant. Unfortunately, most of them are in German, as listed below.

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