Review

Biomass gasification in near- and super-critical water: Status and prospects

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Abstract

The current status of biomass gasification in near- and supercritical water (SCWG) is reviewed. There are two approaches to biomass gasification in supercritical water. The first: low-temperature catalytic gasification, employs reaction temperature ranging from 350 to 600 °C, and gasifies the feedstock with the aid of metal catalysts. The second: high-temperature supercritical water gasification, employs reaction temperatures ranging from 500 to 750 °C, without catalyst or with non-metallic catalysts. Reviews are made on reaction mechanism, catalyst, and experimental results for these two approaches. Engineering technologies for SCWG gasification, and an example of process analysis are also introduced. Finally, the authors' prognostications on the future prospects of this technology are offered.
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Contents

1. Introduction

Following more than 30 years of research, there is now intense worldwide interest in the use of hydrogen as an alternative transportation fuel. This interest is founded upon the expectation that hydrogen will be produced at a competitive price with conventional fossil fuels. One method for producing hydrogen is the steam reforming of biomass [1,2].

$$C_6H_{10}O_5 + 7H_2O \rightarrow 6CO_2 + 12H_2. \qquad (1)$$

In this idealized, stoichiometric equation, cellulose (represented as $C_6H_{10}O_5$) reacts with water to produce hydrogen and carbon dioxide, mimicking the commercial manufacture of hydrogen from methane by catalytic steam reforming chemistry [3–6]. As early as 1978 Antal reported detailed thermochemical equilibrium predictions of the effects of reaction temperature and pressure on the reaction products of 1 mol of cellulose with 7 mol of water (as in Eq. (1)) [2]. Temperatures above 600 °C were predicted to leave no solid carbon product and produce a gas rich in H_2, CH_4, CO, and CO_2. These thermochemical equilibrium calculations were also used to predict the magnitude of the endotherm associated with the cellulose steam-reforming step at 600 °C. At the same time,

studies were reported of the reaction kinetics of cellulose pyrolysis in steam. The presence of steam had little or no measurable effect on the fast pyrolysis reactions under atmospheric pressure [2,7–9].

Of course, a practical technology must convert the cellulose, hemicellulose, lignin, protein, and extractive components of a biomass feedstock into a gas rich in hydrogen and carbon dioxide. Unfortunately, as predicted by the early work with cellulose [2,7–9], biomass does not react directly with steam at atmospheric pressure to produce the desired products. Instead, significant amounts of tar and char are formed, and the gas contains higher hydrocarbons in addition to the desired light gases [7,10–13]. The work of Corella and his co-workers [14] illustrates these obstacles. In a fluid bed operating at atmospheric pressure Corella's group observed char yields of 10–20 wt% from the steam gasification of wood sawdust, and yields of tar decreasing to 4 wt% as the temperature of the bed increased from 650 to 775 °C. Unfortunately, at the highest temperature only 80% of the carbon in the feedstock was converted to gas [14]. By employing a secondary, fluidized bed of calcined dolomite operating at 800 to 875 °C, Corella and his co-workers [15] were able to convert almost all the tar to gas. Nevertheless, the char byproduct remained unconverted. Any production of char represents an effective loss of gas. Many other workers have reported similar results [16]. Thus, the formation of pyrolytic char and tar during gasification sets limits on the efficient production of hydrogen from biomass for the biomass conversion under the atmospheric pressure.

Some of these problems were overcome in 1985, when Modell [17] described experiments involving the quick immersion of maple wood sawdust in supercritical water: water above its critical pressure of 22.1 MPa. The sawdust quickly decomposed to tars and some gas without the formation of char. Measurements of the pyrolysis kinetics of biomass materials offer an explanation for this unexpected result. Cellulose is most stable component of biomass [18]; nevertheless, cellulose decomposes rapidly at temperatures below

the critical temperature of water [19,20]. Thus, Modell's experiments involved pyrolysis of wood sawdust in *liquid* water. The reactions of biomass and its components in liquid water are a focus of current interest. At temperatures above 190 °C a part of lignin and hemicellulose macromolecules undergo solvolysis after only a few minutes of exposure to hot liquid water [17–22]. Hydrothermolysis of the remaining lignocellulosic solid occurs at somewhat higher temperatures. The initial products of these solvolysis reactions subsequently undergo a variety of isomerization, dehydration, fragmentation, and condensations reactions [22–31], that ultimately form gas and tars [32,33]. At temperatures above 600 °C and pressures in excess of the critical pressure, hydrothermolysis transforms biomass into a combustible gas composed of hydrogen, methane, carbon dioxide and carbon monoxide, together with some tar [34–36]. Thus, char formation is suppressed when biomass gasification occurs in liquid water or supercritical water, and tar gasification becomes the chief obstacle to the total steam reforming of biomass.

As evidenced in the work of Corella and his colleagues [14] discussed above, temperatures in excess of 700 °C effectively convert most (but not all) of the tars to gas [2,11,13]. Much work has been reported on the use of heterogeneous catalysts (primarily Ni) to gasify the pyrolytic tars [15,37–55]. These heterogeneous catalysts are also effective in near-critical water and can be used biomass gasification as shown in the following sections, but one problem is that Ni and many of the other metallic catalysts can suffer severe corrosion in supercritical water at temperatures needed to secure high yields of hydrogen. As another approach, Antal overcame this problem by the use of charcoal and other carbons as catalysts for the gasification of tars in supercritical water [36]. Although carbon is perceived to be an unlikely catalyst, there is an extensive literature on its use as both a catalyst support and a catalyst [56,57]. The use of a carbon catalyst resulted in the formation of extraordinary yields of gas ($>2 \, L \, g^{-1}$) from wood sawdust feedstocks, with clean water as the major byproduct of the gasification chemistry.

As shown here, throughout the development of the technology upto today, possibility of biomass gasification in near- and supercritical water (SCWG) has been shown so that complete conversion of biomass into combustible gas is achieved. This technology opens a door to the realization of effective thermochemical gasification of biomass, especially wet ones. Unfortunately, due to the novelty of this technology, it is not widely known to the biomass society. In this paper, the current status of biomass gasification in SCWG is reviewed. First, reactor systems that is employed for SCWG gasification is described. Then, two different approaches in terms of reaction temperature are described. Between the low (350 °C) and high temperature (600 °C) systems, reaction mechanism, catalyst to be used, reactivity of the feedstock, reaction rates, and other important features of the reaction differ. Thus, these two approaches are reviewed in different sections below. Then, engineering technologies for SCWG gasification, and an example of process analysis are introduced. Finally, the authors' prognostications on the future prospects of this technology are offered.

2. Reactor systems

In SCWG gasification, due to the high temperature and pressure, reactor setup needs consideration (see Section 2.1). As characteristic reactors for supercritical water gasification, quartz capillary batch reactor (see Section 2.2), fluidized bed micro reactor (Section 2.3), and PDU tubular reactor (see Section 2.4) are introduced.

2.1. General considerations

Biomass gasification in supercritical water is a novel process, under development (with limited effort) since the late seventies. Large-scale commercial installations do not yet exist. The largest plant, in operation since the beginning of 2003, is the one of Forschungszentrum Karlsruhe (FzK) in Germany [58]. It has a design capacity of about $100 \, L \, h^{-1}$, and was built to demonstrate supercritical gasification of wet residues from wine

production. EU subsidies plus a grant awarded by the Japanese NEDO enabled the construction of a well-equipped process development unit (PDU) in Enschede, The Netherlands [59], with a maximum throughput capacity of $30 \, L \, h^{-1}$. BTG Biomass Technology Group b.v. has been responsible for the technical realization and start-up of the PDU, which will be further used in Ph.D. research work at the University of Twente.

Several small reactors are used in laboratories of e.g. University of Hawaii, Osaka Gas, Pacific Northwest National Laboratory, FzK, Hiroshima University, and in The Netherlands (University of Twente, TNO-MEP and BTG). Batch autoclaves of steel are favored to examine the product yield and distribution for various feedstock materials, process conditions and catalyst formulations. A disadvantage of the steel autoclaves is that it takes quite some time to heat them to reaction conditions. If the gasification rate is larger than the heating rate, the conversion will proceed at undefined temperatures. Moreover, possible catalytic effects of the metal reactor wall have been suggested in the literature [35].

The application at Twente University of quartz capillaries as batch micro-reactors is new. It allows high speed and inexpensive testing, with the additional advantage of possible visual observations. Photo and film techniques can be applied to record the sequence of events inside the transparent capillaries during heating and pressurization. A drawback however is that the pressure inside a capillary cannot be measured. It is derived indirectly from the implied temperature, and the sample plus reactor volume.

When continuous operation is aimed at, tubular steel reactors are often used. Although a stirred tank reactor can be used in a laboratory, it has not yet been considered for practical application. To maintain the same capacity, a stirred tank reactor normally should have a larger volume than a tubular reactor. The biomass concentration is notably lower in a stirred tank reactor, due to the rapid dilution to reactor outlet conditions. An argument in favor of the stirred tank reactor is that the carbon conversion in SCWG of biomass increases at lower biomass concentrations, as observed in the quartz capillary measurements

quoted before. Practical problems may be related to e.g. the efficient insulation of a tank reactor, and the need for stirring power.

One could state that the reactor development for a commercial SCWG process is still to be started. Apart from tubular and (series of) stirred tank reactors, many others may be suitable. In case of heterogeneous catalysis, fixed and fluidized beds could be considered as well.

However, to allow a proper reactor design analysis, data on reaction kinetics obtained for well-defined conditions must be made available, and a model should be developed for the dominant reaction steps. A problem of general nature in SCGW is the required heat exchange between the reactor outlet and inlet streams. To achieve an acceptable thermal efficiency, it is crucial for the process that the heat of the inlet stream is utilized as far as possible to pre-heat the feedstock stream (mainly water) to reaction conditions. At the same time, heating of the biomass slurry in the inlet tube of a reactor is likely to cause fouling/plugging problems because the thermal decomposition ($>250\,°C$) starts already far below the desired reaction temperature ($>600\,°C$). A related phenomenon is that the feed stream will pass through the supercritical point in the heat exchanger with, up to now, unknown consequences.

2.2. Quartz capillary batch reactor

In order to improve the understanding of biomass gasification in supercritical water and to identify the optimal process conditions and possible process bottlenecks, a transparent high-throughput capillary technique has been developed. This technique uses quartz batch reactors of 1 mm ID and 150 mm length (capillaries, see Fig. 1). In the sealed capillaries, different concentrations of the model compounds can be exposed to the various temperatures, pressures and residence times. The capillaries are heated rapidly (within 5 s) in a fluidized sand bed to the desired reaction temperature. Changing the amount of solution in the capillaries enables the variation of the pressure. After the reaction, the capillaries are quenched and smashed after which the released product gases are analyzed with a gas chromato-
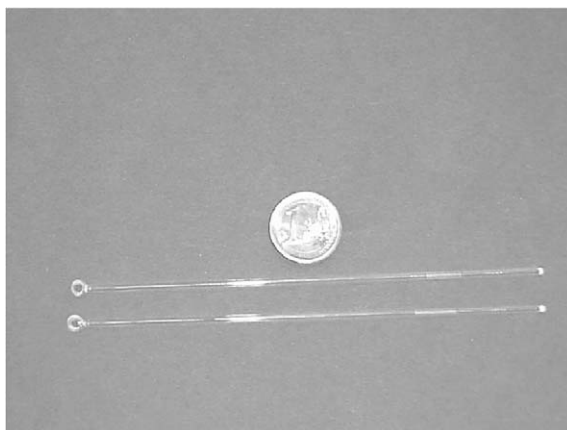

Fig. 1. Photo of the capillary reactors with a 1 EURO coin (diameter: 23 mm).

graph. The capillary technique has several distinct advantages:

- quartz has no or hardly any effect on the reaction kinetics,
- some reaction products are visible (tar, char),
- conducting the experiments is very fast and safe.

Detailed description of the technique is presented elsewhere [60]. Preliminary results are discussed in Section 4.1.1.

2.3. Fluidized bed micro reactor

Experimentation with the capillary method has revealed that, especially at low temperatures and high feed concentrations, char formation occurs. A fluidized bed reactor might be a good alternative to solve the problems related to this char and ash formation (viz. blockage and accumulation). As a part of the NEDO Grant research, the University of Twente constructed a fluidized bed reactor using a quartz tube with an inner diameter of 1 mm and an outer diameter of 3 mm. A quartz ball in the bottom part was employed as gas distributor. Quartz sand particles with an average diameter of 100 μm were used as fluidized bed material. The expected advantages are that a fluid bed (i) enhances the mass/heat transfer rates in the reactor, (ii) can be made catalytically active,

(iii) can be used to collect the minerals (ash) and coke by deposition on the bed particle surface, and (iv) can be used for withdrawal of solid particles from the reactor. From the experiments conducted in the micro FB reactor major observations and conclusions are:

- At supercritical conditions the conventional Darcy-law based relations can be used to calculate minimum fluidization velocity and the bed expansion.
- In low density region ($<90\,kg\,m^{-3}$) only aggregative fluidization was observed.
- For the higher densities ($100<\text{density}<230\,kg\,m^{-3}$), both particulate and aggregative regimes were observed.

2.4. The PDU tubular reactor

To experience all problems possibly related to the development of the SCWG process it was decided to build and test a PDU of simple and straightforward design in the high-pressure (HP) laboratories of Twente University. It has a capacity of $5–30\,L\,h^{-1}$ and is designed for operation temperatures up to $650\,°C$ and a pressure of around $30\,MPa$. A flow sheet of the process is given in Fig. 2. Four liquid containers are installed, represented by only one in the figure.

Two feedstock vessels allow the switching from one to another type of biomass (or another composition). At least 2 h of operation is possible without refilling the feedstock bins. The other two
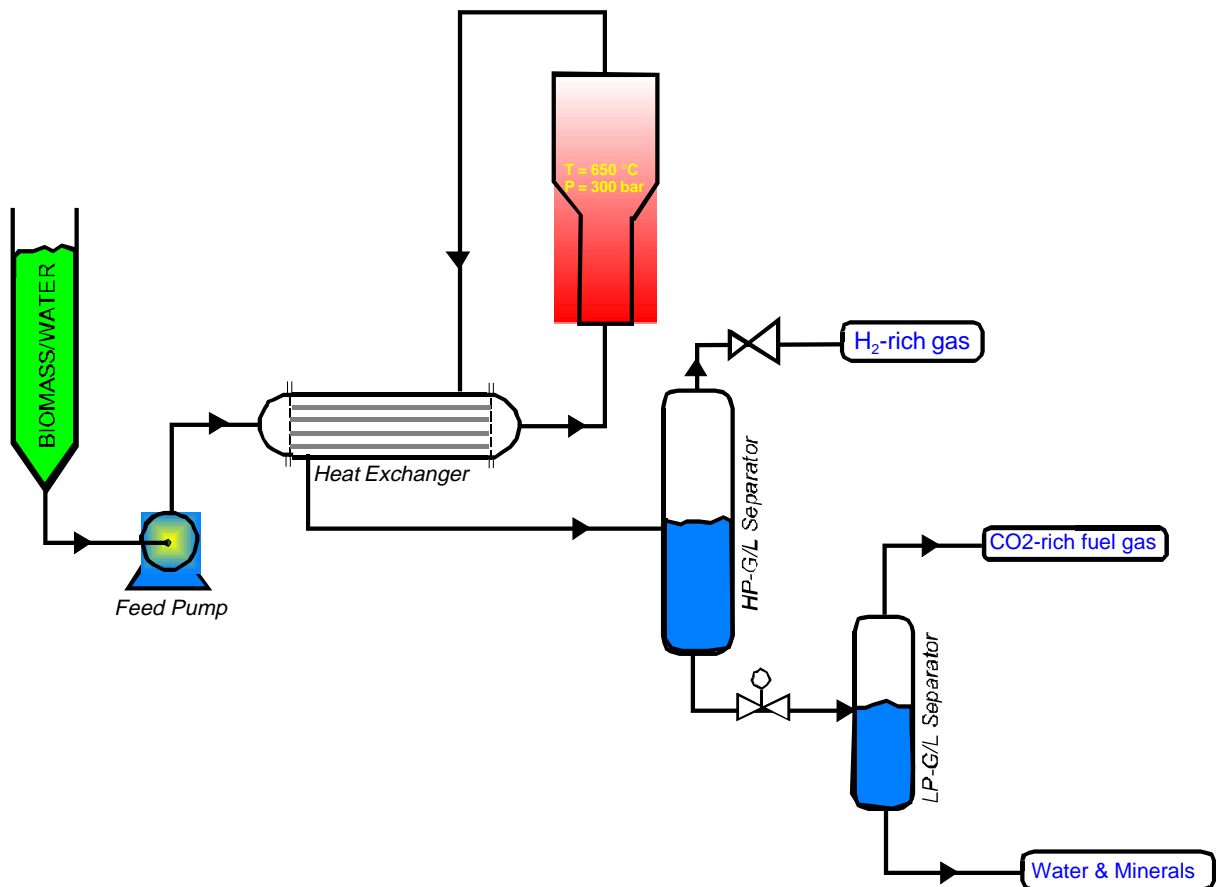

Fig. 2. Simplified scheme of the PDU for biomass gasification in supercritical water, built by BTG for the University of Twente.

storage vessels contain clean and effluent water, respectively.

Heat exchange between the inlet and outlet streams has been implemented in the PDU, as it is essential for achieving acceptable thermal efficiencies. A simple double-walled tube heat exchanger is installed. The feedstock is flowing through the outer tube (5/4″, Incoloy 825), and the reactor effluent through the inner tube (1/2″ Incoloy 825). In this way, about 7 kW of heat can be exchanged between the reactor in- and outlet.

The reactor tube has an inner diameter of 14 mm, a total length of 15 m, and is made also from Incoloy 825. It is heated externally by a 20 kW natural gas burner. A residence time of 0.5–2 min is probably needed to achieve complete carbon conversion.

The two-phase product stream from the reactor arrives in an HP gas–liquid separator ($P = 300$ bar, $T = 25-100\,^\circ$C) from which the liquid phase is further transferred to a low-pressure (LP) gas liquid separator ($P = 1$ bar, $T = 20\,^\circ$C). The gas released from the HP is expected to be rich in hydrogen while the LP separator will presumably produce CO_2 rich gas.

The PDU will first be tested for "simple" components like ethanol, or glycerol. Later trials are intended for the more difficult feedstock types like starch, glucose and, eventually, real biomass. Some technical problems still have to be resolved before a dedicated testing program can be started. The occasional results up to now, however, are quite satisfactory. As an example, 2 h continuous operation with a glycerol solution as a feedstock yielded a gas product distribution of approximately 25 vol% H_2, 15 vol% CH_4, 30 vol% CO, 15 vol% CO_2 and 15 vol% C_2 and C_3 components. The conversion was 83% for a 5wt% and 60% for a 10 wt% glycerol solution.

3. Low-temperature catalytic gasification

In low-temperature catalytic gasification, a temperature range of 350–600 °C is usually employed. Catalysts are applied to enhance the reaction, but complete gasification of feedstock is still difficult. Battelle researchers undertook the first fundamental study (see Section 3.1 below). Since the reaction temperature is low, catalysts play an important role (see Section 3.2). The reaction mechanism has been studied using model compounds (see Section 3.3). A recent study has led to the discovery of interactions between components (see Section 3.4). In engineering studies the biomass feedstock has been treated both by batch (see Section 3.5) and continuous (see Section 3.6) reactors. In an attempt to improve the carbon gasification efficiency, partial oxidation has been also studied (see Section 3.7).

3.1. The Battelle concept—single-step gasification/methane synthesis

Through the use of a metal catalyst, biomass gasification can be accomplished with high levels of carbon conversion to gas at relatively low temperature. In the pressurized-water environment (21 MPa) at sub-critical temperature (350 °C) near-total conversion of the organic structure of biomass to gases has been accomplished in the presence of a ruthenium metal catalyst. The process is strictly a steam reforming reaction as there is no added oxidizer or reagent other than water. In addition, the gas produced is a medium-heating-value gas due to the synthesis of high-levels of methane, as dictated by thermodynamic equilibrium. This type of processing has been accomplished at the bench-scale in continuous-flow reactor systems.

The Battelle concept [61,62] was developed in early research on biomass gasification mechanisms. The results of batch tests suggested that the advantage of the HP environment with a metal catalyst could compensate in the reaction kinetics for operation at lower temperature [63]. Further studies showed that biomass slurries could be processed in continuous-flow reactors at low-temperature gasification conditions and still achieve high-conversion at reasonable processing rates [64,65]. More recent results with improved catalyst formulations, as presented below, have now provided a basis to move the processing forward from the bench-scale to a scaled-up reactor system operated at 6–10 L h^{-1}.

3.2. Review of catalysts

Previous research in low-temperature gasification has shown that new catalyst formulations are required for the pressurized water environment. Only a limited range of catalytic metals can be used in the process because of the oxidation of the metal components in the hot-water environment [66]. In addition, conventional catalyst support materials, such as silica and alumina are also severely degraded in this reaction environment. It is well-known that silica and alumina dissolve in high temperature water [67].

New catalyst formulations for low-temperature gasification include combinations of stable metals, such as ruthenium or nickel bimetallics and stable supports, such as certain titania, zirconia, or carbon. For example, the ruthenium on rutile titania extrudate is particularly effective in this process [68]. The ruthenium is easily reduced to its active form and maintains its activity for long periods of operation. The rutile form of titania is the stable crystalline form of titania at these reaction conditions. Although rutile is the crystalline phase with lower surface area ($\sim$45 m^{2}g^{-1}), active catalysts with up to 3 wt% ruthenium can be synthesized. Catalysts with up to 7 wt% ruthenium on carbon extrudates have also been shown to be valuable in this processing environment.

Although recovery may be a problem, alkali catalysts have also been employed. Sodium carbonate is effective in increasing the gasification efficiency of cellulose [69]. Likewise, homogeneous, alkali catalysts have been employed for high-temperature supercritical water gasification [70]. The effects of these catalysts on gasification are discussed in the next section in connection with the reaction mechanism.

3.3. Fundamental reaction scheme and effect of catalysts

Minowa's group investigated reactions of cellulose and glucose in hot-compressed water to get insight of reaction mechanism of hydrothermal degradation of biomass. They employed an autoclave as a reactor, and ran the reaction in the temperature range from 200 to 350 °C. By running

the reaction with and without catalyst, they also studied the effect of catalyst. Reaction products were gas, aqueous phase, oily material (acetone soluble products) and remained solid material (mixture of non-reacted cellulose and char-like material).

In case of catalyst-free condition [30,50,54, 69,71], cellulose was slightly decomposed over 200 °C to produce water-soluble products, which were almost all sugars; no gas, no oil and no char were produced. This indicated that hydrolysis was the primary step. Then cellulose was decomposed sharply around 250 °C to form water-soluble products (not only sugars, but also non-sugar materials), gas, oil and char. Over 300 °C, char production continued, although no cellulose was left in the reactor, and sugars and oil were decomposed. Finally, char was mainly obtained by the yield of 60% on carbon basis with 10% of gas (almost all CO_2 and small amount of CO), and 15% of non-sugar water-soluble products. From these results, they proposed the overall reaction scheme as follows [30,50,54,69,71],

$$(2)$$
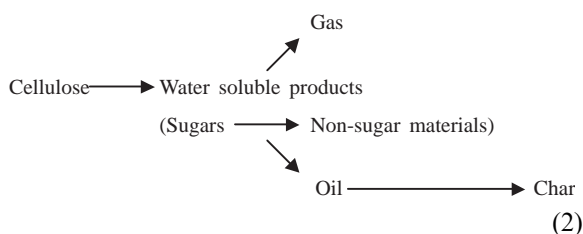
To confirm that hydrolysis is the first step, glucose was used as a starting feedstock [30,50,54,69,71]. The product distribution of gas, oil and char at different reaction temperatures were almost the same as that for cellulose. Thus, the degradation scheme of glucose was known to be almost the same as that of cellulose.

The role of catalyst was examined from the change in the product distribution with or without catalyst. Sodium carbonate was used as alkali catalyst [30,50,54,69,71]. The degradation of cellulose started at 180 °C, showing that alkali catalyst lowered the onset temperature of the cellulose degradation. This is the well-known peeling reaction of carbohydrates [72]. Sodium carbonate also promoted sugar degradation; higher yields of

gas and oil were obtained. In addition, sodium carbonate inhibited the char formation from oil, resulting in high oil yield and low char yield even at high reaction temperature of 350 °C and long holding time of 1 h.

Metal catalyst is well known to catalyze the gasification, and they used a commercial metal nickel catalyst [30,50,54,69,71]. Onset temperature of cellulose degradation was almost the same as that for catalyst-free condition. Then, the nickel catalyst catalyzed the gasification of water-soluble products, and the obtained gas consisted mainly of CO_2, H_2 and CH_4, and no CO. The change of the gas composition showed that CO_2 and H_2 were produced at first, and then CH_4 was formed by methanation. Oil and char yields were minimal. In case of changing the nickel catalyst loading, the gas yield increased linearly with the catalyst loading, and oil and char were also produced [30,50,54,69,71]. To confirm that gasification of oily materials did not occur, the oil produced at 300 °C was collected, put back into the autoclave, and treated under the same condition of glucose gasification. Then the resulting gas production was minimal. From these observations, it was found that water-soluble compounds produced both gas and oily materials and that oily materials once produced were not gasified any more. This supports the competitive reaction mechanism for water-soluble products shown by Eq. (1).

3.4. Interaction between components

The New Energy Development Organization (NEDO), Japan, supported a research project on supercritical water biomass gasification by the University of Tokyo, the Tokyo Gas Chemical Co., and Shinshu University, for 3 years (FY1998-2000) [73]. The purpose of this project was threefold: (1) development of hydrothermal pre-treatments for feedstock delivery to the HP reactor (see Section 5.1); (2) determination of the effect of partial oxidation so that higher gasification efficiency can be obtained at temperatures near 400 °C (see Section 3.7); and (3) development of effective catalysts to produce methanol from the product gas (not shown in this paper). As a part of this project, the interaction between biomass

components are studied, which is presented in this section.

Yoshida and Matsumura [74] were interested in how each component of biomass: cellulose, hemi-cellulose, and lignin behaved during supercritical water gasification. Thus, they treated cellulose, xylan (model compound for hemicellulose), and organosolv lignin with a nickel catalyst in super-critical water using a 4-mL tubing bomb reactor. Afterwards they studied the interaction of these compounds by mixing them in specific ratios and treating them in supercritical water with catalyst under similar conditions. Figs. 3–5 show the behavior of the product gas for the mixture. In these figures, values at null or unity of any compound show the result of treating the pure component. If there were no interaction between the components, data for the mixture should fall on a straight line tying the value at null and unity, which is shown as a dashed line in the figures. The result for treating a mixture of cellulose and hemicellulose falls on this line, indicating the behavior of these two components is summative. On the contrary, a large deviation from the straight line is observed for mixture of lignin and cellulose and that of lignin and hemicellulose. This behavior is clear for production of hydrogen and methane. Thus, it is indicated that when lignin is present, the production of hydrogen is suppressed.
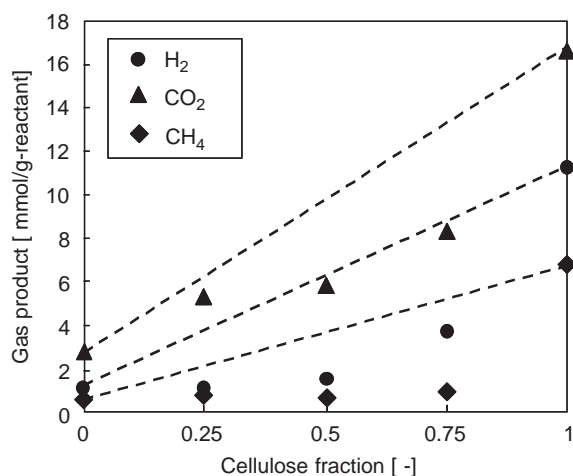

Fig. 3. Product from supercritical water gasification of cellulose–lignin mixture.
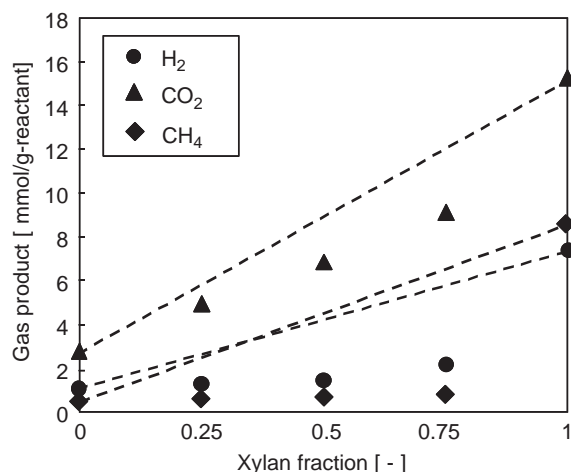
Fig. 4. Product from supercritical water gasification of xylan–lignin mixture.
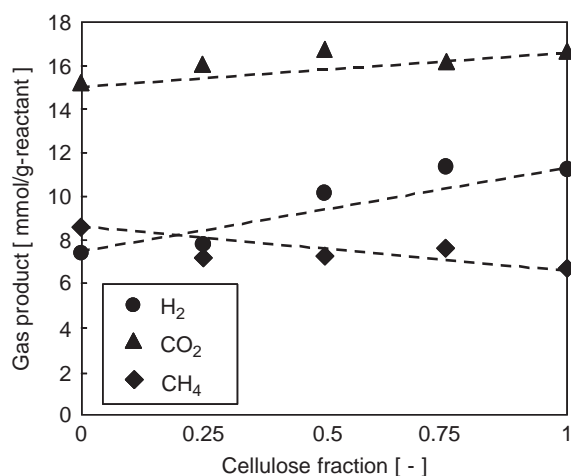

Fig. 5. Product from supercritical water gasification of cellulose–xylan mixture.

In the following article [75] Yoshida and his co-workers showed that this effect depends on the species of lignin. This result reveals the importance of component interaction in the course of supercritical water gasification.

3.5. Review of recent batch biomass results

Batch processing tests have been performed to provide comparative low-temperature gasification

results with different biomass feedstocks and improved catalysts. The reactor was a stirred, 1-L vessel. The feedstocks tested ranged from fermentation ethanol beverage distillation residue to dairy cattle manure solids. The biomass feedstocks were all high-moisture materials that can benefit by use in a gasification process wherein the biomass does not need to be dried. The feedstocks tested also included residues from biorefinery-type operations in which useful components, such as starch or hemicellulose were first recovered from the biomass and the residue was then processed in the low-temperature gasification. The results for 10 wt% dry solids slurries processed for 4 h at temperature are shown in Fig. 6.

The feedstocks shown in Fig. 6 are described in more detail as follows:

WSU manure #2 = dairy cattle manure solids recovered by screening at Washington State University, Pullman, Washington.
deStarched Corn Fiber = corn fiber from Archer Daniels Midland Company, Decatur, Illinois, corn wet mill, processed with hot water at PNNL (Pacific Northwest National Laboratory).
deStarched Millfeed = wheat millfeed from Pendleton Flour Mills, Pendleton, Oregon, processed with hot water at PNNL.
DDG, MGP = Distiller's Dried Grain from Midwest Grain Products, Atchison, Kansas
NREL SSF resid = simultaneous saccharification and ethanol fermentation residue from corn stover from the National Renewable Energy Laboratory, Golden, Colorado.
Washed TVA resid = acid hydrolysis of wood residue from the Tennessee Valley Authority, Muscle Shoals, Alabama, washed with water at PNNL.
BCI wood resid = residue from ethanol fermentation of hydrolyzed wood from BCI Jennings, Louisiana.
The catalysts shown in Fig. 6 are described in more detail as follows:
Ru/TiO2 = 3 wt% ruthenium on rutile titania extrudates produced by Degussa.
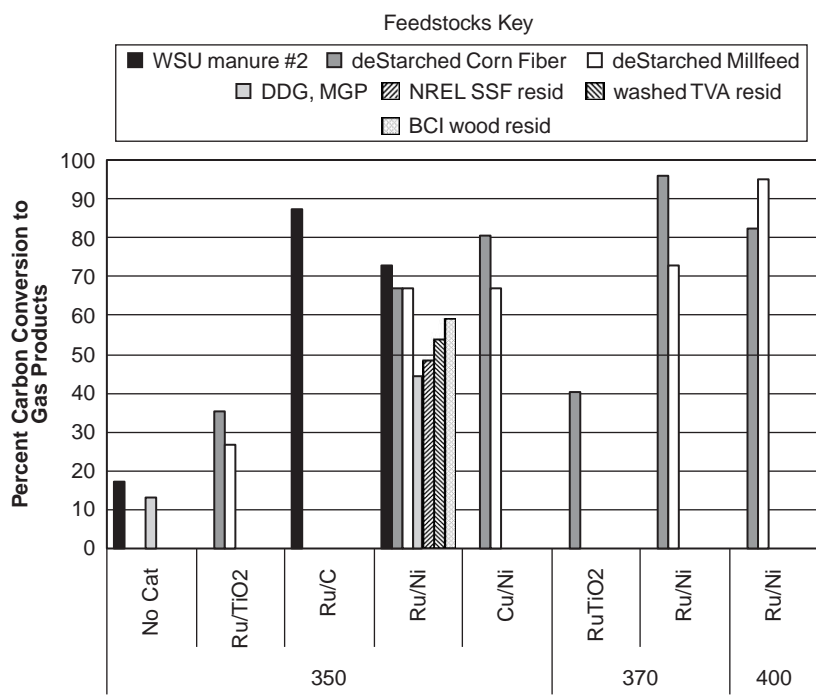Ru/C = 7 wt% ruthenium on carbon produced by Engelhard.

Fig. 6. Gasification results with different biomass feedstocks and catalysts.

Ru/Ni = 1 wt% ruthenium on G1-80 nickel methanation catalyst by BASF.
Cu/Ni = 1 wt% copper on G1-80 nickel methanation catalyst by BASF.

The batch reactor test results show a range of reactivity of the feedstocks in the presence of the various catalysts. Without catalyst the gasification is limited. The ruthenium on titania catalyst (with much lower metal loading) exhibits much lower activity relative to the ruthenium on carbon catalyst. Considering the experimental variability, the two stabilized nickel catalysts appear to be nearly equivalent, at a level of activity intermediate to the two ruthenium catalysts. The comparison of the several feedstocks using the Ru/Ni catalyst shows the highest reactivity with the manure solids followed by the lightly processed grains. The more severely processed lignocellulosic feedstocks showed lower activity as a group. The effect of temperature is obvious, but there is no dramatic effect noticeable at the supercritical point of water (374 °C).

3.6. Review of bench-scale continuous reactor results

Bench-scale processing in a continuous-flow reactor was also accomplished for some of these combinations of feedstock and catalyst. The bench-scale reactor system included a combination of a continuous-flow stirred tank (CSTR) serving as a preheater and a tubular reactor with a fixed catalyst bed. Biomass slurry was fed to the reactor by a progressing cavity (Moyno) pump/reciprocating pump combination. The addition to the existing bench-scale reactor system of both the CSTR and the Moyno pump resulted from difficulties in feeding biomass slurries. Results for manure solids processing (3.5% dry solids content) at 350 °C and 21 MPa with a Ni and Ru combined catalyst bed are shown in Fig. 7. High conversion of organics to a gas with a high level of methane was noted for a range of space velocities. At a 2.1 Liquid Hourly Space Velocity (LHSV = L-feed-slurry (L-catalyst)$^{-1}$ h^{-1}), the chemical oxygen demand (COD) was reduced from 47,000 g L^{-1} in
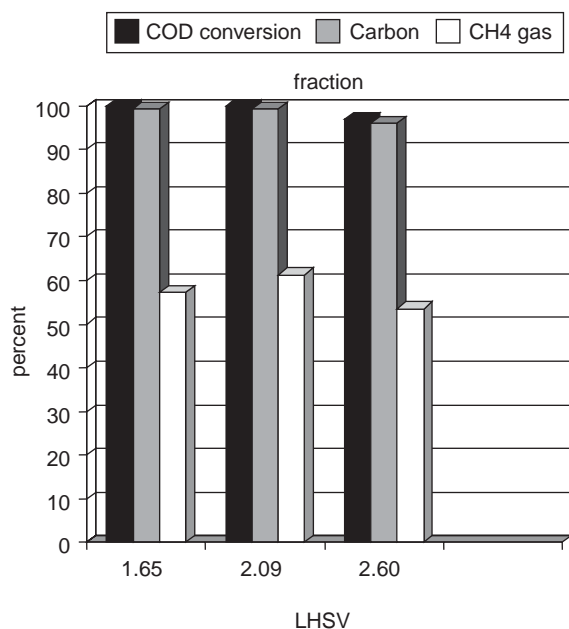
Fig. 7. Gasification of manure (350 °C, 21 MPa, Ru and Ni combined catalyst beds).

the feed slurry to $143 \, \text{g L}^{-1}$ in the effluent. The product yield was $0.76 \, \text{g L}^{-1}$ manure solids of a medium calorific value gas ($23.6 \, \text{MJ m}^{-3}$ in HHV).

3.7. Effect of partial oxidation

Partial oxidation is a common conventional gasification technology [76]. It is expected that partial oxidation will enhance the gasification efficiency even for supercritical water gasification. Matsumura's group tested the effect of partial oxidation on supercritical water gasification [77,78]. They supplied a mixture of hydrogen peroxide and glucose solution, and a mixture of hydrogen peroxide and cabbage slurry prepared as in Section 5.1 to the supercritical water gasification reactor. The reaction temperature ranged from 400 °C, and the pressure employed was 25 MPa. They successfully improved the gasification efficiency by adding hydrogen peroxide, but the cold gas efficiency decreased when the hydrogen peroxide concentration was too high. The maximum cold gas efficiency of 0.87 was obtained with a 2.5 wt% hydrogen peroxide and 6 wt% cabbage slurry mixture.

4. High-temperature supercritical water gasification

In high-temperature, supercritical-water gasification, a temperature range of 500–800 °C is employed. Due to the high reactivity of biomass at these temperatures, high gasification efficiency is possible; but as the concentration of the organic feedstock increases, the gasification efficiency falls. Gasification was studied using single compounds that are soluble in water (see Section 4.1). This approach relieves difficulties associated with feedstock delivery. Then several biomass feedstocks, including baby-food (as standardized biomass of very reproducible composition), sawdust, potato waste, and sewage sludge were tested (see Section 4.2); elucidating the effect of operating conditions. To improve the gasification efficiency, a two-stage gasification procedure was studied, where the biomass was first solubilized, and then gasified (see Section 4.3). The application of metal oxide catalyst was also reported recently (see Section 4.4).

4.1. Treatment of single chemical compounds

4.1.1. Reactions without catalyst: glycerol and glucose

Researchers of the University of Twente investigated gasification of glycerol and glucose without addition of catalytic material using a high-throughput capillary technique (see also Section 2.2). Over 200 experiments were carried out, during which the following parameters were varied: (i) reaction temperature (500–800 °C), (ii) pressure (5–45 MPa) and (iii) concentration (1–20 wt%).

The influence of these different process parameters on the gas-phase product composition and the gasification efficiency was analyzed on basis of the detected gas products. Figs. 8 and 9 show typical results for glycerol and glucose. Figs. 8(a) and 9(a), and Figs. 8(d) and 9(d), show the influence of the reaction temperature on the gas composition and the conversion of carbon in the feed to carbon in the gas products (respectively). Below temperatures of 600 °C, very low carbon conversions (gasification efficiency) were found
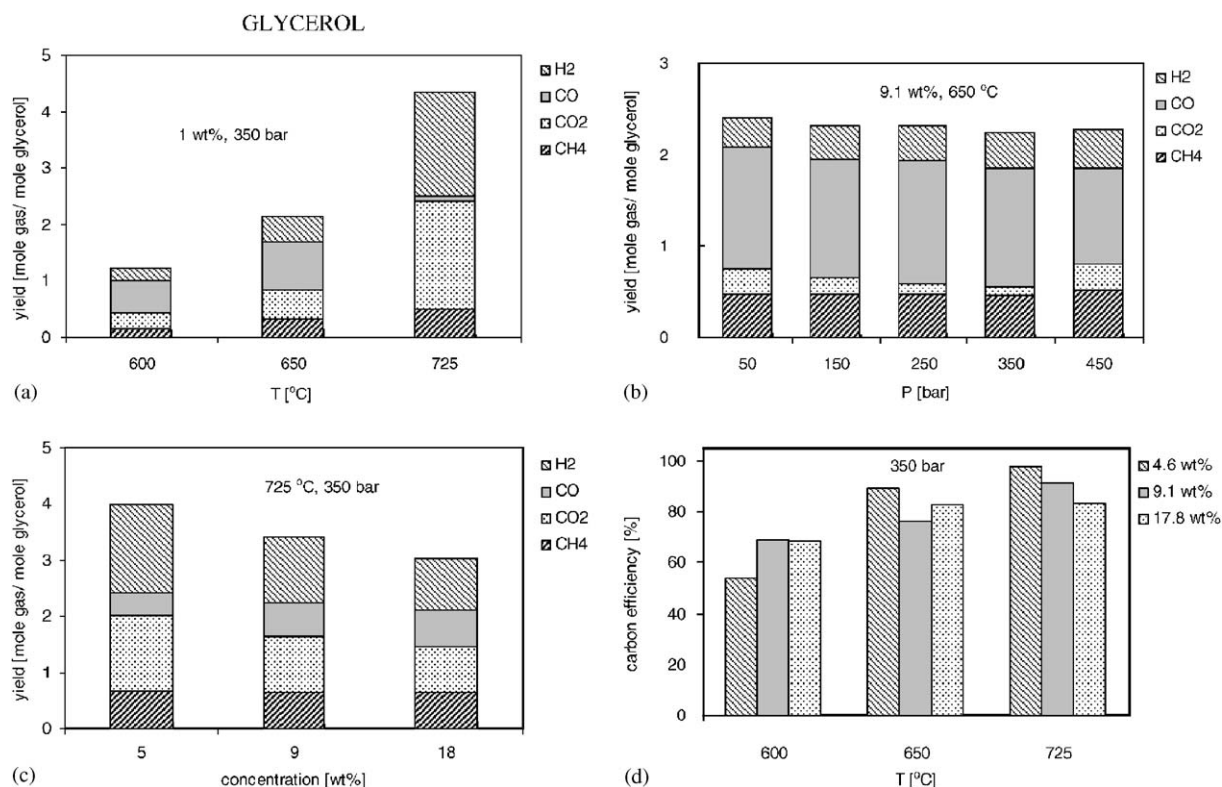
Fig. 8. Glycerol tests: (a) gas yield versus the temperature for 1 wt% solution and 350 bar, (b) gas yield versus pressure for 9.1 wt% solution and 650 °C, (c) gas yield versus the concentration for 350 bar and 725 °C, (d) carbon efficiency (carbon in gas/carbon in glycerol) for different concentrations as function of the temperature at 350 bar.

and dark brown liquid and solid products were clearly visible in the capillaries. Above 600 °C the gasification efficiency steadily increases to asymptotic values around 700 °C (see Figs. 8(d) and 9(d)). Complete carbon conversion to the gas-phase (100% gasification efficiency) was achieved only with very small concentrations (c < 3 wt%) (see Fig. 9(d)). Upon increasing the reaction temperature above 650 °C, the yields of H_2 and CO_2 sharply increase, while the yield of CO decreases (see Figs. 8(a) and 9(a)) and the gasification efficiency (see Figs. 8(d) and 9(d)) remains more or less constant. These observed trends indicate strong(er) water-gas shift activity above 650 °C. The methane yield is not affected by the process temperature and the concentration that much.

Much to our surprise it turned out that process pressure has hardly any influence on both the product gas composition (see Figs. 8(b) and 9(b)) and the gasification efficiency (not shown here) in a very wide range of pressures including supercritical as well as subcritical conditions (5–45 MPa).

The concentration of the organic feedstock exerts a major limitation on the process. Concentrations higher than 5–10 wt% lead to a significant drop of the hydrogen yield (see Figs. 8(c)) and carbon gasification efficiency (not shown here).

4.1.2. Reaction under the influence of catalyst

The University of Hawaii was the first to report studies of the supercritical water gasification of model compounds at high temperatures of 500–600 °C. They intended to conduct gasification of biomass without catalyst using metallic tubular flow reactors. However, with glucose as a feed-stock they found that the gasification efficiency
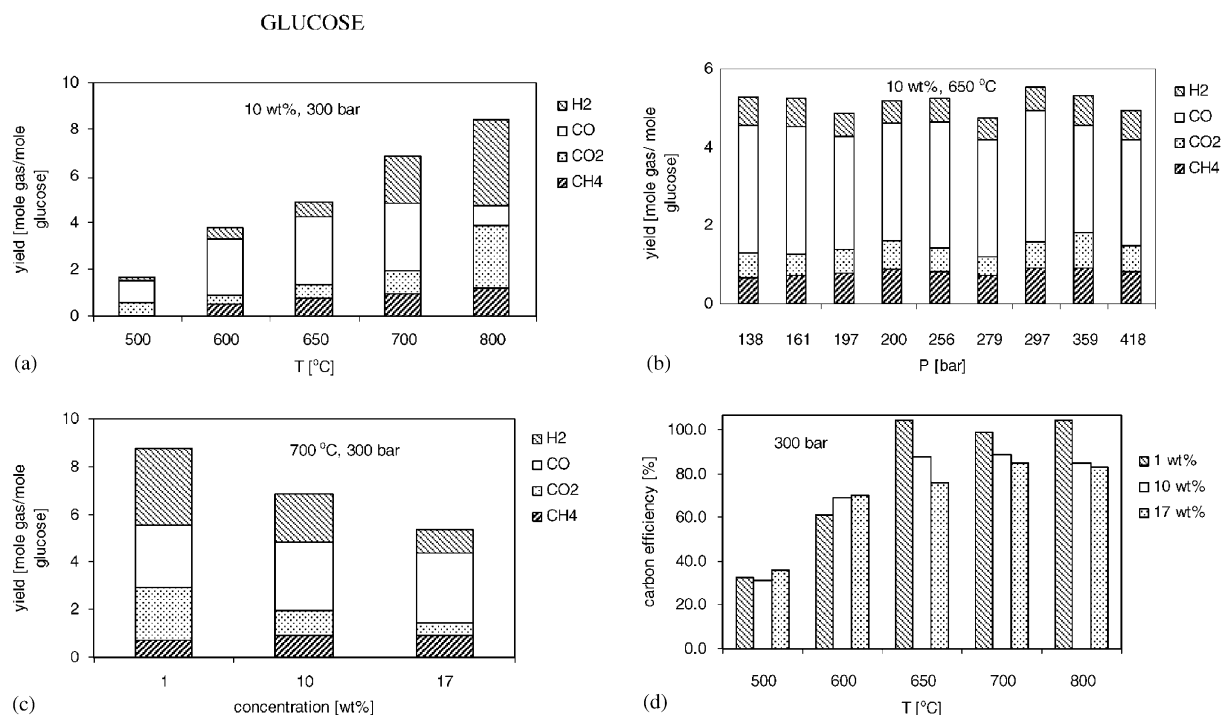
GLUCOSE

Fig. 9. Glucose tests: (a) gas yield versus the temperature for 10 wt% solution and 300 bar, (b) gas yield versus pressure for 10 wt% solution and 650 °C, (c) gas yield versus the concentration for 300 bar and 700 °C, (d) carbon efficiency for different concentrations as function of the temperature at 300 bar.

was affected by the reactor wall material [35]. Later this finding was supported by Lee et al. [79] They pretreated the reactor with sodium chloride to obtain a catalytic effect from the wall. They also measured the temperature distribution along the reactor, and found that at lower temperatures an endothermic reaction took place all along the reactor, while at higher reaction temperatures, the entrance portion of the reactor showed endothermic behavior while latter portion exhibited exothermic phenomena [80].

Researchers at the University of Hawaii also employed carbonaceous catalysts to attain complete gasification of a 20 wt% of glucose solution. In the same work they studied the gasification of single chemical compounds such as acetic acid, phenol, benzene, methanol, and glycerol [36]. Although complete gasification was not always possible, carbonaceous catalysts were found effective for all the compounds tested. It is known that

carbon reacts with water at high temperature and pressure. However, the rate of this reaction was found to be sufficiently slow under typical supercritical water gasification [81,82].

4.2. Treatment of biomass compounds

4.2.1. Results of the conversion of model biomass (baby food) in near- and supercritical water

In addition to investigations of model compounds like glucose or cellulose also scientific studies with real biomass are needed. This biomass must be available in reproducible composition and consistency for years in order to be able to perform all the studies and to have a standard to be compared with other biomass. This standard biomass must have a composition similar to potential feedstocks like residues from the food industry, and it must be a very fine and homogenous sludge to be handled in lab-scale plants.

The Karlsruhe group found this standard biomass; it is baby food (by the company Hipp) consisting mainly of cooked potatoes and carrots [83]. This model biomass consists nearly completely of carbohydrates, has a water content of 89.2 wt% and 6.2 g kg^{-1} ash content (mainly K, Na salts).

4.2.1.1. Identified products and description of the reaction by the choice of "key compounds".

The experiments described here with this model biomass were performed in two different devices, a tumbling batch reactor (up to 500 °C and 50 MPa, 1-L internal volume [84]) and a stirred vessel (up to 700 °C and 100 MPa, 0.190-L internal volume [83,84]), the second reactor can be used in continuous or batch mode. In both modes of the stirred vessel, the unheated biomass was injected into heated water or into the hot mixture and the biomass was immediately heated up by mixing. The tumbling batch reactor was used with a rather low heating rate of 1 or 3 K min^{-1} from room temperature to 500 °C.

It was nearly impossible to quantify or even identify all substances formed during conversion of biomass; therefore we used selected compounds, called key compounds as representatives of different reaction pathways. These key compounds are known from experiments with model compounds and belong to the following chemical groups: sugars, aldehydes, acids, furfurals, phenols and gases [83]. The fact, that the key compounds can be found in experiments with model compounds as well as biomass, and that these key compounds show the same dependencies, e.g. concerning a change in temperature, opens the opportunity to "learn" something about the chemistry with model compounds and apply this knowledge for biomass conversion.

4.2.1.2. Role of alkali salts during biomass gasification.

Studies of the conversion of model substances like glucose and pyrocatechol [70] show a significant influence of salts like KOH, KHCO$_3$ and K$_2$CO$_3$ on the product formation (see also Section 3.3). The addition of these salts leads to an increase in hydrogen and a decrease in CO yield by acceleration of the water-gas shift reaction [85].

Experiments in the tumbling reactor show that the presence of KHCO$_3$ leads additionally to an increased amount of products in the aqueous mixture (measured as total organic carbon), less coke/char formation, a lower concentration of furfurals and a higher concentration of phenols [86]. It has to be pointed out that salts influence a lot of reaction steps and that whenever experiments with model compounds are performed to study biomass conversion, it has to be considered, that real biomass includes salts and therefore leads to a similar gas composition like glucose with alkali salt, which means high hydrogen yields and very low yields of CO [87].

4.2.1.3. Change of product composition as function of temperature and the heating rate.

The temperature dependence of biomass conversion is strongly connected with the effect of the heating rate on the reaction. Slow heating up leads to the formation of coke/char, therefore we found coke/char after every reaction in the tumbling reactor and never in the stirred vessel. In the tumbling reactor a decrease in heating rate leads to a decrease of hydrogen yield [84].

Experiments in the stirred vessel at different temperatures show a rather high yield of furfurals and low gas yields below the critical point of water. Above the critical point the gas yield increases and the yield of furfurals is much lower [83]. This can be explained by a change of the main reaction mechanism from ionic in the subcritical to free radical in the supercritical region. This change is described in detail for the glycerol degradation [88]. Here might be one explanation for the formation of coke at low heating rates: When the biomass water mixtures spends enough time at subcritical temperatures, furfurals or other unsaturated compounds are formed in significant yields that may polymerize when free radicals are formed above the critical temperature. This is, of course, only one possible explanation; and additional studies are still necessary.

It has to be pointed out that the yield of phenols increases with temperature [89]—phenols are the only chemical species in aqueous solution, whose yield increases with temperature. The degradation rate of phenols is slower than that of e.g. furfurals;

therefore we regard phenols as the "last hurdle for complete gasification".

4.2.1.4. Influence of feed dry matter content.

The dependence of the gasification yield on the dry matter content or carbon input is of special interest; the more hydrogen that can be produced from 1 kg biomass, the lower the production price of hydrogen will be.

In the tumbling reactor the researchers at Karlsruhe confirmed what was found at the University of Hawaii (see Section 4.1.2) and at the research center in Karlsruhe in experiments with model compounds in a tubular reactor [70,87]: with increasing dry matter content or carbon input lower gasification efficiencies were found. In the stirred vessel, in contrast, an increased gasification rate at increased dry matter content was found. Thus, two different effects of feed dry matter content were observed depending on what kind of reactor was used. Since the characteristics of the stirred vessel reactor was its fast heating-up and the back-mixing of the products, these characteristics may be the reason for the higher gasification efficiency at higher feed dry matter content, which was observed for the stirred vessel. However, the detail has not been completely understood now. One possible explanation could be, that because of the back-mixing active hydrogen is present in all steps of biomass degradation, which may lead to an inhibition of the unwanted polymerization via saturation of free radicals. This would lead to a preference of small intermediates, which means less coke or tar, and high gas yields.

In both reactors, the relative yield of phenols increases with dry matter content of the biomass [84].

4.2.1.5. Consequences.

The presence of minerals in biomass has a significant effect on the gasification properties of the biomass. Experiments with glucose leads to completely different results than experiments with biomass, here the standardized biomass baby food. On the other hand experiments with glucose and alkali are comparable with gasification results with the cellulose biomass used. Alkali metals influence the reaction pathways of biomass degradation e.g. the presence of alkali decreases coke formation and increases hydrogen yield, which means that in the technical process the alkali content of the feed biomass is an important factor. The alkali content of biomass feedstock should not be too low in order to get high hydrogen yields. Alkali in biomass can also be disadvantageous, because they can cause plugging but this depends very much on the design of the reactor and concentration of the alkali.

The differences found in various reactor types give hints for the chemistry of biomass degradation and optimization of the process. High heating rate and a reductive atmosphere because of the presence of hydrogen also in the early stages of biomass degradation, like in the CSTR experiments, seem to be advantageous by avoiding unwanted polymerization reaction e.g. coke formation. Currently, a combination of a CSTR and a tubular reactor is under construction at Karlsruhe. Here the advantages of the CSTR should be combined with a second reactor to gasify relative stable compounds like phenols and to reach very high conversions.

4.2.2. Sawdust

University of Hawaii researchers succeeded in continuous gasification of sawdust in supercritical water [90]. Sawdust itself is dry feedstock, and probably will not be suitable for supercritical water gasification since conventional gasification processes should be easier and cheaper than supercritical water gasification. However, delivery of this powder feedstock into a supercritical water reactor is a challenge. Furthermore, this work served to demonstrate the possibility of supercritical water gasification with a realistic feedstock containing lignin. The sawdust was suspended in a dilute starch gel for delivery to the reactor (see Section 5.1). When gasification was conducted at temperatures as high as 650 °C, complete gasification was observed. This temperature is about 100 °C higher than was needed for glucose at the same concentration. Nevertheless, this result indicates complete gasification of wood is possible.

4.2.3. Potato waste

The University of Hawaii researcher identified potato waste as a desirable feedstock for supercritical water gasification, and succeeded in demonstrating complete and continuous gasification [91]. Potato waste is produced in large amount by the fast food industry (e.g. McDonalds) and needed no pretreatment. Reactor plugging was observed in the heatup section of their reactor. Depressurizing the reactor, and delivering air from the other end of the reactor successfully removed the carbonaceous product that plugged the reactor. Thus, the reactor was operated in an intermittent manner.

4.3. NEDO supercritical methanation

With NEDO sponsorship the Japan Gas Association undertook an investigation of methane production by supercritical water gasification. Their idea was to solubilize an organic waste feedstock by hydrothermal treatment, and then remove sulfur so that a proprietary metal catalyst—used in the following supercritical water gasification step—would not be poisoned. However, deactivation of the metal catalyst quickly took place in the presence of several ppm of sulfur. It was also found that the presence of salt also damaged the catalyst [92]. They used sewage sludge as target feedstock, and ran a continuous reactor, but found reactor plugging to take place due to the high ash content of the sludge. This result implies the necessity of effective ash removal prior to gasification.

4.4. Metal oxide catalysts

Because alkali catalysts (e.g. sodium carbonate and potassium hydroxide) are difficult to recover from the reactor's effluent, Watanabe et al. tested the ability of a zirconia catalyst to improve the gasification of glucose and cellulose in supercritical water. Unfortunately, the effect of the zirconia catalyst was not as strong as sodium carbonate, but it did double the gasification efficiency [93]. Similar results were obtained for partial oxidative gasification of lignin [94].

5. Engineering of supercritical/subcritical water gasification processes

Supercritical/subcritical water technologies are in their infancy with only a few exceptions. Unit operations that are well established for operation at atmospheric pressure are rarely applicable to supercritical water gasification. Even the delivery of feedstock to the reactor is a difficult task when the temperature and pressure of the reactor are at a supercritical condition. Although these operations are not usually the target of a research paper, an overview of the knowledge of each unit operation should be helpful for technology development, and future research activity in this field.

5.1. Feedstock pretreatment

Often the delivery of biomass to an HP reactor is a technological challenge. Because supercritical water gasification is a reaction in "water", the feedstock is delivered to the reactor with water, resulting in a continuous feeding of slurry or an aqueous solution. However, if the biomass has low moisture content or if it readily absorbs water and leaves only a small amount of "free water", conventional pulverization of the feedstock is insufficient and pretreatment of the feedstock is necessary.

One answer to this problem is to increase viscosity of the slurry. Antal's group succeeded in feeding sawdust continuously by suspending it in a starch gel [90], and delivering the sawdust laden starch gel to the reactor via a "cement pump". Matsumura's group used a hydrothermal pretreatment to successfully deliver cabbage, a model material for herbaceous biomass. It had been observed that treatment in hot compressed water results in softening of the hard structure of herbaceous biomass, as is observed when making a soup in the kitchen. When the temperature and pressure are higher, the effect of this "softening" is larger. This approach was employed successfully as a pretreatment for methane fermentation [95–98]. Matsumura's group used this technology successfully to pre-treat and gasify a cabbage slurry [99]. They fabricated a continuous reactor
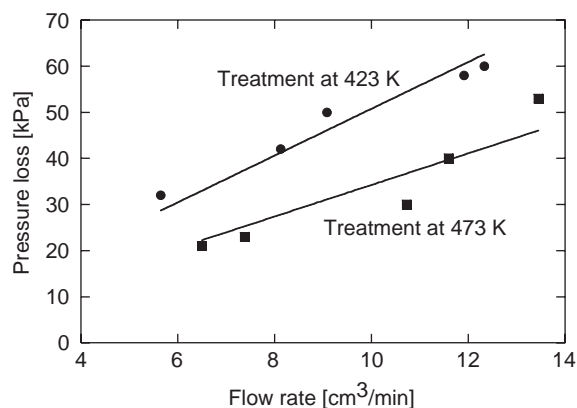
Fig. 10. Relation between flow rate and pressure loss for cabbage and liquidized products.
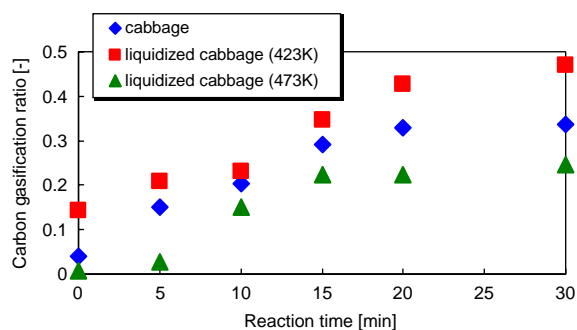

Fig. 11. Carbon gasification conversion of cabbage and its liquidized products (Reprinted from [99] with permission from the Japan Institute of Energy).

for this pretreatment where a slurry pump continuously fed pulverized cabbage to a reactor equipped with a scraper. The temperature in the reactor was 150–200 °C, and residence time was set at around 30 min. The apparent viscosity of the product slurry is shown Fig. 10. The product slurry was only 10 times as viscous as water, and thus easily delivered to the reactor, while pulverized cabbage plugged the line and even a viscosity measurement was not possible. Component analysis and SEM observation suggested that hemicellulose dissolved in water, and thus the structure of the cell was destroyed. The gasification characteristics of the product slurry were also measured using a micro-reactor (see Fig. 11). Treatment at 150 °C resulted in enhancement of

gasification rate and efficiency, while treatment at 200 °C showed reverse effect, indicating the existence of an optimum temperature for this pretreatment.

5.2. Heat recovery unit

It has been mentioned already that heat recovery is essential for SCWG gasification process to be energy-productive. The enthalpy of water at reaction conditions is such that without recovery, heat needed for supercritical water gasification cannot be supplied by the heating value of the feedstock. In other words, from heat balance considerations it is clear that heat exchange between the reactor effluent and the reactor feed is essential for the economics of the process. For supercritical operation, it is desirable to heat the feed to approximately 450 °C in this heat exchanger. In this temperature range biomass in the feed has already finished its decomposition, yielding, primarily, char and tar, as was indicated by capillary experiments. Hence, in a regular shell and tube heat exchanger, blockage and fouling problems are expected. Also, to keep the heat exchanger clean, a particulate system may be interesting. As one of the many possible alternatives, we present here an integrated fluidized bed reactor/heat exchanger system (see Fig. 12). This system combines the advantages of a fluidized bed reactor with concept of particulate heat exchange by using the solids circulation loop of the reactor for this purpose. For more details see [100].

Another important aspect of heat recovery is quick heat-up of the feedstock. Xu et al. found that improving heat transfer in the heating section of the feedstock delays deactivation of catalyst, implying the suppression of tar production [36]. Matsumura's group changed the heating rate of the feedstock and obtained data that indicates a heating rate of several hundreds of degrees Kelvin per minute should be desirable for this purpose [101].

These two requirements, namely, high efficiency of heat recovery and quick heating of the feedstock should be considered in designing the heating-up section.
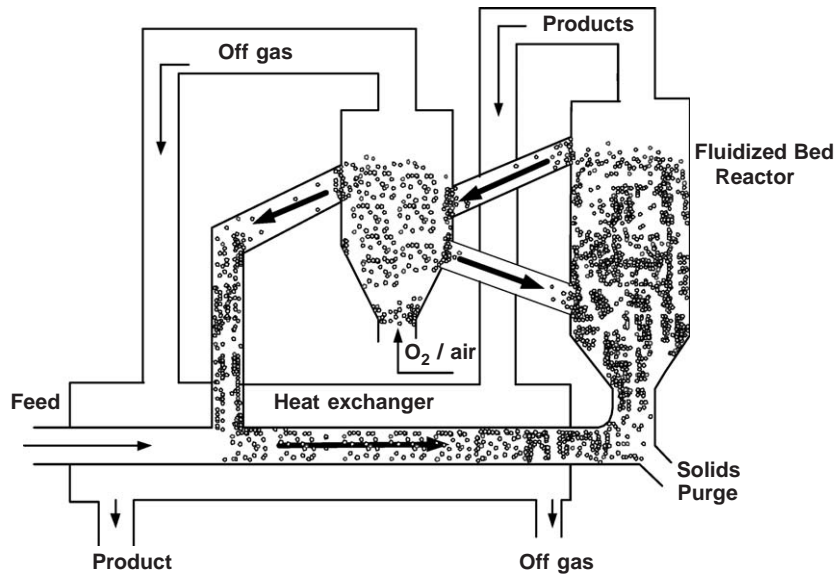
Fig. 12. A possible reactor/heat exchanger configuration for the SWG process.

5.3. Depressurization system

Depressurization of the effluent is conducted following the heat exchanger. Conventional back-pressure regulators are sufficient for this purpose. However, ash and (possibly) solid particles may damage the system; consequently a metal filter should be located before the regulator. Another possibility is the use of capillary tubing that should be effective for the effluent flow with particles.

5.4. Gas recovery

Product gas automatically separates from the liquid phase following the heat exchanger. All tarry materials and char, if any, remain in the liquid phase, and a completely tar free product gas is available, as it is essentially a water-scrubbed product. This is an advantage of supercritical water gasification over conventional gasification processes. Thus, it is expected that product gas may be fed to gas engines or gas turbines without any treatment. To remove carbon dioxide to raise the heating value of the product gas, separation of gas and liquid before depressurization is effective [102]. The effectiveness depends on the feed

concentration and gasification efficiency. Sometimes, when the amount of carbon dioxide to be removed is large, additional water is needed to absorb the carbon dioxide.

6. Advantages and possibilities of near- and supercritical water gasification

Although SCWG is a totally new concept it has, in the present stage of consideration, a number of very interesting aspects (see Fig. 13).

In the first place, the process is suitable to process *very wet* feedstock like for instance algae or water hyacinth. In fact, any agricultural or industrial waste streams can be utilized, provided that its value is low enough to allow economic conversion in the HP/high-temperature SCWG process.

Secondly, it is important to note that the products of SCWG will be available at high pressure, which is practically always needed for any further use.

Thirdly, in case a catalyst or a secondary shift reactor is applied to convert the CO in the product gas, the product will exclusively contain H_2, CH_4
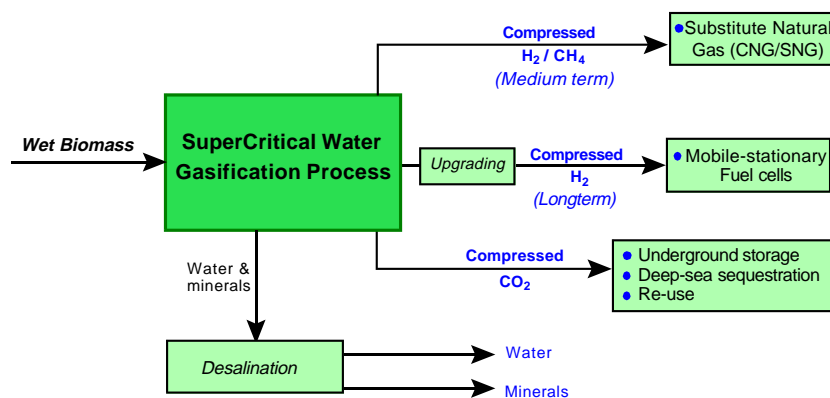
Fig. 13. Scheme for application outlets of SCWG.

and CO_2. Because of its relatively high concentration, it is quite interesting to consider CO_2 sequestration for underground storage.

In the fourth place, mixtures of H_2 and CH_4 are on a short to medium term applicable to mix into any distribution network for natural gas and make it partially green. In The Netherlands, this co-feeding application has a huge potential because of the large scale of natural gas utilization.

Last but not least, hydrogen from SCWG can be used for fuel cell applications, in which case the CH_4 and any other hydrocarbons should be converted in a secondary reformer. Upgrading steps like water-gas shift and steam reforming are known technologies and are not expected to hinder the development of that particular application seriously.

7. Concluding remarks

SCWG may become an important technology for converting wet biomass or organic waste to a pressurized and clean medium caloric value gas with high hydrogen content. Technical hurdles are not yet solved completely but significant progress has been made through experimentation with a variety of equipment, including millimeter sized quartz capillaries, bench-scale laboratory set-ups, and fully automated pilot-plants. For continuously operated plants, unusual process and reactor technology will be required to cope with fouling and necessary heating rates. At present, wet biomass species are gasified by methane fermentation. A recent paper compared the process cost, energy efficiency, and carbon dioxide emissions of these two approaches to wet biomass gasification [103]. Considering the costs of treating wastewater and fermentation sludge, supercritical water gasification can be competitive with biomethanation.

Acknowledgments

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